



Efficient degradation of sulfamethazine in simulated and real wastewater at slightly basic pH values using Co-SAM-SCS /H₂O₂ Fenton-like system

Min Cheng^{a, b}, Guangming Zeng^{a, b, *}, Danlian Huang^{a, b, **}, Cui Lai^{a, b}, Yang Liu^{a, b}, Chen Zhang^{a, b}, Jia Wan^{a, b}, Liang Hu^{a, b}, Chengyun Zhou^{a, b}, Weiping Xiong^{a, b}

^a College of Environmental Science and Engineering, Hunan University, Changsha, Hunan 410082, China

^b Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha, Hunan 410082, China

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ABSTRACT

The presence of antibiotics in aquatic environments has attracted global concern. Fenton process is an attractive yet challenging method for antibiotics degradation, especially when such a reaction can be conducted at neutral pH values. In this study, a novel composite Fe/Co catalyst was synthesized via the modification of steel converter slag (SCS) by salicylic acid–methanol (SAM) and cobalt nitrate (Co(NO₃)₂). The catalysts were characterized by N₂-Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), Fourier transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The results indicated that the Co-SAM-SCS/H₂O₂ Fenton-like system was very effective for sulfamethazine (SMZ) degradation at a wide pH range. At initial pH of 7.0, the degradation rate of SMZ in Co-SAM-SCS/H₂O₂ system was 2.48, 3.20, 6.18, and 16.21 times of that in Fe-SAM-SCS/H₂O₂, SAM-SCS/H₂O₂, Co(NO₃)₂/H₂O₂ and SCS/H₂O₂ system, respectively. The preliminary analysis suggested that high surface area of Co-SAM-SCS sample and synergistic effect between introduced Co and SAM-SCS are responsible for the efficient catalytic activity. During the degradation, three main intermediates were identified by high performance liquid chromatography–mass spectrometry (HPLC–MS) analysis. Based on this, a possible degradation pathway was proposed. The SEM images, XRD patterns and XPS spectra before and after the reactions demonstrate that the crystal and chemical structure of Co-SAM-SCS after five cycles are almost unchanged. Besides, the Co-SAM-SCS presented low iron and cobalt leaching (0.17 mg/L and 2.36 mg/L, respectively). The studied Fenton-like process also showed high degradation of SMZ in river water and municipal wastewater. The progress will bring valuable insights to develop high-performance heterogeneous Fenton-like catalysts for environmental remediation.

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1. Introduction

Antibiotics have been excessively abused in veterinary and human medicine. As emerging contaminants, they have drawn increasing attention in recent years owing to their potential adverse effects on human health and aquatic ecology (Cheng et al.,

2016c; Zeng et al., 2013a). Due to their antibacterial and polarity nature, conventional waste-water treatment plants (WWTPs) can only partially remove antibiotics, demonstrating the potential for these compounds to be consistently presented in effluents (Lai et al., 2016; Li et al., 2017; Yang et al., 2010). As a result, antibiotics have been repeatedly detected in surface water and sediment (Cheng et al., 2018b; Guo et al., 2017; Huang et al., 2016; Liu et al., 2017; Zhang et al., 2016). Thus, an effective elimination of these compounds from the environment is important and necessary.

Advanced oxidation processes (AOPs) are promising techniques for the disposal of toxic and persistent organic pollutants in wastewaters (Cheng et al., 2017b; Huang et al., 2017a; Yang et al., 2016, 2017). Among these techniques, Fenton process, based on

* Corresponding author. College of Environmental Science and Engineering, Hunan University, Changsha, Hunan 410082, China.

** Corresponding author. College of Environmental Science and Engineering, Hunan University, Changsha, Hunan 410082, China.

E-mail addresses: zgming@hnu.edu.cn (G. Zeng), huangdanlian@hnu.edu.cn (D. Huang).

the generation of highly reactive hydroxyl radicals ($\text{HO}\bullet$), has received particular attention (Cheng et al., 2016b). The Fenton process holds many advantages, including high degradation efficiency, mild reaction conditions and simple operation (Cheng et al., 2016a). However, Fenton process also suffers from some drawbacks, such as, (1) it requires strict pH regulation (pH 2–4) (Liu et al., 2016), (2) it requires the post-treatment of the dissolved iron ions and sludge (Guo et al., 2014), and (3) it may cause secondary pollution of acids (Burbano et al., 2005), which make this technique complex and uneconomical.

In order to overcome these drawbacks, Fenton-like processes using heterogeneous catalysts containing iron materials have been developed (Navalon et al., 2010). In recent years, hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), magnetite (Fe_3O_4), pyrite (FeS_2) and goethite ($\alpha\text{-FeOOH}$) have been applied as heterogeneous Fenton-like catalysts for the degradation of many organic contaminants over a wider pH range. Steel converter slag (SCS), a final waste material of the steel making process, has high potential to be used in the Fenton-like process as heterogeneous catalyst owing to its abundance of iron oxides (FeO and Fe_2O_3) (Yi et al., 2012). On the other hand, SCS also contains calcium minerals, which can negatively impact the performance of Fenton-like process. It was reported that after adding SCS into the system, solution pH could be rapidly increased from 6.4 to 10, due to the dissolution of calcium minerals (Cheng et al. 2017a, 2018a). Under this condition, the Fenton/Fenton-like reaction would be inefficient. In our previous study, salicylic acid–methanol (SAM) solution was used to dissolve calcium silicate minerals in SCS and successfully improved the catalytic property of SCS (Cheng et al., 2017a). However, like other iron based heterogeneous Fenton-like processes, the degradation was preferentially operated at acidic solutions (pH < 3) (Fan et al., 2009; Ozcan et al., 2017; Shen et al., 2017; Tang et al., 2008). Such a requirement of acidic environment, however, limited the industrial application of the technology because the pollutant solutions always have neutral or slightly basic pH values (Fan et al., 2008; Shen et al., 2017; Zeng et al., 2013b).

Previous studies have shown cobalt based Fenton/Fenton-like process can be operated in neutral pH condition (Bokare and Choi, 2014). On the one hand, the homogeneous $\text{Co}^{2+}/\text{H}_2\text{O}_2$ system was found able to completely decompose the dye pollutant without the control of pH (Ling et al., 2010). On the other hand, the degradation of organic pollutants by heterogeneous Co catalysts was also studied in the presence of H_2O_2 . In one study, Co^{2+} loaded periodic mesoporous aluminum phosphate was utilized as heterogeneous catalyst for the degradation of phenol (Mahamallik and Pal, 2016). In a more recent work, Co^{2+} adsorbed alumina was applied as heterogeneous catalyst to decompose methylene blue and methyl orange (Mahamallik and Pal, 2017). In both cases, Co-based heterogeneous catalysts can effectively degrade the pollutants at neutral or even basic pH.

Inspired by the above idea, in this study, we used Co^{2+} to further improve the catalytic property of SCS in order to deal with the real wastewater, which always has neutral or slightly basic pH values. The sulfamethazine (SMZ), one of the most commonly used antibiotics, was selected as model antibiotics contaminant because of its adverse effects on living being and frequently occurrence in natural water environment (Sopaj et al., 2016). In recent years, chemical oxidation methods, especially the AOPs, have been used for degradation of SMZ, including Fenton reaction based processes (Wan et al., 2016; Wan and Wang, 2017; Wang et al., 2017; Zhou et al. 2013, 2014), photo-catalysis (Babić et al., 2015; Yap et al., 2012), gamma irradiation (Liu et al., 2014; Liu and Wang, 2013), ozonation (Bai et al., 2016; Garoma et al., 2010) and dielectric barrier discharge plasma (Kim et al., 2013). According to the literature, Fenton reaction based processes have been most widely used

for the degradation of SMZ mainly due to their low cost and high efficiency. The other methods may either suffer from high energy consumption or low efficiency. Many works have demonstrated the degradation of SMZ by Fenton reaction based processes; however, most of them were conducted at acidic condition (Wan and Wang, 2017; Wang et al., 2017; Zhou et al. 2013, 2014). Besides, few studies have considered the degradation pathways of SMZ in the system.

The main objectives of this work were to (1) produce a new heterogeneous Fenton-like catalyst and elucidate its morphology evolution process; (2) study the degradation performance of SMZ at neutral pH values in this Fenton-like system and investigate affecting experimental parameters; (3) clarify the Fenton-like reaction mechanism and reveal the promotional role of Co^{2+} in the Fenton-like process; and (4) examine the degradation intermediates of SMZ and propose the possible degradation pathways.

2. Experimental section

2.1. Reagents and materials

The SCS was provided by Valin Iron and Steel Corp (VISTC), Xiangtan, China. The SCS is mainly composed of CaO , SiO_2 , FeO , Fe_2O_3 , MgO , MnO , Al_2O_3 , P_2O_5 and TiO_2 (Table S1). The raw SCS was grinded with a planetary ball mill (YXQM-4L, MITR, China) and sieved with a 0.05 mm mesh sieve to remove the large particles. Sulfamethazine ($\text{C}_{14}\text{H}_{20}\text{ClN}_2\text{O}_2$, standard grade) was obtained from Sigma-Aldrich (Missouri, USA). Cobalt nitrate hexahydrous ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, analytical grade), methanol (chromatographic grade), salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$, analytical grade) and hydrogen peroxide (H_2O_2 , 30% in water) were obtained from Beijing Sinopharm Chemical Reagent Corp (China). Ultrapure water ($18.3 \text{ M}\Omega\cdot\text{cm}^{-1}$) was used in all the batch experiments.

2.2. Preparation of SAM-modified SCS

The preparation of SAM-modified SCS (SAM-SCS) was reported in a previously work (Cheng et al., 2017a). Briefly, 50 g of the dried SCS powder was added in 100 mL SAM solution (50 g/L) and stirred at 200 rpm for 4 h at 25 °C. The mixture was then filtered with the suction filter machine using a 0.45 μm filter membrane. The filtration residue was washed repeatedly with ultrapure water and then dried at 105 °C for 24 h.

2.3. Preparation of Co-SAM-SCS

Co^{2+} was introduced to the surface of SAM-SCS by a simple adsorption process. At first, 1 g of prepared SAM-SCS was dispersed in a glass beaker containing 50 mL of ultrapure water. The beaker was placed in a constant temperature (25 °C) ultrasonic bath to obtain homogeneous SAM-SCS dispersion. After 30 min, 2 mL of $\text{Co}(\text{NO}_3)_2$ solution (0.2 M) was equally and slowly added to the beaker and maintained for another 0.5 h ultrasonic treatment. The beaker was then transferred to a magnetic stirrer and constantly stirred for 4 h at 25 °C. After that, the suspension was filtered and filtration residue (Co^{2+} loaded SAM-SCS, Co-SAM-SCS) was washed with ultrapure water for several times and dried in an oven at 80 °C for 24 h. As a comparison, Fe^{2+} loaded SAM-SCS (Fe-SAM-SCS) catalyst was also prepared according to the above method, where Fe^{2+} was used to replace Co^{2+} .

2.4. Characterization

Characterization of the catalysts (SCS, SAM-SCS, Co-SAM-SCS) was performed by using Brunauer–Emmett–Teller (BET), scanning

electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectrum (XPS), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR). The specific surface area, pore volume and pore size of SCS, SAM-SCS and Co-SAM-SCS were measured by the N₂-BET adsorption method (Micromeritics Instrument Corporation, TRI-STAR3020, USA). The morphology of the catalysts was examined by SEM scanning (Carl Zeiss, EVO-MA10, Germany). EDS of the samples was performed with an energy dispersive X-ray detector (Oxford Instruments, UK). The crystal structure of the catalysts was examined with a D/max-2500 X-ray diffractometer (Rigaku, Japan) with Cu K α radiation, testing in the region of 2 θ from 5° to 80°. FTIR absorption spectra were obtained from a GX spectrophotometer (Perkin Elmer, USA) with the standard KBr disk method. In addition, XPS was adopted to investigate the chemical states of elements by using an Axis Ultra spectrometer (Kratos, Japan) with Al K α source ($h\nu = 1486.6$ eV). In the electron paramagnetic resonance (EPR) measurements, 50 mL of solution was sampled out from the heterogeneous Fenton-like system and mixed with 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO, 50 mM) to create DMPO- \bullet OH adducts.

2.5. Adsorption experiments

The adsorption characteristics of the prepared catalysts were evaluated by adsorption experiments using SMZ solution. The initial SMZ concentration used in this study was 5 mg/L. All batch experiments were performed in 250 mL flasks containing 100 mL of SMZ solution and 50 mg of SCS, SAM-SCS, Fe-SAM-SCS or Co-SAM-SCS, which were stirred in a water bath shaker at 160 rpm and 25 ± 0.5 °C. For certain time intervals, 0.5 mL of solution was sampled out for measurement of the concentration of SMZ. The adsorbed amount of SMZ was calculated as follow:

$$Q_t = (C_0 - C_t) V/m \quad (1)$$

Where Q_t is the adsorption quantity of SMZ on SCS, SAM-SCS or Co-SAM-SCS (mg/g); C_0 and C_t are the initial concentration and the measured concentration of SMZ (mg/L), respectively; m is the weight of SCS, SAM-SCS or Co-SAM-SCS (g) and V is the volume of SMZ solution (L).

The pseudo-first order kinetic model (2) (Lagergren, 1898) and pseudo-second order kinetic model (3) (Ho and McKay, 1998) were adopted to study the adsorption kinetics.

$$\log (Q_e - Q_t) = \log Q_e - k_f t / 2.303 \quad (2)$$

$$t/Q_t = 1/k_s Q_e^2 + t/Q_e \quad (3)$$

Where Q_t and Q_e are the adsorbed amount (mg/g) of SMZ on adsorbents at t and equilibrium, respectively. k_f is pseudo-first rate constant (1/h), and k_s is the pseudo-second rate constant (g/mg \cdot h), respectively.

2.6. Fenton-like reaction

The heterogeneous Fenton-like reaction was performed in 250 mL glass conical flasks containing 100 mL of reaction solution at 25 °C and stirred at 160 rpm. SMZ concentration in all experiment groups was 50 mg/L. The initial pH of SMZ solution was set as 7.0 unless other mentioned. Typically, in the comparative degradation experiment, 50 mg of SCS, SAM-SCS, Fe-SAM-SCS or Co-SAM-SCS was added in 100 mL SMZ solution, and then a certain amount of H₂O₂ solution (30 wt%) was added to trigger the Fenton-like reactions. For certain time intervals, 0.5 mL of reaction solution was sampled out for measurement of the concentration of SMZ. In

the preliminary experiment on the real wastewater treatment, tap water (derived from Changsha running-water company), river water (Xiangjiang River, Changsha, China) and municipal wastewater (obtained from Changsha 1st sewage treatment plant, Changsha, China) were used as the solution for the preparation of 50 mg/L SMZ wastewater. In these experiments, the catalyst loading is 0.7 g/L, H₂O₂ dosage is 4%, and the initial pH of the solution was adjusted to 9.0. The experiments were performed in 250 mL glass conical flasks containing 100 mL of reaction solution at 25 °C and stirred at 160 rpm. All the experiments (including the adsorption experiments) were performed in triplicate.

2.7. Analytical methods

The concentration of SMZ was measured according to a published method (Teixido et al., 2013) by high performance liquid chromatography (HPLC, Agilent 1100 series, USA) with an Agilent TC-C18 column (4.6 \times 250 mm, 5 μ m). In addition, SMZ mineralization was evaluated by detecting the TOC with a TOC-5000A model analyzer (Shimadzu, Japan). The intermediates analysis was performed by an ultra-high-performance liquid chromatography mass spectrometry (UPLC-MS, Agilent 1290/6460, Triple Quad MS, USA) system equipped with an Symmetry C18 column (50 mm \times 2.1 mm \times 5 μ m). The detailed description of detecting condition was provided in [supplementary material](#). Total iron concentration in the solution after the reaction was determined using the 1, 10-phenanthroline-based method (HACH method 8146) with a HACH DR2000 spectrophotometer (Hach, USA). Cobalt concentration in the solution after the reaction was measured by flameless atomic absorption spectroscopy (AAS, PEA700, Perkin Elmer, USA). The filtrate of the reaction solution was used in above mentioned measurements.

3. Results and discussion

3.1. Physicochemical characterization of the prepared catalysts

The prepared catalysts (SCS, SAM-SCS, Co-SAM-SCS and used-Co-SAM-SCS) were characterized via different methods. Firstly, the surface properties of the catalysts were investigated by BET analysis. We found that specific surface areas of SCS increased from 67.14 to 179.62 m²/g (Table S2) after SAM modification, suggesting that SAM modification significantly changed the morphology of SCS. The remarkable increase in specific surface area is because calcium silicate minerals in the surface of SCS were selectively removed by SAM treatment, resulting in forming irregular surfaces (Cheng et al., 2017a). Compared to SAM-SCS, Co-SAM-SCS showed an even larger specific surface area, this could be ascribed to the fact that Co formed new structure on the surface of SAM-SCS. Only a slight decrease was observed in the surface areas of used-Co-SAM-SCS, indicated that no significant change occurred in the morphology of SAM-SCS during the Fenton-like experiments. On the other hand, the hysteresis of modified-SCS (SAM-SCS, Co-SAM-SCS and used-Co-SAM-SCS) was observed (Fig. S1), indicating that the modified-SCS presented the larger number of mesoporous compared to SCS.

SEM was applied to further study the morphologies changes of SCS. As seen from Fig. 1a, the surface of SCS was relatively flat and smooth. After SAM modification, there was an obvious change in the surface morphology of SCS. As displayed in Fig. 1b, SAM-SCS presented irregular shapes and sizes. Fig. 1c revealed that after Co²⁺ deposition SAM-SCS surface was covered by a rather uniform Co layer. SEM image of used-Co-SAM-SCS is very similar to that of Co-SAM-SCS (Fig. 1c), further demonstrating that no significant change occurred in the morphology of Co-SAM-SCS during the

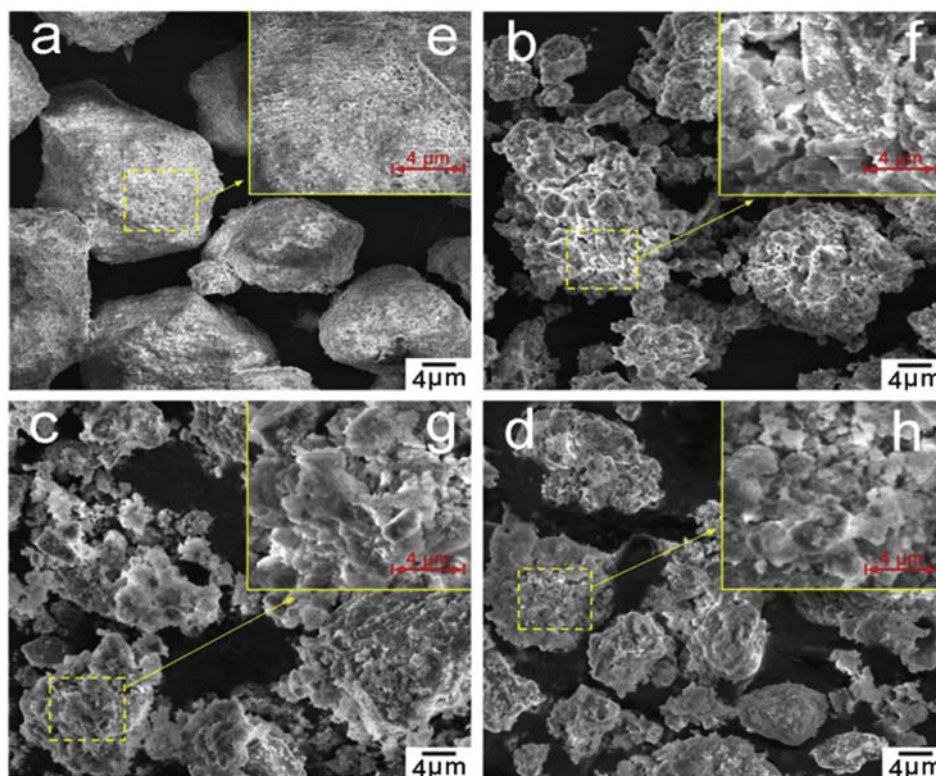


Fig. 1. SEM images of SCS (a), SAM-SCS (b), Co-SAM-SCS (c) and Used-Co-SAM-SCS (d), and the enlarged SEM images of SCS (e), SAM-SCS (f), Co-SAM-SCS (g) and Used-Co-SAM-SCS (h).

Fenton-like degradation experiments.

Additional elemental mappings combined with EDS analysis for the prepared catalysts were also performed. EDS analysis showed that the unmodified SCS mainly consists of O, Ca, Fe, Si, Mg, Mn and Al (Fig. S2a). After SAM modification, these elements are still detected (Fig. S2b), but a distinct variation in the signals of them was observed. As illustrated in Table S3, the content of Ca was remarkably decreased, while Fe content was increased after SAM modification. In particular, the mass ratio of Ca to Fe was decreased from 2.27 to 1.29 after SAM modification. The results from element mapping coincided well with the EDX analysis. For example, we can clearly see from Fig. 2 that the signal intensity of Ca gradually reduced after the modifications. The Co element distributed throughout the film of Co-SAM-SCS (Fig. 2O) and used-Co-SAM-SCS (Fig. 2T), suggesting that Co had been evenly dispersed on the surface of SAM-SCS and maintained good stability.

XRD diffraction patterns of SCS, SAM-SCS, Co-SAM-SCS and used-Co-SAM-SCS were obtained to evaluate the modification of SCS with SAM and Co^{2+} (Fig. 3). As can be seen in Fig. 3a, the intensities of dicalcium silicate peaks (2θ : 32.02° and 32.92° , JCPDS 77–0409) prominently decreased after SAM modification. On the contrary, the intensities of iron oxide peaks (2θ : 36.21° , 42.07° and 61.16° , JCPDS 74–1880) of SAM-SCS were enhanced as compared to those of unmodified SCS. XRD analysis indicated that the SAM modification removed a portion of calcium silicate minerals from SCS. As for SAM-SCS and Co-SAM-SCS, the similar XRD patterns were found (Fig. 3). That is to say, the introduction of Co in the catalyst had no noticeable influence on its crystalline structure. The peaks for CoO (2θ : 36.37° , 42.26° and 61.38° , JCPDS 48–1719) were found in Co-SAM-SCS, suggesting that Co was successfully introduced onto the surface of SAM-SCS. No obvious decline in Co peaks after 5 cycles of degradation test revealed that a negligible amount

of Co on the surface of SAM-SCS was lost during the Fenton-like processes. The decrease in the peak at 2θ values of 29.36° belongs to CaCO_3 (JCPDS 05–0586) in Co-SAM-SCS and used-Co-SAM-SCS may attribute to that part of CaCO_3 in SAM-SCS was removed under acidic condition during the preparation of Co-SAM-SCS.

The structure of the catalysts was also studied by FT-IR spectra. As displayed in Fig. 3b, the FT-IR spectra of SCS and SAM-modified SCS are similar. The broad bands in the range of $1400\text{--}1500\text{ cm}^{-1}$ and $800\text{--}1000\text{ cm}^{-1}$ are primarily associated to the stretching vibrations of Ca–O (Gadsden, 1975) and Si–O (Criado et al., 2007), respectively. The bands of Ca–O and Si–O decreased obviously after SAM modification, which was in agreement with XRD analysis. For Co-SAM-SCS, no discernible discrepancy was observed, which is likely due to the small amount of Co in the catalyst, and it also inferred that the introduction of Co has no impacts on the initial chemical structure of SAM-SCS.

Fig. 4A displays the comparison of the survey spectra of SCS and SAM-modified SCS. The elements of Si (102.3 eV), Ca (347.5 eV, 351.2 eV), Fe (711.7 eV, 724.9 eV), O (531.1 eV) and Mg (1303.7 eV) can be clearly observed on the spectra of all the four samples, while the elements of Co can only be observed on the spectra of Co-SAM-SCS and used-Co-SAM-SCS. Fig. 4B and C presents the high resolution XPS spectra of Ca and Fe, respectively. It can be clearly seen from Fig. 4B that Ca 2p peaks with the binding energy of 347.5 eV and 351.2 eV in SAM-SCS are much weaker than that in SCS, and these peaks in the spectra of Co-SAM-SCS and used-Co-SAM-SCS further decreased as compared to those in SAM-SCS. Fig. 4C shows the Fe 2p spectrum with two individual peaks located at 724.6 eV for Fe $2p_{1/2}$ and the other one with the binding energy of 711.7 eV is assigned to Fe $2p_{3/2}$. It was found that Fe 2p peaks in the spectra of modified SCS (SAM-SCS, Co-SAM-SCS and used-Co-SAM-SCS) were enhanced as compared with those in the spectra of SCS.

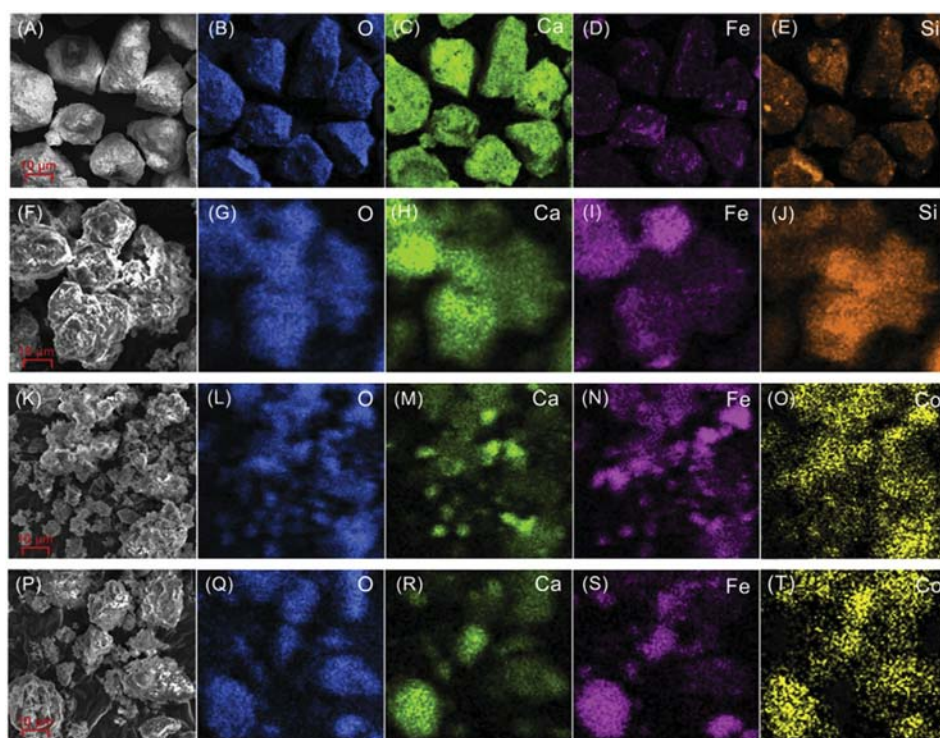


Fig. 2. SEM-EDS elemental mapping images of SCS (A–E), SAM-SCS (F–J), Co-SAM-SCS (K–O) and Used-Co-SAM-SCS (P–T).

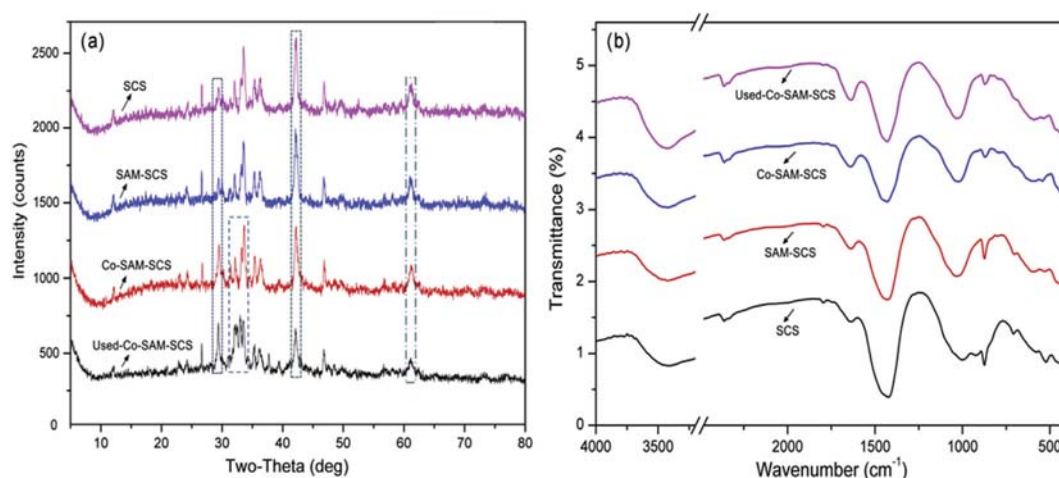


Fig. 3. XRD patterns (a) and FTIR absorption spectra (b) of SCS, SAM-SCS, Co-SAM-SCS and Used-Co-SAM-SCS.

We found there was no discernible change in the XPS spectra of Co for Co-SAM-SCS and used-Co-SAM-SCS (Fig. 4D). Two major peaks with binding energies at 797.6 eV and 781.6 eV are attributed to Co 2p_{3/2} and Co 2p_{1/2} of Co, and the satellite peaks were found at 786.4 eV and 803.7 eV (Li et al., 2016). Overall the XPS results coincided well with the SEM, EDS, and XRD analysis.

3.2. Adsorption of SMZ by the catalysts

The adsorption of organic pollutants onto the surface of catalysts are important for the catalytic degradation since the heterogeneous Fenton-like degradation mainly occurs at the solid–liquid interface (Xie et al., 2014). Thus, in the first step, the adsorption of SMZ by SCS, SAM-SCS and Co-SAM-SCS was studied by using 5 mg/

L of SMZ solution. As revealed in Fig. 5, the adsorption of SMZ increased quickly in 30 min and achieved adsorption equilibrium within 2 h in all three studied systems. Fig. 5 demonstrates that the adsorption performance of Co-SAM-SCS is similar to that of SAM-SCS, whereas SCS shows much lower adsorption capability. The remarkable adsorption rate can be ascribed to the changes of surface structure and chemical composition of SCS. As shown in Table S2 and Fig. 1, the surface area, total porosity and total pore volume of SCS increased largely after SAM modification. Further study showed that the sorption kinetics of SMZ on SCS, SAM-SCS and Co-SAM-SCS can be well fitted by pseudo-second order kinetic model ($R^2 = 0.9995$, 0.9994 and 0.9997 , respectively), suggesting chemisorption is the rate-limiting step for sorption (Brusseau et al., 1991; Gong et al., 2009; Xu et al., 2012).

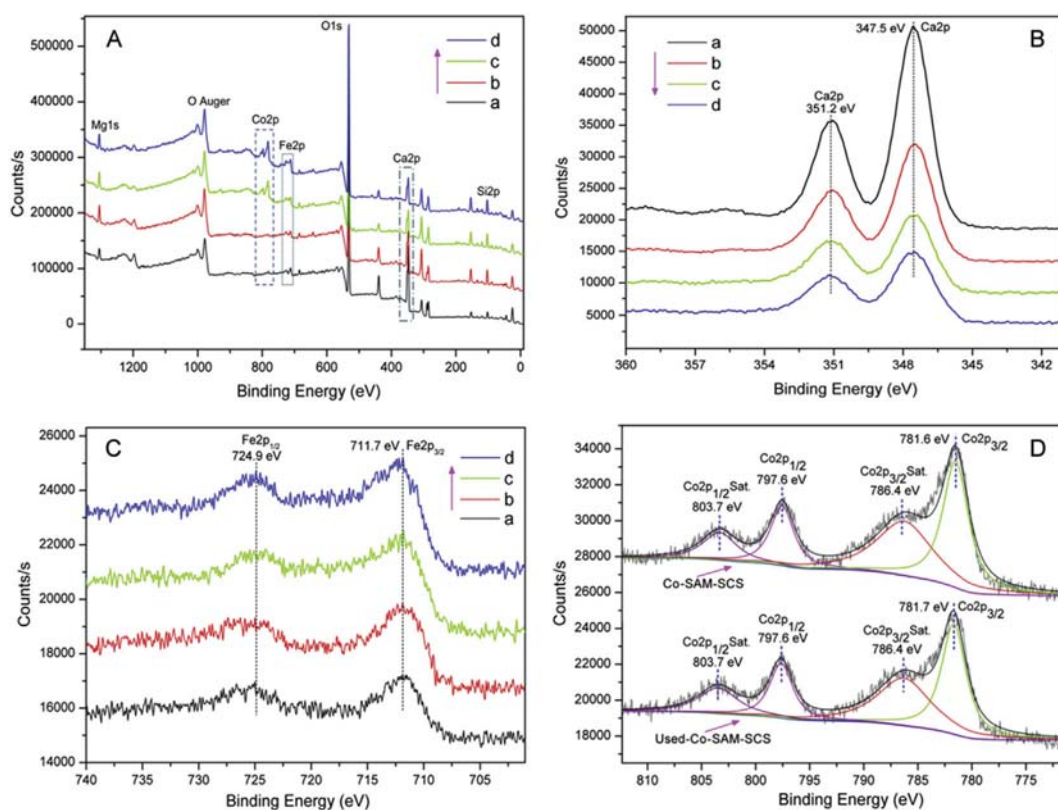


Fig. 4. XPS spectra of the SCS-based catalysts: (A) survey, (B) Ca 2p, (C) Fe 2p and (D) Co 2p. (a): SCS, (b): SAM-SCS, (c): Co-SAM-SCS, (d) used-Co-SAM-SCS.

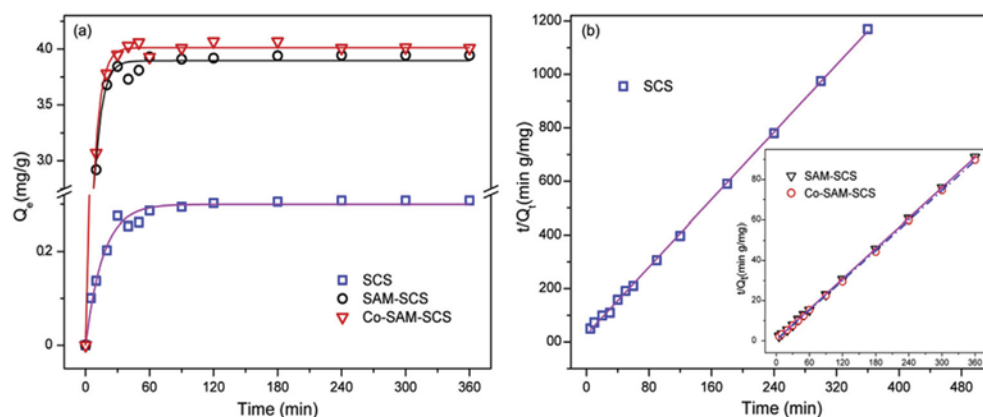


Fig. 5. The sorption kinetics of SMZ on SCS SAM-SCS and Co-SAM-SCS. (a) fitted by pseudo-first order kinetic; (b) fitted by pseudo-second order kinetic.

3.3. Comparative degradation behavior of SMZ in different Fenton-like systems

Degradation behaviors of SMZ were investigated by homogeneous and heterogeneous Fenton-like processes to evaluate the catalytic activity of Co-SAM-SCS (Fig. 6). The degradation experiments were conducted at pH 7.0 with 50 mg/L of SMZ solution. Fig. 6a illustrated that the degradation rates of SMZ were very different to each other in these systems. It was found that 4.79% of SMZ was removed in the SCS/H₂O₂ system within the first 1 h and then the concentration of SMZ did not significantly change during the subsequent 3 h (Fig. 6a). The SAM modification enhanced the catalytic ability of SCS, approximately 20% degradation efficiency enhancement, which mainly due to the reduction of calcium

mineral and the formation of higher surface area. What's more, the removal rate of SMZ could reach to 77.62% when Co²⁺ was introduced to SAM-SCS.

For comparison, Co(NO₃)₂ and Fe-SAM-SCS were also taken into consideration. As shown in Fig. 6a, the efficiency of heterogeneous Co²⁺/H₂O₂ Fenton-like process was relatively low, only 12.56% of SMZ was degraded in 240 min. This is because high H₂O₂ concentration (H₂O₂/Co²⁺ = 6) is required to achieve efficient oxidation in heterogeneous Co²⁺/H₂O₂ system (Bokare and Choi, 2014; Ling et al., 2010). Compared with SAM-SCS, Fe-SAM-SCS exhibited higher catalytic activity and SMZ concentration was reduced by 31.63%. However, this value is not comparable with that of Co-SAM-SCS, which could be ascribed to the fact that Fe-based Fenton/Fenton-like reactions are more efficient at acidic condition. Over all,

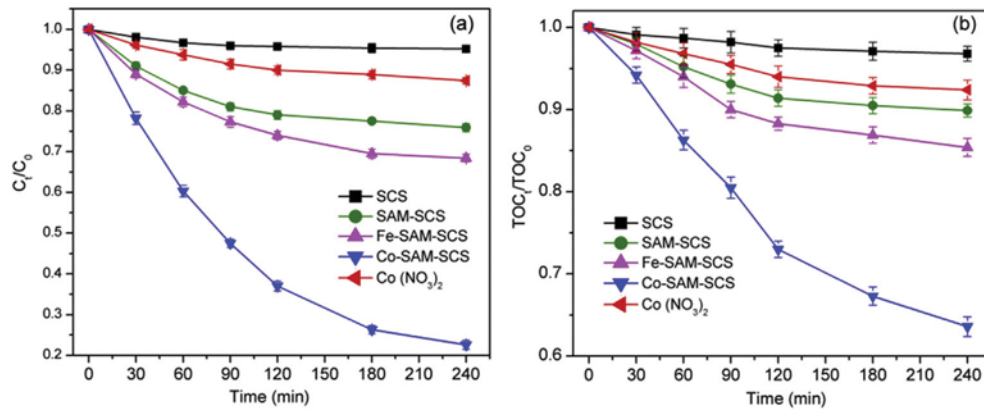
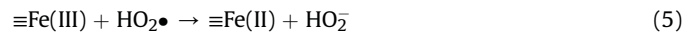


Fig. 6. The variation of SMZ concentration (a) and TOC (b) in different operation systems. Experiment condition: H_2O_2 dosage = 2%; catalyst loading = 0.7 g/L; SMZ concentration = 50 mg/L; Temperature = 25 °C; initial pH = 7.

the corresponding degradation rates of all the catalysts were in the following order: Co-SAM-SCS > Fe-SAM-SCS > SAM-SCS > $\text{Co}(\text{NO}_3)_2$ > SCS. Besides, these results are in good accordance with the results of TOC analysis (Fig. 6b), demonstrating that Co-SAM-SCS has high potential in practical applications.

3.4. Effects of catalyst loading, H_2O_2 dosage and pH on SMZ degradation

The effects of catalyst concentration on the degradation rates of SMZ were evaluated by performing experiments with the presence of increasing amounts of Co-SAM-SCS. As seen in Fig. 7a, SMZ removal in 240 min increased from 29.31% to 82.57% along with the increase of catalyst dosage from 0.1 to 0.7 g/L. This is probably due to that the number of active sites increased as the increased Co-SAM-SCS loadings, which accelerated the decomposition of H_2O_2 and the generation of $\text{HO}\cdot$. On the other hand, the decline in SMZ removal was observed when increasing Co-SAM-SCS loading up to 1.0 g/L. The probable reason was that the excessive Co-SAM-SCS decreased the density of surface adsorbed H_2O_2 , and reduced the concentration of $\text{HO}\cdot$ on the solid-liquid inter-surface (Wang et al., 2016). Besides, there also research suggested that iron surfaces would then cause the undesirable consumption of radicals (e.g., $\text{HO}\cdot$ and $\text{HOO}\cdot$) through the following equations (Cheng et al., 2014; Hu et al., 2011b; Huang et al., 2012).



The effect of H_2O_2 dosage (0%–6%) on the degradation of SMZ was then examined. The experimental results (Fig. 7b) showed the removal of SMZ was quite limited (less than 5%) in the absence of H_2O_2 . In fact, this part of SMZ was removed by the adsorption of Co-SAM-SCS. The introduction of H_2O_2 into the SMZ solution significantly accelerated the removal of SMZ. The degradation rate of SMZ increased along with the increase of H_2O_2 dosage from 1% to 4%, indicating that the concentration of H_2O_2 was directly related to the degradation of SMZ. That makes sense, because H_2O_2 is directly involved in the generation of the reactive radicals. However, the degradation rate of SMZ decreased when the H_2O_2 dosage further increased to 6%, which is possibly due to the scavenging of $\text{HO}\cdot$ by excessive H_2O_2 through equations (6) and (7) (Hu et al., 2011a; Huang et al., 2008; Xia et al., 2011).



It has been well established that pH of the solution plays a critical role in the efficiency of the Fenton/Fenton-like oxidation. In

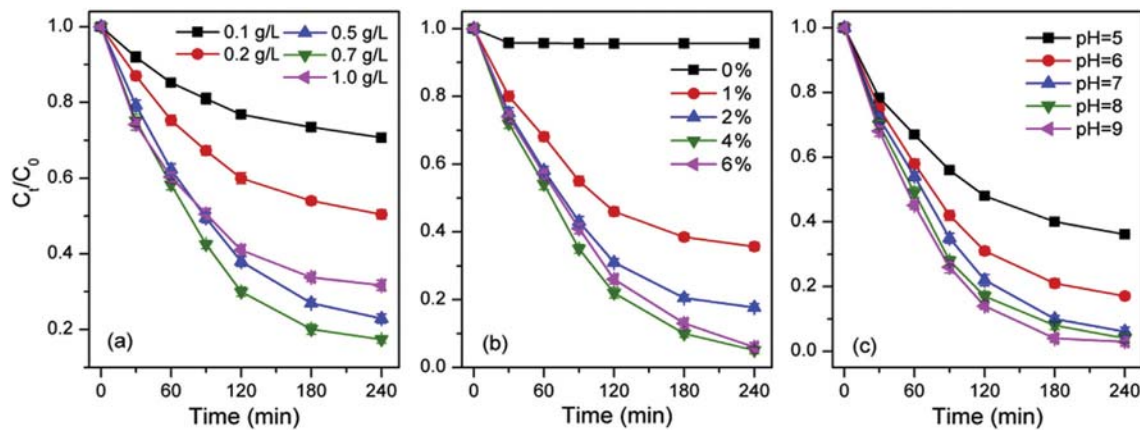


Fig. 7. Effects of (a) catalyst loading, (b) H_2O_2 dosage, and (c) initial pH in degradation rates of SMZ. Experimental conditions: (a) SMZ concentration = 50 mg/L; H_2O_2 dosage = 2%; Temperature = 25 °C; pH = 7; (b) catalyst loading = 0.7 g/L; SMZ concentration = 50 mg/L; Temperature = 25 °C; initial pH = 7; (c) catalyst loading = 0.7 g/L; SMZ concentration = 50 mg/L; H_2O_2 dosage = 4%; Temperature = 25 °C.

the tested pH range (5–9), at least 60% of SMZ can be degraded after 240 min, suggesting that Co-SAM-SCS could be used for degradation of organic contaminants over a wide range of pH values. As illustrated in Fig. 7c, the degradation efficiency increased gradually as pH increased from 5.0 to 9.0, which indicated that the increase of pH favored the catalytic degradation of SMZ in the Co-SAM-SCS/H₂O₂ system. This result would be ascribed to the fact that Co rather than Fe played the major role in the catalytic degradation of SMZ under low pH condition. In this regard, the Co-SAM-SCS catalyzed heterogeneous Fenton-like process showed a remarkable advantage due to the working environment.

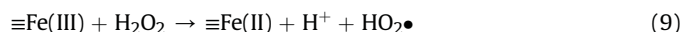
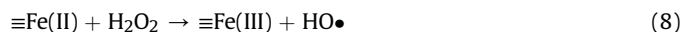
3.5. Identification of the dominant radicals

It has been widely accepted that the degradation of pollutants is attributed to the generation of radicals originated from the activation of H₂O₂ in the Fenton/Fenton-like process (Centi and Perathoner, 2003). In order to elucidate the reaction mechanism in depth, the dominant radical that contributes to the degradation of SMZ was identified by free radical trapping experiments. In this study, *tert*-butyl alcohol (TBA) was utilized for hydroxyl radical (HO•) scavenger and 1,4-benzoquinone (BQ) was used for superoxide radical (•O₂⁻) scavenger (Feng et al., 2010; Ozcan et al., 2017). As seen from Fig. 8a, addition of BQ caused a slight decrease in the degradation rate of SMZ, indicating that O₂•⁻ played a minor role in SMZ degradation. On the other hand, TBA caused prominently deactivation of the Co-SAM-SCS catalyst. The degradation rate of SMZ declined from 96.72% to 37.13% in the presence of 20 mM of TBA, which demonstrated the crucial role of HO• in the catalytic degradation process. According to these results, it can be concluded that the major active specie in this heterogeneous Fenton-like reaction should be HO•. The formation of HO• was also verified by EPR spin trapping experiment. Fig. 8b reveals that HO• were generated in Co-SAM-SCS/H₂O₂ and SAM-SCS/H₂O₂ systems. The intensity of the generated HO• was found to be almost 3 times higher for Co-SAM-SCS than for SAM-SCS. These results were consistent with the observed enhancement in SMZ removal.

3.6. Possible activation mechanisms of H₂O₂

It is generally accepted that in iron oxides based Fenton oxidation systems, HO• is believed to be generated by the decomposition of H₂O₂ on the surface of the heterogeneous catalyst through Eqs. (8) and (9) (Zhao et al., 2017). In these processes, Fe(II) is produced

via reduction of Fe(III), while HO• is continuously generated from the decomposition of H₂O₂. Meanwhile, it should be noted that competitive reactions (e.g., Eqs. (1) and (2)) could occur (Hu et al., 2011b; Huang et al., 2012; Zhang et al., 2007), which negatively influence the Fenton process.



By contrast, the generation of HO• by Co²⁺-mediated activation of H₂O₂ has been documented only in a few studies. Based on previous researches (Bokare and Choi, 2014; Shen et al., 2017) and the experimental results obtained in this work, a possible HO• formation mechanism by Co can be proposed as Eqs. (10–12). Very interesting, HO₂⁻ produced in the competitive reaction (Eq. (5)) of iron based Fenton processes, plays an important role in the reduction of Co(III) (Eq. (12)). What's more, HO₂• generated from Eqs. (9) and (12) can react with Fe(III) to produce HO₂⁻ via Eq. (5). That is to say, Co and Fe on the surface of Co-SAM-SCS present synergistic effects on the efficient generation of HO• (Fig. 9).

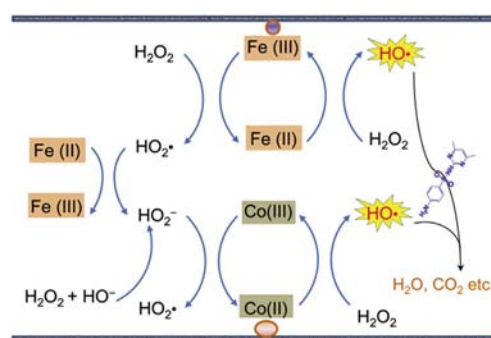
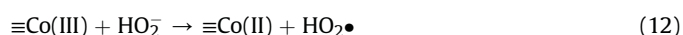
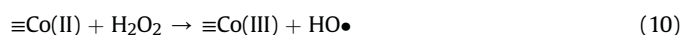


Fig. 9. Possible activation mechanisms of H₂O₂ in Co-SAM-SCS/H₂O₂ system.

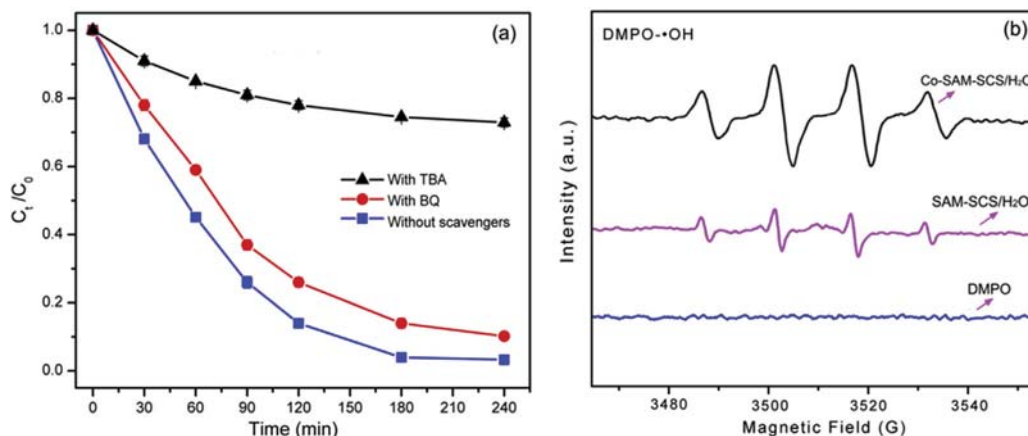


Fig. 8. (a) Effect of radical scavengers on SMZ degradation. Reaction conditions: catalyst loading = 0.7 g/L; H₂O₂ dosage = 4%; Concentration of radical scavenger = 20 mM; Temperature = 25 °C; pH = 9. (b) DMPO spin-trapping EPR spectra obtained from different systems. All the spectra were recorded 10 min after mixing. Reaction conditions: catalyst loading = 0.7 g/L; H₂O₂ dosage = 4%; DMPO concentration = 50 mM; Temperature = 25 °C; pH = 9.0.

As shown in Eq. (11), HO^- plays an important role in the Co(II)/Co(III) circulation, which has been varied by our result in section 3.3 that the Co-SAM-SCS catalyst exhibited better catalytic performance in alkaline solutions (pH = 9) than acidic solution (pH = 5). At higher pH, a larger number of perhydroxyl anions (HO_2^-) were present in the solution (Eq. (11)). Compared with H_2O_2 molecules, HO_2^- is more nucleophilic and show higher activity to interact with Co(III) in the Co-SAM-SCS catalyst (Eq. (12)) (Nguyen et al., 2013).

3.7. Degradation intermediates and pathway of the SMZ degradation

To fully understand the degradation process of SMZ by the Co-SAM-SCS catalyzed Fenton-like reaction, LC-MS analyses were further performed to identify the oxidation products of SMZ. The LC patterns showed that intensity of SMZ peak (3.52 min) decreased quickly after H_2O_2 was added to the system (Fig. 10a). Meanwhile, two peaks emerged between 0.60 min and 1.10 min, and the intensity of them increased gradually with the reaction time. In our study, three main degradation intermediates of SMZ were detected by LC-MS, which included N-(4,6-dimethylpyrimidin-2-yl)benzene-1,4-diamine (A, m/z 215), 4-aminophenol (B, m/z 110) and 4,6-dimethylpyrimidin-2-ol (C, m/z 125) (Fig. S3). Further, we found that A was the dominant product at 60 min, but C became the most abundant product after 120 min. On the basis of these information and the studies (Guo et al., 2013; Li et al., 2017) published previously, a possible degradation pathway of SMZ in the Co-SAM-SCS/ H_2O_2 system was proposed in Fig. 10b. First, SO_2 elimination driven by $\text{HO}\cdot$ led to the formation of A, which is a phenomenon frequently observed in the degradation of sulfonamides (Boreen et al., 2005; Huang et al., 2017b; Neafsey et al., 2010). Then, C–N bond on the benzene ring was cleaved to form the degradation products of B and C. Finally, B and C could be further attacked by $\text{HO}\cdot$, leading to the formation of harmless inorganic species and small-molecule organic acids.

3.8. The stability and the degradation of SMZ in natural samples

The stability of the catalyst is an important issue that should be considered before actual application. The reusability is commonly used for evaluating the stability of Co-SAM-SCS. As shown in Fig. 11, the degradation efficiency was nearly maintained at the level of fresh sample after five successive runs. Furthermore, the structural

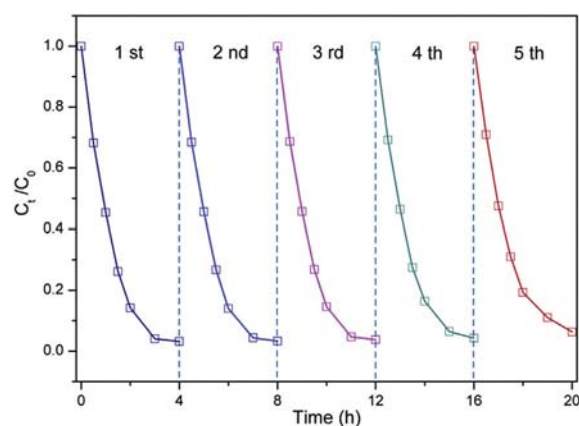


Fig. 11. Cycling runs for the degradation of SMZ in the presence of Co-SAM-SCS and H_2O_2 . Experimental conditions: catalyst loading = 0.7 g/L; SMZ concentration = 50 mg/L; H_2O_2 dosage = 4%; Temperature = 25 °C.

stability of the Co-SAM-SCS catalyst was examined by SEM (Fig. 1), EDS (Fig. 2), XRD (Fig. 3) and XPS (Fig. 4), as can be seen, the crystal structure and morphology of used-Co-SAM-SCS are very similar to those of fresh Co-SAM-SCS. In addition, the leached Co and Fe after reaction were only 2.36 mg/L and 0.17 mg/L, respectively.

In real applications, the composition of actual wastewater is extremely complex. Therefore, huge differences could be obtained between removal efficiencies in a simulated wastewater and an actual polluted wastewater. In this work, the removal efficiency of SMZ by Co-SAM-SCS/ H_2O_2 was studied using ultrapure water, tap water (Changsha Running-water Company), river water (taken from Xiangjiang River, Changsha), and municipal wastewater (obtained from Changsha 1st sewage treatment plant, China). The results showed that, after the Fenton-like process, more than 95% of SMZ is removed by Co-SAM-SCS/ H_2O_2 for ultrapure water, ultrapure water and river water (Fig. S4). While relatively lower removal of SMZ (about 86%) was observed in wastewater, this is probably due to the competition of $\text{HO}\cdot$ by the abundant organic matters in municipal wastewater. The obtained results greatly suggested that this novel catalyst exhibited good stability, and also has a great potential for practical treatment of real wastewater. The versatility of this Co-SAM-SCS/ H_2O_2 system is also enhanced by the fact that it can work efficiently in neutral or slightly basic pH condition. More

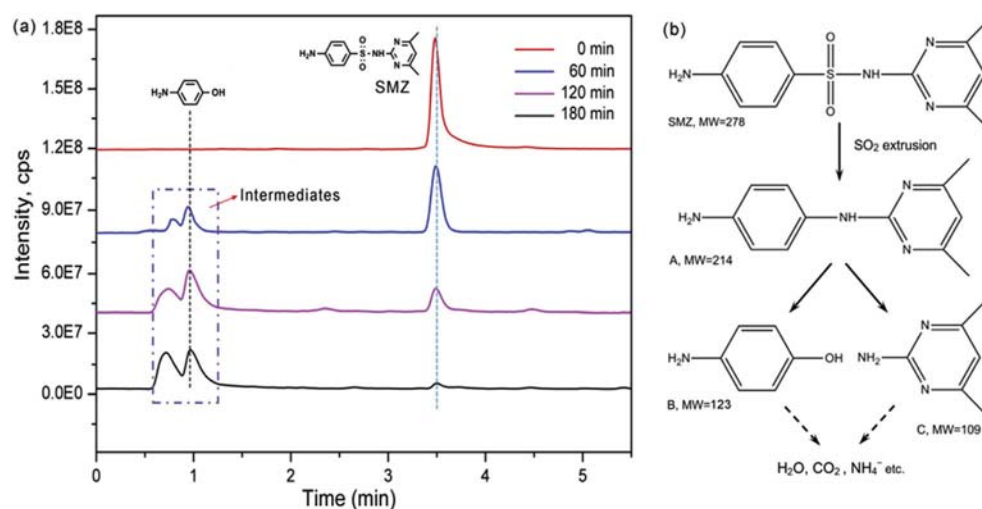


Fig. 10. LC spectra of the intermediates detected in the Co-SAM-SCS/ H_2O_2 system (a.), and the proposed degradation pathways of SMZ in this system (b.).

Table 1

Summary of the treatment costs of different AOPs. The total treatment cost includes the energy and chemical costs.

Process	Pollutants and the concentrations	Chemicals and the concentrations	Operating conditions	Removal efficiency	Total treatment cost	Reference
Hydrodynamic cavitation + O ₃ + H ₂ O ₂	Carbamazepine: 10 mg/L	O ₃ flow rate: 400 mg/h H ₂ O ₂ : 50 mg/L	Volume: 4 L; pH: 4; inlet pressure: 5 bar	100%	4.55 US\$/m ³	Thanekar et al., 2018
O ₃ + sonication	Dichlorvos: 20 mg/L	O ₃ flow rate: 576 mg/h	Volume: 7 L; pH: 3; 100% ultrasonic: 36 kHz		9.1 US\$/m ³	Patil and Gogate, 2015
iO ₂ + solar	Dichlorvos: 20 mg/L	TiO ₂ : 100 mg/L	Volume: 7 L; pH: 3	78.4%	4.23 US\$/m ³	Patil and Gogate, 2015
enton-like + sonication	Reactive black 5: 49.6 mg/L	Fe (0): 1000 mg/L H ₂ O ₂ : 350 mg/L	Volume: 1 L; pH: 3; 99% ultrasonic: 60 kHz		2.25 US\$/m ³	Weng et al. 2013
Fenton-like + sonication	Reactive orange 107: 50 mg/L	Fe ₃ O ₄ : 800 mg/L H ₂ O ₂ : 340 mg/L	Volume: 0.7 L; pH: 3; ultrasonic: 24 kHz	100%	13.07 US\$/m ³	Jaafarzadeh et al., 2018
Fenton-like	Sulfamethazine: 50 mg/L	Co-SAM-SCS: 700 mg/L H ₂ O ₂ : 12 g/L	Volume: 0.1 L; pH: 9	96.7%	10.0 US\$/m ³	This study

importantly, the catalyst can be recovered by a simple settling and separation process, which enables the reuse of the catalyst.

3.9. Operating cost-efficiency comparison

The raw materials and chemicals used in the preparation of Co-SAM-SCS can be cheaply provided by the industrial supplies. The wholesale price of grinded SCS, salicylic acid, methanol, Co(N-O₃)₂·6H₂O and H₂O₂ (30%) is about 0.15 US\$/kg, 1.5 US\$/kg, 0.4 US\$/L, 1.8 US\$/kg and 0.22 US\$/L, respectively. In this study, the cost for the production of Co-SAM-SCS is about 1.7 US\$/kg. According to the preliminary results abstained in this work, the chemical cost for the treatment of 50 mg/L SMZ wastewater is about 10 US\$/m³, which is higher than the costs of some reported AOPs (Table 1) (Boczkaj and Fernandes, 2017; Patil and Gogate, 2015; Thanekar et al., 2018; Weng et al., 2013). For example, in a recent work, Thanekar et al. (2018) reported the total cost of a hydrodynamic cavitation/H₂O₂/O₃ system is 4.55 US\$/m³. The higher chemical cost in our study is mainly because relatively high H₂O₂ dosage (4%) was adopted for the fast degradation of SMZ at slightly basic pH condition. It should be noted that over 80% of SMZ can be removed in 240 min with 2% of H₂O₂ (Fig. 7). Under this condition, the chemical cost can be reduced to 5.6 US\$/m³. Furthermore, the chemical cost can also be reduced by recycling the catalyst. As shown in Table 1, the studied process (Co-SAM-SCS/H₂O₂) is more economical than a recently reported sonication/Fenton-like process (Jaafarzadeh et al., 2018). If the studied Fenton-like process can be put into practical application, it will provide a feasible way to reuse SCS and also achieve excellent environmental benefit.

4. Conclusions

- In this study, a novel heterogeneous Fenton-like system with Co-SAM-SCS as the catalyst was developed for the degradation of antibiotic SMZ in wastewater.
- The Co-SAM-SCS/H₂O₂ system can work efficiently in neutral or slightly basic pH conditions. Furthermore, the catalyst showed good stability and reusability.
- Co and Fe on the surface of Co-SAM-SCS present synergistic effects on the efficient generation of HO•, which was mainly responsible for the degradation of SMZ.
- Three main degradation intermediates were detected during the degradation process, based on which a possible degradation pathway of SMZ in the Co-SAM-SCS/H₂O₂ system was proposed.

- A further study conducted in three kinds of wastewater confirmed the application feasibility of this heterogeneous Fenton-like process for wastewater treatment. Meanwhile, further research conducted with more complex wastewater is still needed before the full-scale implementation.
- Our findings provide useful information to develop efficient and cost-effective approaches to degrade organic pollutants in wastewater.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.watres.2018.03.022>.

References

- Babić, S., Zrnić, M., Ljubas, D., Čurković, L., Skorić, I., 2015. Photolytic and thin TiO₂ film assisted photocatalytic degradation of sulfamethazine in aqueous solution. *Environ. Sci. Pollut. Res.* 22, 11372–11386.
- Bai, Z., Yang, Q., Wang, J., 2016. Catalytic ozonation of sulfamethazine antibiotics using Ce_{0.1}Fe_{0.9}OOH: catalyst preparation and performance. *Chemosphere* 161, 174–180.
- Boczkaj, G., Fernandes, A., 2017. Wastewater treatment by means of advanced oxidation processes at basic pH conditions: a review. *Chem. Eng. J.* 320, 608–633.
- Bokare, A.D., Choi, W., 2014. Review of iron-free Fenton-like systems for activating H₂O₂ in advanced oxidation processes. *J. Hazard Mater.* 275, 121–135.
- Boreen, A.L., Arnold, W.A., McNeill, K., 2005. Triplet-sensitized photodegradation of sulfa drugs containing six-membered heterocyclic Groups: identification of an SO₂ extrusion photoproduct. *Environ. Sci. Technol.* 39 (10), 3630–3638.
- Brusseau, M.L., Jessup, R.E., Rao, P.S.C., 1991. Nonequilibrium Sorption of Organic Chemicals: Elucidation of Rate-limiting Processes.
- Burbano, A.A., Dionysiou, D.D., Suidan, M.T., Richardson, T.L., 2005. Oxidation kinetics and effect of pH on the degradation of MTBE with Fenton reagent. *Water Res.* 39 (1), 107–118.
- Centi, G., Perathoner, S., 2003. Remediation of water contamination using catalytic

- technologies. *Appl. Catal. B Environ.* 41 (1–2), 15–29.
- Cheng, M., Zeng, G., Huang, D., Lai, C., Liu, Y., Xu, P., Zhang, C., Wan, J., Hu, L., Xiong, W., Zhou, C., 2017a. Salicylic acid–methanol modified steel converter slag as heterogeneous Fenton-like catalyst for enhanced degradation ofalachlor. *Chem. Eng. J.* 327, 686–693.
- Cheng, M., Zeng, G., Huang, D., Lai, C., Liu, Y., Zhang, C., Wang, R., Qin, L., Xue, W., Song, B., 2018a. High adsorption of methylene blue by salicylic acid-ethanol modified steel converter slag and evaluation of its mechanism. *J. Colloid Interface Sci.* 515, 232–239.
- Cheng, M., Zeng, G., Huang, D., Lai, C., Xu, P., Zhang, C., Liu, Y., 2016a. Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: a review. *Chem. Eng. J.* 284, 582–598.
- Cheng, M., Zeng, G., Huang, D., Lai, C., Xu, P., Zhang, C., Liu, Y., Wan, J., Gong, X., Zhu, Y., 2016b. Degradation of atrazine by a novel Fenton-like process and assessment the influence on the treated soil. *J. Hazard Mater.* 312, 184–191.
- Cheng, M., Zeng, G., Huang, D., Liu, L., Zhao, M., Lai, C., Huang, C., Wei, Z., Li, N., Xu, P., Zhang, C., Li, F., Leng, Y., 2014. Effect of Pb^{2+} on the production of hydroxyl radical during solid-state fermentation of straw with *Phanerochaete chrysosporium*. *Biochem. Eng. J.* 84, 9–15.
- Cheng, M., Zeng, G., Huang, D., Yang, C., Lai, C., Zhang, C., Liu, Y., 2018b. Tween 80 surfactant-enhanced bioremediation: toward a solution to the soil contamination by hydrophobic organic compounds. *Crit. Rev. Biotechnol.* 38 (1), 17–30.
- Cheng, M., Zeng, G., Huang, D., Yang, C., Lai, C., Zhang, C., Liu, Y., 2017b. Advantages and challenges of Tween 80 surfactant-enhanced technologies for the remediation of soils contaminated with hydrophobic organic compounds. *Chem. Eng. J.* 314, 98–113.
- Cheng, Y., He, H., Yang, C., Zeng, G., Li, X., Chen, H., Yu, G., 2016c. Challenges and solutions for biofiltration of hydrophobic volatile organic compounds. *Biotechnol. Adv.* 34 (6), 1091–1102.
- Criado, M., Fernández-Jiménez, A., Palomo, A., 2007. Alkali activation of fly ash: effect of the SiO_2/Na_2O ratio. *Microporous Mesoporous Mater.* 106 (1), 180–191.
- Fan, H.-J., Huang, S.-T., Chung, W.-H., Jan, J.-L., Lin, W.-Y., Chen, C.-C., 2009. Degradation pathways of crystal violet by Fenton and Fenton-like systems: condition optimization and intermediate separation and identification. *J. Hazard Mater.* 171 (1), 1032–1044.
- Fan, T., Liu, Y., Feng, B., Zeng, G., Yang, C., Zhou, M., Zhou, H., Tan, Z., Wang, X., 2008. Biosorption of cadmium (II), zinc (II) and lead (II) by *Penicillium simplicissimum*: isotherms, kinetics and thermodynamics. *J. Hazard Mater.* 160 (2), 655–661.
- Feng, Y., Gong, J.-L., Zeng, G.-M., Niu, Q.-Y., Zhang, H.-Y., Niu, C.-G., Deng, J.-H., Yan, M., 2010. Adsorption of Cd (II) and Zn (II) from aqueous solutions using magnetic hydroxyapatite nanoparticles as adsorbents. *Chem. Eng. J.* 162 (2), 487–494.
- Gadsden, J.A., 1975. *Infrared Spectra of Minerals and Related Inorganic Compounds*. Butterworths.
- Garoma, T., Umamaheshwar, S.K., Mumper, A., 2010. Removal of sulfadiazine, sulfamethizole, sulfamethoxazole, and sulfathiazole from aqueous solution by ozonation. *Chemosphere* 79 (8), 814–820.
- Gong, J.-L., Wang, B., Zeng, G.-M., Yang, C.-P., Niu, C.-G., Niu, Q.-Y., Zhou, W.-J., Liang, Y., 2009. Removal of cationic dyes from aqueous solution using magnetic multi-wall carbon nanotube nanocomposite as adsorbent. *J. Hazard Mater.* 164 (2), 1517–1522.
- Guo, C., Xu, J., Wang, S., Zhang, Y., He, Y., Li, X., 2013. Photodegradation of sulfamethazine in an aqueous solution by a bismuth molybdate photocatalyst. *Catal. Sci. Technol.* 3 (6), 1603–1611.
- Guo, J., Li, J., Chen, H., Bond, P.L., Yuan, Z., 2017. Metagenomic analysis reveals wastewater treatment plants as hotspots of antibiotic resistance genes and mobile genetic elements. *Water Res.* 123, 468–478.
- Guo, S., Zhang, G., Wang, J., 2014. Photo-Fenton degradation of rhodamine B using Fe_2O_3 -Kaolin as heterogeneous catalyst: characterization, process optimization and mechanism. *J. Colloid Interface Sci.* 433, 1–8.
- Ho, Y.S., McKay, G., 1998. Kinetic models for the sorption of dye from aqueous solution by wood. *Process Saf. Environ. Protect.* 76 (2), 183–191.
- Hu, X.-j., Wang, J.-s., Liu, Y.-g., Li, X., Zeng, G.-m., Bao, Z.-l., Zeng, X.-x., Chen, A.-w., Long, F., 2011a. Adsorption of chromium (VI) by ethylenediamine-modified cross-linked magnetic chitosan resin: isotherms, kinetics and thermodynamics. *J. Hazard Mater.* 185 (1), 306–314.
- Hu, X., Liu, B., Deng, Y., Chen, H., Luo, S., Sun, C., Yang, P., Yang, S., 2011b. Adsorption and heterogeneous Fenton degradation of 17 α -methyltestosterone on nano Fe_3O_4 /MWCNTs in aqueous solution. *Appl. Catal. B Environ.* 107 (3), 274–283.
- Huang, D.-L., Zeng, G.-M., Feng, C.-L., Hu, S., Jiang, X.-Y., Tang, L., Su, F.-F., Zhang, Y., Zeng, W., Liu, H.-L., 2008. Degradation of lead-contaminated lignocellulosic waste by *Phanerochaete chrysosporium* and the reduction of lead toxicity. *Environ. Sci. Technol.* 42 (13), 4946–4951.
- Huang, D., Hu, C., Zeng, G., Cheng, M., Xu, P., Gong, X., Wang, R., Xue, W., 2017a. Combination of Fenton processes and biotreatment for wastewater treatment and soil remediation. *Sci. Total Environ.* 574, 1599–1610.
- Huang, D., Liu, L., Zeng, G., Xu, P., Huang, C., Deng, L., Wang, R., Wan, J., 2017b. The effects of rice straw biochar on indigenous microbial community and enzymes activity in heavy metal-contaminated sediment. *Chemosphere* 174, 545–553.
- Huang, D., Xue, W., Zeng, G., Wan, J., Chen, G., Huang, C., Zhang, C., Cheng, M., Xu, P., 2016. Immobilization of Cd in river sediments by sodium alginate modified nanoscale zero-valent iron: impact on enzyme activities and microbial community diversity. *Water Res.* 106, 15–25.
- Huang, R., Fang, Z., Yan, X., Cheng, W., 2012. Heterogeneous sono-Fenton catalytic degradation of bisphenol A by Fe_3O_4 magnetic nanoparticles under neutral condition. *Chem. Eng. J.* 197, 242–249.
- Jaafarzadeh, N., Takdastan, A., Jorfi, S., Ghanbari, F., Ahmadi, M., Barzegar, G., 2018. The performance study on ultrasonic/ Fe_3O_4/H_2O_2 for degradation of azo dye and real textile wastewater treatment. *J. Mol. Liq.* 256, 462–470.
- Kim, K.-S., Yang, C.-S., Mok, Y.S., 2013. Degradation of veterinary antibiotics by dielectric barrier discharge plasma. *Chem. Eng. J.* 219, 19–27.
- Lagergren, S., 1898. Zur theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenska Vetenskapsakademiens Handlingar* 24, 1–39.
- Lai, C., Wang, M.-M., Zeng, G.-M., Liu, Y.-G., Huang, D.-L., Zhang, C., Wang, R.-Z., Xu, P., Cheng, M., Huang, C., Wu, H.-P., Qin, L., 2016. Synthesis of surface molecular imprinted TiO_2 /graphene photocatalyst and its highly efficient photocatalytic degradation of target pollutant under visible light irradiation. *ApS* 390, 368–376.
- Li, H., Wan, J., Ma, Y., Wang, Y., Chen, X., Guan, Z., 2016. Degradation of refractory dibutyl phthalate by peroxymonosulfate activated with novel catalysts cobalt metal-organic frameworks: mechanism, performance, and stability. *J. Hazard Mater.* 318, 154–163.
- Li, M., Wang, C., Yau, M., Bolton, J.R., Qiang, Z., 2017. Sulfamethazine degradation in water by the VUV/UV process: kinetics, mechanism and antibacterial activity determination based on a mini-fluidic VUV/UV photoreaction system. *Water Res.* 108, 348–355.
- Ling, S.K., Wang, S., Peng, Y., 2010. Oxidative degradation of dyes in water using Co^{2+}/H_2O_2 and Co^{2+} /peroxymonosulfate. *J. Hazard Mater.* 178 (1–3), 385–389.
- Liu, Y., He, X., Fu, Y., Dionysiou, D.D., 2016. Degradation kinetics and mechanism of oxytetracycline by hydroxyl radical-based advanced oxidation processes. *Chem. Eng. J.* 284, 1317–1327.
- Liu, Y., Hu, J., Wang, J., 2014. Fe^{2+} enhancing sulfamethazine degradation in aqueous solution by gamma irradiation. *Radiat. Phys. Chem.* 96, 81–87.
- Liu, Y., Wang, J., 2013. Degradation of sulfamethazine by gamma irradiation in the presence of hydrogen peroxide. *J. Hazard Mater.* 250–251, 99–105.
- Liu, Y., Zeng, G., Zhong, H., Wang, Z., Liu, Z., Cheng, M., Liu, G., Yang, X., Liu, S., 2017. Effect of rhamnolipid solubilization on hexadecane bioavailability: enhancement or reduction? *J. Hazard Mater.* 322, 394–401.
- Mahamallik, P., Pal, A., 2016. Photo-Fenton process in a Co(II)-adsorbed micellar soft-template on an alumina support for rapid methylene blue degradation. *RSC Adv.* 6 (103), 100876–100890.
- Mahamallik, P., Pal, A., 2017. Degradation of textile wastewater by modified photo-Fenton process: application of Co(II) adsorbed surfactant-modified alumina as heterogeneous catalyst. *J. Environ. Chem. Eng.* 5 (3), 2886–2893.
- Navalon, S., Alvaro, M., Garcia, H., 2010. Heterogeneous Fenton catalysts based on clays, silicas and zeolites. *Appl. Catal. B Environ.* 99 (1), 1–26.
- Neafsey, K., Zeng, X., Lemley, A.T., 2010. Degradation of sulfonamides in aqueous solution by membrane anodic Fenton treatment. *J. Agric. Food Chem.* 58 (2), 1068–1076.
- Nguyen, T.T.M., Park, H.-J., Kim, J.Y., Kim, H.-E., Lee, H., Yoon, J., Lee, C., 2013. Microbial inactivation by cupric ion in combination with H_2O_2 : role of reactive oxidants. *Environ. Sci. Technol.* 47 (23), 13661–13667.
- Ozcan, A., Ozcan, A.A., Demirci, Y., Sener, E., 2017. Preparation of Fe_2O_3 modified kaolin and application in heterogeneous electro-catalytic oxidation of enoxaciri. *Appl. Catal. B Environ.* 200, 361–371.
- Patil, P.N., Gogate, P.R., 2015. Degradation of dichlorvos using hybrid advanced oxidation processes based on ultrasound. *J. Water Process Eng.* 8, 58–65.
- Shen, Y., Zhou, Y., Zhang, Z., Xiao, K., 2017. Cobalt–copper oxalate nanofibers mediated Fenton degradation of Congo red in aqueous solutions. *J. Ind. Eng. Chem.* 52, 153–161.
- Sopaj, F., Oturan, N., Pinson, J., Podvorica, F., Oturan, M.A., 2016. Effect of the anode materials on the efficiency of the electro-Fenton process for the mineralization of the antibiotic sulfamethazine. *Appl. Catal. B Environ.* 199, 331–341.
- Tang, L., Zeng, G.-M., Shen, G.-L., Li, Y.-P., Zhang, Y., Huang, D.-L., 2008. Rapid detection of picloram in agricultural field samples using a disposable immunomembrane-based electrochemical sensor. *Environ. Sci. Technol.* 42 (4), 1207–1212.
- Teixido, M., Hurtado, C., Pignatello, J.J., Beltran, J.L., Granados, M., Peccia, J., 2013. Predicting contaminant adsorption in black carbon (Biochar)-Amended soil for the veterinary antimicrobial sulfamethazine. *Environ. Sci. Technol.* 47 (12), 6197–6205.
- Thanekar, P., Panda, M., Gogate, P.R., 2018. Degradation of carbamazepine using hydrodynamic cavitation combined with advanced oxidation processes. *Ultrason. Sonochem.* 40 (Part A), 567–576.
- Wan, Z., Hu, J., Wang, J., 2016. Removal of sulfamethazine antibiotics using CeFe-graphene nanocomposite as catalyst by Fenton-like process. *J. Environ. Manage.* 182, 284–291.
- Wan, Z., Wang, J., 2017. Degradation of sulfamethazine using Fe_3O_4 - Mn_3O_4 /reduced graphene oxide hybrid as Fenton-like catalyst. *J. Hazard Mater.* 324 (Part B), 653–664.
- Wang, M., Fang, G., Liu, P., Zhou, D., Ma, C., Zhang, D., Zhan, J., 2016. Fe_3O_4 @ β -CD nanocomposite as heterogeneous Fenton-like catalyst for enhanced degradation of 4-chlorophenol (4-CP). *Appl. Catal. B Environ.* 188, 113–122.
- Wang, Y., Feng, C., Li, Y., Gao, J., Yu, C.-P., 2017. Enhancement of emerging contaminants removal using Fenton reaction driven by H_2O_2 -producing microbial fuel cells. *Chem. Eng. J.* 307, 679–686.
- Weng, C.-H., Lin, Y.-T., Yuan, H.-M., 2013. Rapid decoloration of Reactive Black 5 by an advanced Fenton process in conjunction with ultrasound. *Separ. Purif. Technol.* 117, 75–82.

- Xia, M., Long, M., Yang, Y., Chen, C., Cai, W., Zhou, B., 2011. A highly active bimetallic oxides catalyst supported on Al-containing MCM-41 for Fenton oxidation of phenol solution. *Appl. Catal. B Environ.* 110, 118–125.
- Xie, Y., Yan, B., Xu, H., Chen, J., Liu, Q., Deng, Y., Zeng, H., 2014. Highly regenerable mussel-inspired Fe_3O_4 @Polydopamine-Ag core-shell microspheres as catalyst and adsorbent for methylene blue removal. *Acs Appl. Mater. Int.* 6 (11), 8845–8852.
- Xu, P., Zeng, G.M., Huang, D.L., Feng, C.L., Hu, S., Zhao, M.H., Lai, C., Wei, Z., Huang, C., Xie, G.X., 2012. Use of iron oxide nanomaterials in wastewater treatment: a review. *Sci. Total Environ.* 424, 1–10.
- Yang, C., Chen, H., Zeng, G., Yu, G., Luo, S., 2010. Biomass accumulation and control strategies in gas biofiltration. *Biotechnol. Adv.* 28 (4), 531–540.
- Yang, Y., Lu, X., Jiang, J., Ma, J., Liu, G., Cao, Y., Liu, W., Li, J., Pang, S., Kong, X., Luo, C., 2017. Degradation of sulfamethoxazole by UV, $\text{UV}/\text{H}_2\text{O}_2$ and $\text{UV}/\text{persulfate}$ (PDS): formation of oxidation products and effect of bicarbonate. *Water Res.* 118, 196–207.
- Yang, Y., Pignatello, J.J., Ma, J., Mitch, W.A., 2016. Effect of matrix components on $\text{UV}/\text{H}_2\text{O}_2$ and $\text{UV}/\text{S}_2\text{O}_8^{2-}$ advanced oxidation processes for trace organic degradation in reverse osmosis brines from municipal wastewater reuse facilities. *Water Res.* 89, 192–200.
- Yap, P.-S., Cheah, Y.-L., Srinivasan, M., Lim, T.-T., 2012. Bimodal N-doped $\text{P25-TiO}_2/\text{AC}$ composite: preparation, characterization, physical stability, and synergistic adsorptive-solar photocatalytic removal of sulfamethazine. *Appl. Catal. Gen.* 427–428, 125–136.
- Yi, H., Xu, G., Cheng, H., Wang, J., Wan, Y., Chen, H., 2012. An overview of utilization of steel slag. *Procedia Environ. Sci.* 16, 791–801.
- Zeng, G., Chen, M., Zeng, Z., 2013a. Risks of neonicotinoid pesticides. *Sciences* 340 (6139), 1403.
- Zeng, G., Chen, M., Zeng, Z., 2013b. Shale gas: surface water also at risk. *Nature* 499 (7457), 154.
- Zhang, C., Lai, C., Zeng, G., Huang, D., Yang, C., Wang, Y., Zhou, Y., Cheng, M., 2016. Efficacy of carbonaceous nanocomposites for sorbing ionizable antibiotic sulfamethazine from aqueous solution. *Water Res.* 95, 103–112.
- Zhang, Y., Zeng, G.-M., Tang, L., Huang, D.-L., Jiang, X.-Y., Chen, Y.-N., 2007. A hydroquinone biosensor using modified core-shell magnetic nanoparticles supported on carbon paste electrode. *Biosens. Bioelectron.* 22 (9–10), 2121–2126.
- Zhao, H., Chen, Y., Peng, Q., Wang, Q., Zhao, G., 2017. Catalytic activity of $\text{MOF}(2\text{Fe}/\text{Co})/\text{carbon aerogel}$ for improving H_2O_2 and OH generation in solar photo-electro-Fenton process. *Appl. Catal. B Environ.* 203, 127–137.
- Zhou, T., Wu, X., Mao, J., Zhang, Y., Lim, T.-T., 2014. Rapid degradation of sulfonamides in a novel heterogeneous sonophotochemical magnetite-catalyzed Fenton-like ($\text{US}/\text{UV}/\text{Fe}_3\text{O}_4/\text{oxalate}$) system. *Appl. Catal. B Environ.* 160–161, 325–334.
- Zhou, T., Wu, X., Zhang, Y., Li, J., Lim, T.-T., 2013. Synergistic catalytic degradation of antibiotic sulfamethazine in a heterogeneous sonophotolytic goethite/oxalate Fenton-like system. *Appl. Catal. B Environ.* 136, 294–301.