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# An easily applicable and recyclable Fenton-like catalyst produced without wastewater emission and its performance evaluation

Lu Liu <sup>a</sup>, Shiquan Liu <sup>a, \*</sup>, Shivani Bhardwaj Mishra <sup>b</sup>, Liping Sheng <sup>a</sup>

<sup>a</sup> School of Materials Science and Engineering, University of Jinan, Jinan, 250022, Shandong, PR China <sup>b</sup> Nanotechnology and Water Sustainability Unit, University of South Africa (Florida Campus), Johannesburg, South Africa

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# ABSTRACT

A thin disc-shaped Fenton-like catalyst sized 28.59\*1.39 mm in diameter and thickness was produced by ball milling a hemi-dried silica xerogel with iron (III) acetylacetonate, followed by mold pressing and calcination. The developed compact catalyst facilitated its application and recovery. The whole fabrication process was free of wastewater emission. Plasticizers or binders indispensable for shaping commercial powders into compact green bodies were not necessary in the present method. The bulky catalyst was mesoporous and had a large surface area of 580 m<sup>2</sup>/g, providing access to the activation of  $H_2O_2$  by the active iron sites inside the sample. It removed 100% of methylene blue (MB) in solution with a total TOC reduction by 92.13% mainly via the Fenton degradation. No washing, chemical elution of the adsorbed dye before the next application was applied. After five cycles, *ca*.93% of the initial capacity was kept after the 5th cycle, while the iron leaching was only 0.021% of the applied catalyst. The excellent performance of the bulky catalyst was due to its large surface area, uniformly distributed and chemically bonded iron species. The present work provides a scalable and green way to produce Fenton-like catalysts for environmental application.

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# 1. Introduction

Dyes are used in industries including textile, leather manufacturing and printing, etc., leading to the formation of wastewaters containing dye molecules. Most synthetic dyes are difficult to degrade and have detrimental environment effects (Holkar et al., 2016). Using Fenton (-like) catalysts is an effective way to remove the dyes from wastewaters via degradation. It mainly utilizes iron-containing catalysts reacting with  $H_2O_2$  to form free radicals as oxidants for the degradation of organic pollutants to carbon dioxide and water or to small molecules (Zhang et al., 2016). Li et al., 2019).

Many different types of Fenton-like catalysts have been developed and applied in wastewater treatment (Nidheesh, 2015). Ironcontaining silica-based porous composites are among the developed Fenton-like catalysts which exhibited good dye removal performance. They were mostly prepared via hydrothermal reaction (Meng et al., 2016), sol-gel method (Chae et al., 2016) or

\* Corresponding author. E-mail addresses: liusq\_ujn@hotmail.com, mse\_liusq@ujn.edu.cn (S. Liu). impregnation (Ursachi et al., 2012; Rostamizadeh et al., 2018). These methods face a great challenge due to the emission of wastewater during the production of catalysts.

Some of the Fenton-like catalysts have been proved efficient in removing methylene blue (MB), a commonly used dye in industries, from wastewaters (Zhang et al., 2016; Chai et al., 2016; Li et al., 2017; Mohamed et al., 2017; Li et al., 2018; Li et al., 2018; Li et al., 2018; He et al., 2018; Hu et al., 2019). However, with few exceptions (Li et al., 2018; Shi et al., 2019), most of such catalysts so far are in powder form, which makes their dispersion in wastewater and the recovery after the application a difficult work. In addition, the collection of used catalysts via filtration or centrifugation which are normally used in labs is actually not applicable at industrial scale, because of the small dosage of powders added in wastewaters. Efforts have been made to make magnetic Fenton-like catalysts so that the catalysts can be recovered using external magnets (Li et al., 2017; Chai et al., 2016; Li et al., 2018; Hu et al., 2019). Alternatively, Fenton-like catalysts were incorporated into membranes or fibers or foams (Li et al., 2018; Shi et al., 2019), which may facilitate an easier collection of catalysts compared in the cases of using powder form catalysts.







In this work, a silica xerogel was first facilely synthesized by solgel method. All reactants were enclosed in the formed wet gel and no wastewater was generated during the synthesis. After the gel was hemi-dried, it was ball milled with iron source forming a precursor powder. The powder mixture was formed under pressing into a disc-shaped green body which was further turned into a porous Fenton-like catalyst. The catalyst was used to degrade MB without dispersion in the wastewater. Its degradation performance toward highly concentrated dye in wastewater was superior to other reported Fenton-like catalysts. Since most of the dye molecules adsorbed by the porous catalyst was degraded, it was reused up to five cycles without washing or chemical elution after it was easily recovered from the treated wastewater.

# 2. Materials and methods

#### 2.1. Reagents

Tetraethyl orthosilicate (TEOS,  $C_8H_{20}O_4Si$ ) was bought from Sinopharm Chemical Reagent Co. Ltd. and anhydrous ethyl alcohol (EtOH,  $C_2H_5OH$ ,  $\geq 99.7\%$ ) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd.; n-Butylamine (BA,  $C_4H_{11}N$ ,  $\geq 99.0\%$ ) and Iron (III) acetylacetonate (FeAA,  $C_{15}H_{21}FeO_6$ , 98%) were from Aladdin Industrial Corporation; Methylene blue (MB,  $C_{16}H_{18}CIN_3S\bullet 3H_2O$ , 97%) and Hydrogen peroxide ( $H_2O_2$ , 30%) were from Tianjin Da Mao Chemical Reagent Co., Ltd.) and Fine Chemical Plant of Laiyang Economic and Technological Development Zone. All reagents were analytic grade and used without any further purification. Distilled water was used in all the experiments.

#### 2.2. Materials synthesis

The SiO<sub>2</sub> xerogel was prepared by the hydrolysis and condensation of TEOS in a mixed butylamine and EtOH solution. The relative molar ratios of reactants were 1TEOS:30.6H<sub>2</sub>O: 1.68BA:12.4EtOH. First, EtOH and distilled water were mixed and magnetically stirred for 10 min. Then, BA was added into the solution under vigorous stirring for 30 min. Finally, TEOS was added. After continues stirring of 6 min, the mixed solution became turbid. The stirring was immediately stopped and the solution gelled quickly. The gel was further aged for 1 h. Then, the wet gel was dried at 80 °C for 4 h in an oven.

To prepare the FeOx/SiO<sub>2</sub> catalyst, FeAA was mixed with the xerogel in an agate jar. The Fe/SiO<sub>2</sub> molar ratio was 0.05. Agate balls were added according to the total weight of the xerogel and FeAA. The weight ratio between the balls and the mixture to be milled was 1:25. The mixture was milled in a planetary ball mill (W-QMJ, Sangli electronic equipment factory, Nanjing, China) for 30min under a rotating speed of 150 r/min to obtained composite powder precursor. Then, 1 g of the composite powder was uniaxially pressed under 34 MPa in a cylindrical steel mold with a diameter of 30 mm. Finally, the pressed samples were calcined at 550 °C for 6 h. The final size of the resultant sample was measured by a vernier caliper.

#### 2.3. Materials characterizations

Cationic MB was chosen as a model pollutant to evaluate the degradation performance of the prepared FeOx/SiO<sub>2</sub> composite. MB solution was prepared by dissolving MB in distilled water. The volume of solution and the dosage of catalyst were fixed at 50 ml and 0.5 g in all tests. Specified amount of  $H_2O_2$  (Conc. 30%) was added into the MB solutions. The mixtures were in conical flasks (250 ml) under shaking continuously for 24–72 h at room temperature. For the recyclability tests, a new sample was used and it

was taken out from the solution after each preceding experiment simply by a tweezer and dried at 80 °C for 2 h. Then it was reused under the specified conditions.

The total dye removal efficiency was calculated using the formula:

Removal efficiency  $(\%) = [(C_0-C_t))/C_0] \times 100\%$ 

Where  $C_0$  (mg/L) and  $C_t$  (mg/L) are the concentrations of MB solutions at the beginning and the time *t*.

The concentrations of MB in water were measured on a 722type spectrometer (Shanghai Jinghua, China) at the wavelength of 665 nm. The contents of C, N, S in the used samples were measured on a Vario EL Cube (Elementar, German) element analyzer. TOC measurements were carried out on TOC-L CSH type analyzer (Shimadzu, Japan). The TOC reduction efficiency was determined by comparing the original TOC in solution and the final TOC in the treated solution. The iron leaching in the solution was measured by ICPOES or ICPMS technique on 730 or 7700ce spectrometers (Agilent, USA) depending on the concentration.

N<sub>2</sub>-sorption measurements were performed on a Quantachrome Auotsorb iQ-C equipment (Quantachrome, USA). The surface area of sample was calculated based on the Brunauer-Emmett-Teller (BET) model and the pore size distribution (PSD) curve was derived using the Barrett-Joyner-Halenda (BJH) method using the adsorption branch of isotherm. EDS elemental analysis of the FeO<sub>x</sub>/SiO<sub>2</sub> composite was carried out on a QUANTAN FEG250 scanning electron microscope (SEM). X-ray diffraction (XRD) analysis was on a D8 Advanced diffractor (Bruke, Germany). Thermogravimetric (TG-DTG) analysis of the silica xerogel was performed in air with a ramp rate of 5 °C/min on a Synchro thermal analyzer (Fast STA 449 F3, Germany). X-ray photoelectron spectroscopy (XPS, Thermo escalab 250Xi, Thermo Electron Corporation, USA) was used to investigate the valence state of iron species in the FeO<sub>x</sub>/SiO<sub>2</sub> composite.

#### 3. Results and discussion

SiO<sub>2</sub> xerogel was quickly synthesized by the hydrolysis and condensation of tetraethyl orthosilicate in water with the addition of ethanol as solvent and 1-butylamine as catalyst [Cheng et al., 2007]. All the reactants were fully transformed into a wet gel without the formation of waste liquid. After the wet gel was dried at 80 °C for 4 h, it still contained ca.14.6% enclosed water, ethanol and amine which were identified by the FTIR (SI-1) and TG analysis results (SI-2). This hemi-dried xerogel afforded its powder plasticity (ductility) and consequently capability to be pressed into robust compacts. During the shaping process, no plasticizer or binder was added. The formation of the robust bulky sample was dependent on the organics and water remained in the hemi-dried silica xerogel (Schiavo et al., 2018; Fontes et al., 2019). Experiments confirmed that powders from either commercial silica gels or the present xerogel which had been calcined at 500 °C for 4 h were unable to be pressed into compact green bodies with any strength (Kumar et al., 2014; Younes et al., 2019).

The hemi-dried xerogel and iron acetylacetonate (FeAA) were ball milled and the mixed powder was uniaxially pressed into a compact precursor. After the green body was calcined at 550 °C for 4 h, a FeO<sub>x</sub>/SiO<sub>2</sub> composite was obtained. Presented in Fig. 1 are the digital photo, SEM image and EDS mapping analysis result of the product. The diameter of the sample is 28.59 mm and the thickness is 1.39 mm (Fig. 1a).

The SEM image (Fig. 1b) shows that the catalyst consists of nanoparticles and the interparticle voids contribute to a highly porous texture of the composite (see the later N<sub>2</sub>-soprtion results). The EDS mapping analysis results (Fig.1c~e) evidence a



Fig. 1. The digital photo (a), SEM image (b) and EDS mapping analysis results of the sample: (c) O; (d) Si; (e) Fe; (f) EDS spectrum.

homogenous distribution of iron species in the prepared composite. The iron content was 8.65 wt% in the sample (Fig. 1f). However, XRD pattern of the composite (SI-3) only showed a broad diffraction peak centered at  $20-30^{\circ}$  indicative of the amorphous silica, suggesting that crystallites of iron or its oxides did not form in the composite. A comparison of the FTIR spectrum of the sample with that of calcined xerogel shows that the absorption band at 956 cm<sup>-1</sup> related to the -OH groups on the surface of silica xerogel is significantly weaker that in the case of the iron-containing silica composite, suggesting that the iron species were chemically bonded with the silica skeleton by forming Si–O–Fe bonds (Fig. 2) (Alotaibi et al., 2017; Fu et al., 2017). This is to be further confirmed by the O1s XPS spectrum result. The formation of Si–O–Fe bonds might be a result similar to the mechanical alloying of powders as reported by many researchers (Muaz et al., 2017).

The N<sub>2</sub>-sorption isotherm and pore size distribution (PSD) curve of the sample are shown in Fig. 3a&b. The type IV isotherm (Fig. 3a) indicates the composite is mesoporous. The surface area, pore volume and pore size are  $580 \text{ m}^2/\text{g}$ , 1.14 ml/g and 17.4 nm, respectively. The surface area is much larger than those of other similar catalysts used for the MB degradation (see the values listed in Table 1). And the PSD curve is broad, covering small mesopores to macropores (Fig. 3b), facilitating not only the adsorption and diffusion of dye molecules, but also the accessibility of active sites



Fig. 2. Comparison of the FTIR spectra of the xerogel and the composite.

for catalytic reactions inside the bulky composite (Li et al., 2019; Kalaparthi et al., 2017).

Shown in Fig. 4a is the Fe 2p XPS spectrum of the sample. It shows that the core energy levels of Fe 2p are split into two peaks at 711 and 725 eV, which correspond to Fe  $2p_{3/2}$  and Fe $2p_{1/2}$  respectively due to spin orbit coupling (Balamurugan et al., 2013). According to the literature, the B.E. of Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$  strongly depends on the valence state of iron species (Boroń et al., 2015). The major peak of Fe  $2p_{3/2}$  is deconvoluted into Fe<sup>3+</sup> peaks at 713.1eV and 714.8 eV, and Fe<sup>2+</sup> peaks at 710eV and 712 eV (Gurgul et al., 2013). The peaks of Fe  $2p_{1/2}$  can be fitted as Fe<sup>3+</sup> doublet. The presence of Fe<sup>2+</sup> could be due to the defects of ill-crystallized or amorphous iron oxide (Wang et al., 2014). In addition, carbon or carbon monoxide formed due to the decomposition of ACAC ligands of FeAA and the xerogel combined amine during the calcination process, locally generated reducing atmosphere, leading to formation of  $Fe^{2+}$  (Liu et al., 2004). The calculated percentages of  $Fe^{2+}$  and  $Fe^{3+}$  in the sample were 39.1% and 60.9%, respectively. The O1s spectrum in Fig. 4b are deconvoluted into three peaks at 532.3, 533.0 and 533.7 eV, respectively. These peaks indicate the presence of Si-O-Si, Si-O-Fe and Si-O-H bonds on the sample surface, further proving the formation of Si–O–Fe bonds (Jusoh et al., 2015).

For the evaluation of dye degradation performance of the prepared bulky form composite, the sample was used to degrade MB solution with a high initial concentration,  $C_0$ , of 1000 mg/L. The test was at room temperature for 72 h with the addition of 5 ml of H<sub>2</sub>O<sub>2</sub>. The H<sub>2</sub>O<sub>2</sub> concentration in the tested MB solution was 0.03 g/ml. The molar ratio of H<sub>2</sub>O<sub>2</sub> to Fe<sup>2+</sup> was ca.163.

The time-dependent removal of MB from solution was monitored by measuring the residual MB concentration in the treated solution via spectroscopy method. It should be mentioned that in order to carry out a continuous test, the residual solution was not allowed to be diluted intermediately for the residual concentration test at different time intervals. Therefore, the first point was recorded when the residual MB concentration was below the upper detection limit of the applied spectrometer. Due to the very high initial concentration of the MB solution, the residual MB concentration of the solution treated for 34 h was not detectable. After an overnight, the first residual MB concentration was recorded at 48 h, which gave a removal of 98.81%. As shown in Fig. 5a, the removal increases with further prolonging the time and reaches 100% at 72 h. After the test, the treated water became fully clear and the



Fig. 3. N<sub>2</sub>-sorption isotherm (a), PSD curve (b) of the sample.

## Table 1

A comparison of the performance of Fenton-like catalysts toward MB degradation in water.

Catalyst	Surface	Maximum efficiency		Capacity of the	Catalyst recovery	Percentage of remained Iron leaching (%) <sup>c)</sup> Refs.		
	area (m²/g)	MB removal	TOC reduction	ັcatalyst (mg/g) <sup>a</sup> າ	method	efficiency in 5th cycle		
Fe <sub>3</sub> O <sub>4</sub> /carbon octahedra	87.3	nearly 100%	58%	20	Magnetic separation	97 <sup>e)</sup> TOC 72.41 <sup>e)</sup>	Not available	Li, 2018
MnO <sub>2</sub> /Fe <sub>3</sub> O <sub>4</sub> /diatomite	103.6	100% (PMS) d)	57.2%	100	Magnetic separation	86.78	Not available	Li, 2018
Fe <sub>3</sub> O <sub>4</sub> @MnO <sub>2</sub>	247.9	99.8% (PMS) d	<sup>)</sup> 55%	99.8	Magnetic separation	>90 <sup>f)</sup>	0.73-1.5%	Zhang (2016)
Fe-based MOF	163.9	97%	54.6%	64.67	Centrifuga-tion	90	0.067%	He (2018)
Bulky form FeO <sub>x</sub> /SiO <sub>2</sub> composit	e 580	100%	92.13%	100	Manually with a tweeze	r 92.57 TOC 87.93	0.021%	This work

(Note: a) calculated using the maximum total removal efficiency and the solution volume, MB concentration and the dosage of catalyst applied; b) Percentage of remained efficiency = [(the efficiency of the first cycle - the efficiency of the final cycle)/the efficiency of the first cycle] $^{*100\%}$ ; c) calculated using the total iron in the treated solution/the catalyst applied; d) PMS: peroxymonosulfate activation; e) ten cycles were applied; f) six cycles were applied).



Fig. 4. Fe 2p (a) and O 1s XPS spectra (b) of the sample.

used sample was dark brown (Fig. 5b). However, the residual TOC in the treated water was 47.2 mg/L. Therefore, the TOC removal efficiency of the composite was 92.13% (MB solution with a concentration of 1000 mg/L has 600 mg/L of carbon. Thus, the TOC removal efficiency was calculated as [(600-47.2)/600] \*100% = 92.13%). The residual carbon in the treated water was from the degraded or mineralized MB, which existed as elemental carbon or small molecules and not detectable by the spectroscopy used for determining the removal of dye (Hartmann et al., 2010; Nidheesh, 2015; He et al., 2018; Hu et al., 2019). This explains why the used sample is brown. In addition, the color change of the used sample may also be partially contributed by the variation of iron species during the Fenton reaction.

In principle, the 100% removed MB could be divided into three parts: (1) remained as MB molecules in the used sample; (2) fully degraded into  $CO_2$  and  $H_2O$  by the catalyst via the Fenton reactions; (3) transformed into elemental carbon or small molecules under

catalytic reactions and existed in either the used sample or the treated solution (Hartmann et al., 2010; Mohamed et al., 2017).

Elemental analysis revealed that the TOC in the used sample was 0.53%, which could be equivalent to 8.83 mg MB/g used sample, indicative of a possible MB removal of 8.83% by adsorption. However, the elemental analysis also showed that the contents of N and S originated from MB molecules remained in the used sample were 0.45% and 0.25%, respectively. It indicates that the ratios of N and S to C in the used sample are 0.85:1 and 0.47:1. Both are much higher than those in MB molecules (N,S ratios to C in the MB molecules are respectively 0.22:1 and 0.17:1), suggesting at least part of the detected C in the used sample did not exist as MB molecules, instead, it existed as small molecules due to the degradation occurred inside the sample (Hartmann et al., 2010; Mohamed et al., 2017).

The above results suggest that the 100% removal of MB and TOC reduction in the present case was mainly due to the catalytic dye



Fig. 5. (a) Time-dependent removal of MB from synthetic wastewater by the bulky sample and (b) the photos of the solution and sample after the MB removal.

degradation by the bulky form iron/silica composite. Both the initial concentration of MB applied in the test and the TOC removal efficiency of the present bulky form catalyst, to our knowledge, have not been reported (See later discussion and comparative data in Table 1).

The hemi-dried silica gel not only afforded the ball-milled composite powder necessary plasticity for the shaping via pressing, but also provided the catalyst a large surface area and porous texture which facilitated the adsorption of MB and provided more accessible iron active sites for the activation of  $H_2O_2$  (Hartmann et al., 2010; Li et al., 2018). The iron species (mainly Fe<sup>2+</sup>) were involved in the Fenton-like reactions, which are shown by the following equations (1)~(4). The reaction (1) led to the formation of large amounts of free radicals of OH. The •OH which has a high oxidation-reduction potential can oxidize organic dye molecules into inorganic substances such as CO<sub>2</sub> and H<sub>2</sub>O (Hartmann et al., 2010; Wang et al., 2013)

$$Fe^{2+} + H_2O_2 \rightarrow \cdot OH + OH^- + Fe^{3+}$$
(1)

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HOO \cdot$$
<sup>(2)</sup>

$$Fe^{3+} + HOO \cdot \rightarrow Fe^{2+} + H^+ + O_2$$
(3)

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^{-}$$
(4)

Since the main advantage of the present catalyst lies in its easy recyclability, the recycling performance the catalyst was tested. To reduce the experimental time, MB solution with  $C_0 = 200 \text{ mg/L}$  was applied and the treatment time was reduced to 24 h. And 2 ml of  $H_2O_2$  was added, giving a  $H_2O_2$  concentration of 0.012 g/ml and a

 $H_2O_2/Fe^{2+}$  molar ratio of ca.65. As concluded earlier, the dye was removed mostly by catalytic degradation, while only very small amount of dye was remained in the used catalyst. No special regeneration (chemical elution or washing of dye molecules) of the used catalyst (Soon and Hameed, 2013; Chai et al., 2016; Li et al., 2018; Sun et al., 2019), except a single drying at 80 °C for 2 h, was performed before the next cycle of application.

Fig. 6 depicts both the total MB removal efficiency as well as the TOC reduction in the treated solutions after different cycles of application of the bulky catalyst. It is seen that the total removal efficiency is still above 90% after five cycles. The decrease of efficiency for the five cycles is totally 7.43%, suggesting that 92.57% of the initial efficiency was maintained after 5 cycles. However, the TOC removal actually increases from 47.15% for the first to 56.10 and 75.61% for the second and third cycles, respectively. Similar to the photo-Fenton catalyst reported by Hu et al. (2019), our catalyst also exhibited self-activation behavior in the cyclic application. Two main reasons are responsible for this phenomenon. One is that the  $Fe^{2+}/Fe^{3+}$  ions inside the bulky catalyst were not fully utilized in the first cycle. Another is that the  $Fe^{3+}$  ions either formed by the oxidation of Fe<sup>2+</sup> from preceding cycle or originally existed inside the bulky catalyst had the reactions (2) and (3), leading the formation of new active  $Fe^{2+}$  ions (Cao et al., 2018).

With further increasing the cycles, the total removal efficiency became to decrease again, reaching 54.47% and 41.46% for the fourth and fifth cycles. Comparing with the TOC reduction in the first run, 87.93% of TOC removal efficiency was maintained after five cycles. The decrease in the total removal efficiency was mainly due to the decrease in the surface area of the catalyst. This was confirmed by the N<sub>2</sub>-sorption result that the surface area of the sample after 5 cycles was reduced to  $250 \text{ m}^2/\text{g}$  due to the aforementioned residues of organic molecules in the used catalyst (He



Fig. 6. Cyclic performance of the prepared catalyst.

et al., 2018). The decreases in the TOC reduction in the fourth and fifth cycles are not comparable with those of the total removal efficiency, suggesting that the oxidation of MB was partial in these two cycles and then intermediate species formed.

Compared in Table 1 are the recyclability data of other Fentonlike catalysts used for the MB degradation reported in the references (Photo-Fenton catalysts were not compared herein, because in most cases, without light irradiation, their efficiencies decreased obviously (Chai et al., 2016; Li et al., 2017; Li et al., 2018; Hu et al., 2019)). It can be seen that after 5 cycles the total removal efficiency of the present catalyst is among the highest one and only smaller than that reported for Fe<sub>3</sub>O<sub>4</sub>/carbon octahedra. However, the maximum TOC removal efficiency and especially the capacity of unit mass of catalyst (mg/g) of our sample in either single use or recycled use is much higher than those of reported samples, including the mentioned Fe<sub>3</sub>O<sub>4</sub>/carbon octahedra (Li et al., 2018). The stability of the catalyst was evaluated by measuring the iron leaching in solution. The leaching after the first to the fifth run was in the range of 0.0045-0.037% with an average of 0.021% of the applied catalyst, which is much lower than the reported data (see Table 1), suggesting a good stability of the bulky catalyst. This good stability is due to fact that iron species was chemically bonded with the silica skeleton, which had been evidenced by the FTIR and the XPS results (see Fig. 2 & Fig. 4b and the related discussion). In addition, the confinement of iron species inside the bulky form catalyst also contributed to the observed low leaching of iron into the solution (Hartmann et al., 2010).

The above results indicated that the bulky form catalyst developed herein showed better catalytic performance, stability and recyclability in dye degradation than the reported powder form catalysts. Moreover, the bulky form catalyst can be placed or hung in wastewater and there is no need to disperse the catalyst. They can be conveniently recovered manually with the help of simple tools (e.g. a tweezer) or a simple machine (e.g. a hoister). No special facility or equipment (e.g. high intensity magnetic separator) is needed to collect the used catalyst.

## 4. Conclusions

A bulky form FeO<sub>x</sub>/SiO<sub>2</sub> Fenton-like catalyst was prepared by combining a sol-gel process with industrialized ceramic pressing technique without adding any plasticizer or binder. The catalyst has a large surface area, pore volume and pore size. Its total removal efficiency toward methylene blue in water was 100%, and the TOC reduction was 92.13% mainly due to the iron species-involved Fenton-like catalytic degradation. The catalytic performance (especially the unit mass capacity), recyclability and stability of the developed bulky form catalyst were higher than those of reported powder form Fenton-like catalysts for the degradation of methylene blue, due to its large surface area, uniformly distributed and chemically bonded iron species. The developed bulky catalyst has the following advantages over the others:1)The fabrication process is highly efficient and free of wastewater emission; 2) It can be conveniently used in wastewater treatment without special dispersion; 3) It can be easily recycled. No filtration, centrifugation or magnetic separation facility or equipment is needed for the recovery. These advantages facilitate a scalable production and application of Fenton-like catalyst in real dye contaminated wastewater treatment. However, the reduction of catalyst cost by searching for cheap iron source is needed.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/i.jclepro.2019.06.230.

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