



Salicylic acid–methanol modified steel converter slag as heterogeneous Fenton-like catalyst for enhanced degradation of alachlor

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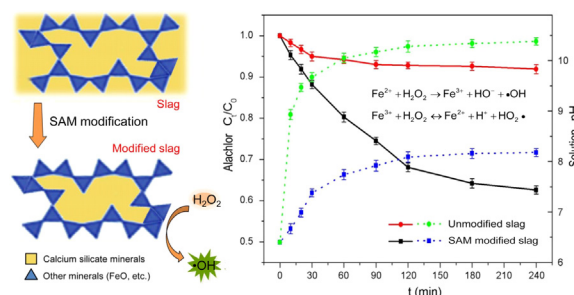
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HIGHLIGHTS

- SAM treatment significantly improved the catalytic property of steel slag.
- SAM can selectively dissolve calcium silicate minerals on the surface of steel slag.
- SAM modified slag shows high activity and good reusability for alachlor degradation.
- The degradation rate decreased along with the increase of initial pH from 2 to 6.0.

GRAPHICAL ABSTRACT



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ABSTRACT

Significant effort has recently been directed toward the use of advanced oxidation processes (AOPs) to degrade organic pollutants. In this work, an affordable and effective heterogeneous Fenton-like process was proposed and studied. Preparation and utilization of an iron-rich catalyst, salicylic acid–methanol (SAM) modified steel converter slag (SCS), were investigated for the degradation of alachlor in wastewater. Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), Fourier transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) were used to assess the morphology and crystal structure of the prepared catalysts. Results showed that SAM modification can selectively remove calcium silicate minerals from surface of SCS. The modification decreased the alkalinity of SCS and led to a prominent decrease in the specific surface areas and iron content, which dramatically improved the catalytic property of SCS. The removal rate of alachlor at initial pH 3.0 in SAM-modified SCS/H₂O₂ system was 3.07 times of that in SCS/H₂O₂ system. Further studies showed that this heterogeneous Fenton-like process was more suitable to be performed at relative higher temperature (30–40 °C) and lower initial pH (2.0–3.0). A small decrease (2.1%) was found in the activity of SAM-modified SCS after four runs, indicating a feasible way to utilize SCS and also achieve excellent environmental benefit.

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1. Introduction

The treatment of persistent organic pollutants is a very important task to protect the environment and water resources. Water treatment technologies applied nowadays such as membrane technologies, sedimentation, or adsorption merely concentrate

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the pollutants by transferring them to other phases, but they do not eliminate pollutants residues [1,2]. Oxidation technology, particularly advanced oxidation processes (AOPs) in which highly reactive intermediates (such as hydroxyl radical, $\cdot\text{OH}$) are used as the oxidant, has been identified as one of the most promising solutions for this problem [3–8].

Among the AOPs, Fenton reactions have been extensively studied due to their simplicity, high efficiency, low cost and environmental friendliness [9–11]. However, the traditional homogeneous Fenton reactions based methods suffer from some drawbacks such as (i) the precipitation of soluble iron ions as hydroxide precipitate under neutral pH or alkaline conditions [12,13], (ii) the requirement of strict pH regulation around 3 [14,15], and (iii) the requirement of post-treatment prior to discharge, such as neutralization of the treated solutions [16]. To overcome these drawbacks in classical Fenton processes, a lot of attempts have been made on the development of heterogeneous Fenton-like processes in which iron oxides based catalysts were used instead of soluble iron salts [17,18]. In the recent years, hematite, pyrite and goethite have been utilized as the heterogeneous catalyst in the treatment of many persistent organic pollutants over a wider pH range [19–21]. Nevertheless, these catalysts were often found to have poor stability or low activity or recyclability [22]. Therefore, developing affordable and durable heterogeneous catalysts remains a challenge.

Steel converter slag (SCS) is a final waste material in the steel making process [23]. SCS is mainly constituted by CaO , SiO_2 , FeO , Fe_2O_3 , MgO , and MnO . In most cases, the weight content of iron oxides (FeO and Fe_2O_3) in SCS is above 20%. Therefore, SCS has high potential to be used as catalyst in the heterogeneous Fenton-like process [24,25]. However, even adjust the initial pH value to around 3, SCS could rapidly increase the solution pH up to 10 due to the dissolution of calcium minerals. Although heterogeneous Fenton-like processes could be used in a wider pH range than homogeneous Fenton, they would be inefficient at high pH conditions [26]. This makes the SCS based Fenton-like process complex and uneconomical. To overcome the mentioned shortcomings, in this study, salicylic acid–methanol (SAM) solution was used to dissolve calcium silicate minerals in SCS and thus to improve the catalytic property of SCS.

Alachlor was used as a model organic pollutant to investigate the performance of the Fenton-like processes in this study. Alachlor, a chloroacetanilide, was first registered in 1969, has been widely used to control grassy weeds and broadleaf in sorghum, soybeans, as well as corn [27,28]. Alachlor is also known as an endocrine disruptor, it may cause problems with spleen, kidneys, eyes, liver or experience anemia [29,30]. And according to the U. S. Environmental Protection Agency, alachlor is a Group B2 human carcinogen. Compared with organochlorine pesticides, alachlor is more soluble in water. As a result, it is easy to be leached from soil to surface and ground water that are used as sources of drinking water. This problem has been exacerbated by the vast and increasing use of alachlor Worldwide and the fact that alachlor is relatively resisted to biodegradation due to its high toxicity and chemical stability [31]. Therefore, the effective removal of alachlor from wastewater is a problem of great practical importance and interest. A lot of studies have reported the degradation of alachlor by Fenton chemistry including classical Fenton [7], photo-Fenton [32], ultrasound assisted Fenton [33] and Fenton-like processes [8]. However, there is no literature reported the degradation of alachlor by SCS catalyzed heterogeneous Fenton-like process.

The aim of the present work is to develop a SCS based heterogeneous Fenton-like process for the effective degradation of organic pollutants in aqueous solutions. Apart from the production and characterization of the SCS catalysts, our experimental work also focused on the optimization of degradation process. The effects

of different doses of catalyst, initial pH values, temperatures and alachlor concentrations on the degradation were evaluated. The variation in total organic carbon (TOC) and the concentrations of short-chain carboxylic acids during the Fenton process were also monitored in this work. Finally, we performed continuous degradation experiments to verify the reusability of the catalyst.

2. Experimental

2.1. Materials

The SCS was provided by Valin Iron and Steel Corp (VISTC), Xiangtan, China. The SCS is composed of CaO , SiO_2 , FeO , Fe_2O_3 , MgO , MnO , Al_2O_3 , P_2O_5 and TiO_2 (Table S1). The alachlor ($\text{C}_{14}\text{H}_{20}\text{ClNO}_2$, standard grade) was obtained from Sigma-Aldrich (Missouri, USA). Hydrogen peroxide (H_2O_2 , 30% in water), methanol (chromatographic grade) and salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$, analytical grade) were obtained from Sinopharm Chemical Reagent (Beijing, China). Ultrapure water ($18.3 \text{ M}\Omega\cdot\text{cm}$) was used in all the batch experiments.

2.2. Preparation of catalyst

The raw SCS was grinded and sieved with a 0.15 mm mesh sieve to remove the large particles. The obtained SCS powder was fully washed with ultrapure water and dried at 80°C in a drum wind drying oven, and then collected in a desiccator. 20 g of the dried SCS powder was added in 1 L SAM solution (50 g/L) and shaken on a shaking bed with a constant shaking rate of 300 rpm at 25°C for 4 h. The mixture was then filtered using a $0.45 \mu\text{m}$ filter paper. The filtration residue was washed repeatedly with ultrapure water. After drying at 105°C for 24 h, the SAM-modified SCS catalyst was obtained.

2.3. Characterization methods

The specific surface area, pore volume and pore size of SCS and SAM-modified SCS were determined by the Brunauer-Emmett-Teller (BET) analysis (Micromeritics Instrument Corporation, TRI-STAR3020, USA). Their morphology was examined by scanning electron microscope (SEM) scanning (Carl Zeiss, EVO-MA10, Germany) at a magnification of 1400. Energy dispersive X-ray spectroscopy (EDS) of the samples was performed with an energy dispersive X-ray detector (Oxford Instruments, UK). The crystal phase of the prepared steel catalysts was measured by using a D/max-2500 X-ray diffractometer (XRD; Rigaku, Japan) using in the region of 2θ from 5° to 80° . X-ray photoelectron spectrum (XPS) of the samples was obtained by using Al $K\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$) with an ESCALAB 250Xi spectrometer (Thermo Fisher, USA) with. The Fourier transform infrared (FT-IR) spectra of the samples were obtained from a Nicolet 5700 Spectrometer (Nicolet, USA).

2.4. Fenton-like reaction

The Fenton-like reaction was performed in 50 mL plastic centrifuge tubes containing 20 mL of reaction solution at $20 \pm 0.5^\circ\text{C}$ and shaken at 120 rpm. Except the optimization experiments, alachlor concentration in all the other experiment groups was 0.15 mM. Typically, in the comparative degradation experiment, 0.1 g of SAM-modified SCS (or SCS) was added in 20 mL alachlor solution, and then 250 μL of 30% H_2O_2 was added to trigger the Fenton-like reaction. The initial pH of alachlor solution was set as 6.4 (without pH adjusting) and 3.0 (adjusting by 10% HCl solution). For certain time intervals, some centrifugal tubes were sacri-

ficed for analysis of alachlor concentration. For each tube, 0.4 mL of ethanol and 0.1 mL of 10% HCl solution were added to quench the reaction. All the experiments were performed in triplicate.

The concentration of alachlor was measured according to a published method [31] by high performance liquid chromatography (HPLC, Agilent 1100 series, Germany) with an Agilent TC-C18 column (4.6×250 mm, $5 \mu\text{m}$). In addition, alachlor mineralization was evaluated by measuring the TOC with a TOC-5000 A model analyzer (Shimadzu, Japan). Released carboxylic acids were determined by HPLC according a previous study [34], running with mobile phase of KH_2PO_4 /methanol 75/25 (v/v) and the absorption wavelength was set at 210 nm. Total iron concentration in the solution was determined by a DR2000 spectrophotometer (Hach, USA) using the 1, 10-phenanthroline-based method (HACH module No. 8146).

3. Results and discussion

3.1. Characterization of the catalysts

The prepared catalysts were characterized via different methods. Firstly, the textural properties of the samples was investigated by BET analysis (Table S2). The specific surface areas of SCS and SAM-modified SCS were determined as 1.55 ± 0.14 and $8.47 \pm 0.32 \text{ m}^2/\text{g}$, respectively. BET analysis reveals that SAM modification led to a remarkable alteration in the morphology of SCS. SEM was further used to study the morphology of the samples (Fig. 1). The surface of untreated SCS was relatively flat, smooth and continuous. As can be seen, there was a noticeable change in the surface morphology of SCS after SAM treatment, the external surface area was clearly increased by forming more holes (Fig. 1). The remarkable increase in holes was probably because calcium silicate minerals in SCS were selectively removed by SAM treatment.

EDS analysis of the unmodified SCS shows that SCS mainly consists of O, Ca, Fe, Si and Mg (Fig. 2a). After the SAM treatment, these elements are still detected (Fig. 2b) but a distinct change in the signal of these elements was observed. The variation in the signal of these elements verified the selectively removal of calcium silicate minerals from SCS. As can be seen from Fig. 2, the relative signal intensity of Fe increased obviously after SAM modification. EDS analysis shows the mass ratio of Fe to Ca was increased from 0.46 to 1.34 after SAM modification (Table S3).

Fig. 3 illustrates the XRD patterns of SCS and SAM-modified SCS. The observed diffraction peaks (2θ : 22.98° , 29.41° , 32.08° , 32.98° , 33.70° , 35.30° , 36.06° , 37.68° , 39.38° , 40.86° , 42.00° , 43.14° , 46.86° , 47.52° , 48.48° , 57.42° , 60.80° , 65.22° , 72.96° , and 77.27°) showed the complexity of the constituents of SCS. As can be seen, the intensities of tricalcium silicate peaks (2θ : 29.41° and 42.00°) [35] and dicalcium silicate peaks (2θ : 32.08° and 32.98°) [36] prominently decreased after SAM modification process. Similar results were found in FT-IR analysis. As shown in Fig. S1, the broad bands in the range of $1400\text{--}1500 \text{ cm}^{-1}$ (Ca–O) [37] and $800\text{--}1000 \text{ cm}^{-1}$ (Si–O) [38] decreased obviously after SAM modification. By contrast, the intensities of iron oxides peaks (2θ : 33.70° and 35.30°) [39,40] of the modified SCS were found enhanced as compared with those of unmodified SCS. These results indicated that the SAM modification indeed can selectively remove calcium silicate minerals from SCS.

XPS analyses were conducted to probe the surface chemical composition of the samples. Fig. 4a displays the comparison of the survey spectra of SCS and SAM-modified SCS. The elements of Mg (1303.7 eV , 311.2 eV), O (978.2 eV , 531.1 eV), Fe (724.2 eV , 710.3 eV), Ca (350.6 eV , 347.0 eV) and Si (102.0 eV) can be detected on the surface of both the two samples [41,42]. Fig. 4b–d presents the high resolution XPS spectra of Ca and Fe. It can be clearly seen that the intensity of Ca peaks at 350.6 eV and 346.9 eV for SAM-modified SCS are much weaker than that of unmodified SCS, while the intensity of the Fe peaks at 724.3 eV and 710.9 eV for SAM-modified SCS are much stronger than that of unmodified SCS, revealing that more Fe minerals were exposed on the surface of SCS after SAM modification.

3.2. Release of iron from the catalysts

In acidic condition, iron ions would be generated by the dissociation of iron oxides in the SCS catalysts. Fig. 5a shows the formation of iron ions by SCS and SAM-modified SCS in the presence of H_2O_2 at an initial pH of 3.0. In SCS/ H_2O_2 system, the concentration of iron ions increased rapidly in the first 30 min and decreased gradually after that. The quick increase in iron concentration is due to the dissociation of iron oxides in the surface of SCS, and the subsequent decline in dissolved iron concentration is probably caused by the increase of solution pH (Fig. 5b). The variation tendency of iron ions in SAM-modified SCS/ H_2O_2 system is quite similar to that in SCS/ H_2O_2 system, but the concentrations of iron ions are much higher than those in the later one. These results reveals

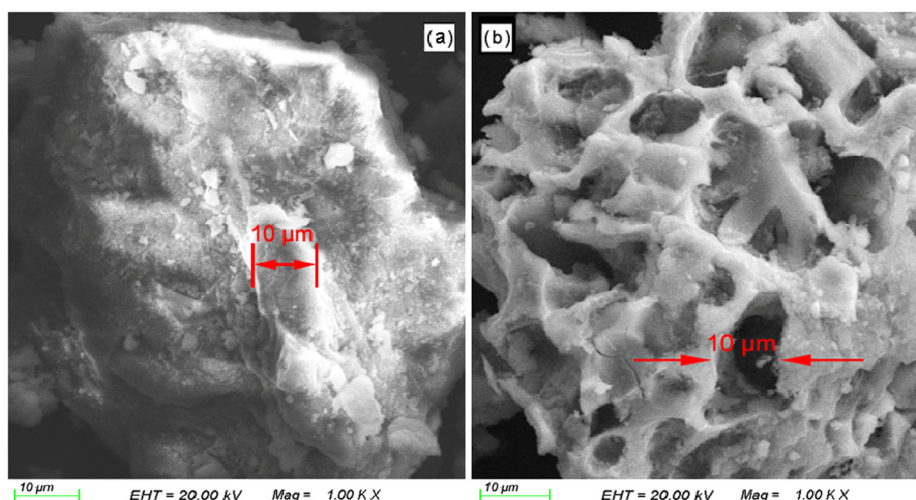


Fig. 1. SEM images of SCS (a) and SAM-modified SCS (b).

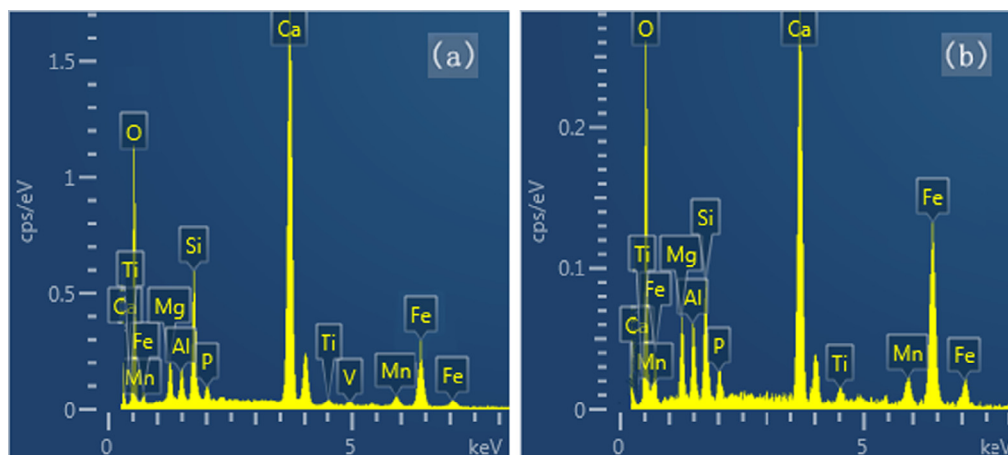


Fig. 2. EDS patterns of SCS (a) and SAM-modified SCS (b).

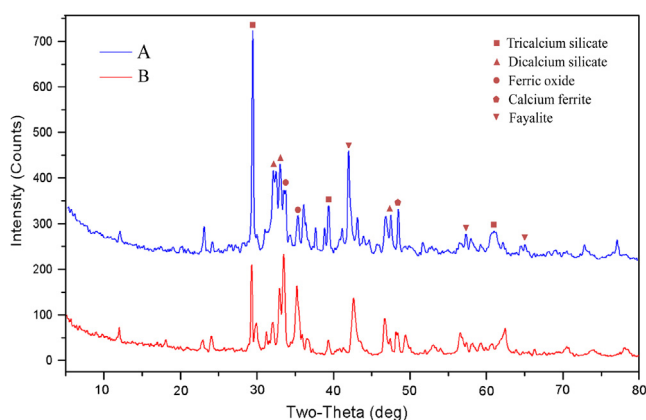


Fig. 3. XRD patterns of SCS (A) and SAM-modified SCS (B).

that SAM modification can improve the release of iron from SCS thus more efficiently catalyze the decomposition of H_2O_2 in the solution to produce more $\cdot\text{OH}$ for thealachlor oxidation. On the one hand, as shown in Fig. 1, the SAM treatment is able to dramatically increase the specific surface area of SCS, providing more liquid–solid interface for the dissociation. On the other hand, SAM treatment removed considerable amounts of calcium minerals from SCS, and thus can prevent the quick precipitation of iron ions due to the increase in solution pH. Fig. 5b shows the changes of pH versus time in different systems. It was found that although the initial pH value of the system was adjusted to 3.0, the addition of SCS quickly changed the pH to 7.43 within 60 min. By comparison, the pH value did not obviously change in the SAM-modified SCS system within 30 min, and then only increased to 6.27 with prolonging the process time to 120 min.

3.3. Comparative degradation behavior ofalachlor

Degradation behavior ofalachlor was investigated to evaluate the catalytic activity of SAM-modified SCS (Fig. 6). Firstly, the degradation experiments were conducted without any pH adjustment at 6.4, which is the native pH ofalachlor solution. It was found that 5.8% ofalachlor was decomposed in the SCS/ H_2O_2 system within the first 1 h and then the concentration ofalachlor did not significantly change during the subsequent 3 h (Fig. 6a), suggesting the termination of Fenton-like reactions after 1 h. This is probably because the pH value of the solution rapidly rise up

to 10.05 in 1 h after SCS was added in the system (Fig. 6a). The rapidly increase in solution pH is because SCS is a kind of alkaline materials which can neutralize H^+ and release OH^- ions. It has long been known that alkali condition is undesired for Fenton and Fenton-like reactions [43,44]. By comparison, the pH value maintained near neutral for over 1 h in SAM-modified SCS system, and consequently a noticeable degradation (37.4%) ofalachlor was obtained after the treatment. In the other two groups, the initial pH value of thealachlor solution was adjusted to 3.0 with HCl. Comparing with the results from Fig. 6a, we found that the addition of HCl solution can effectively slow down the increase in pH value and also promote the degradation ofalachlor, especially for SAM-modified SCS system (Fig. 6b).

Taken together, SAM modification successfully improved the catalytic property of SCS. Alachlor removal rates of SAM-modified SCS/ H_2O_2 system at initial pH of 3.0 and 6.4 were 462% and 307% of those of SCS/ H_2O_2 system, respectively. SAM modification can not only prevent the rapid increase in solution pH, but also produce more surface area for the heterogeneous Fenton-like reaction and the dissolution of iron (Fig. S2). Particularly, the big enhancement (446.5%, Table S2) in specific surface area is crucial for the heterogeneous Fenton-like oxidation. Previous studies suggested that heterogeneous Fenton-like oxidation mainly occurs at solid–liquid interface and the increased specific surface areas can provide more reaction areas for the oxidation [20,45].

3.4. Optimization of parameters for the heterogeneous Fenton-like process

3.4.1. Optimization of catalyst amount

The effects of catalyst load on the degradation performance ofalachlor were evaluated by conducting experiments in the presence of increasing amounts of SAM-modified SCS (Fig. 7a). As expected, thealachlor removal in 240 min increased from 42.1% to 75.7% along with increase of the catalyst dosage from 2.5 to 15 g/L (Fig. 7a). The increase in the amount of SAM-modified SCS could increase the amount of dissolved iron ions and solid–liquid interfaces, leading to higher reaction rate. However, the degradation efficiency ofalachlor began to decrease when the catalyst dosage further increased to 20 g/L. This happens for two reasons. Firstly, the increased SAM-modified SCS amount would cause superfluous fresh iron surfaces, which would then cause the consumption of oxidants (e.g., H_2O_2 and $\cdot\text{OH}$) and thus reduce the oxidation efficiency [46,47]. Secondly, the pH value of solution increases gradually with increase of the loaded catalyst (Fig. S3), negatively affecting the activity of Fenton-like reactions.

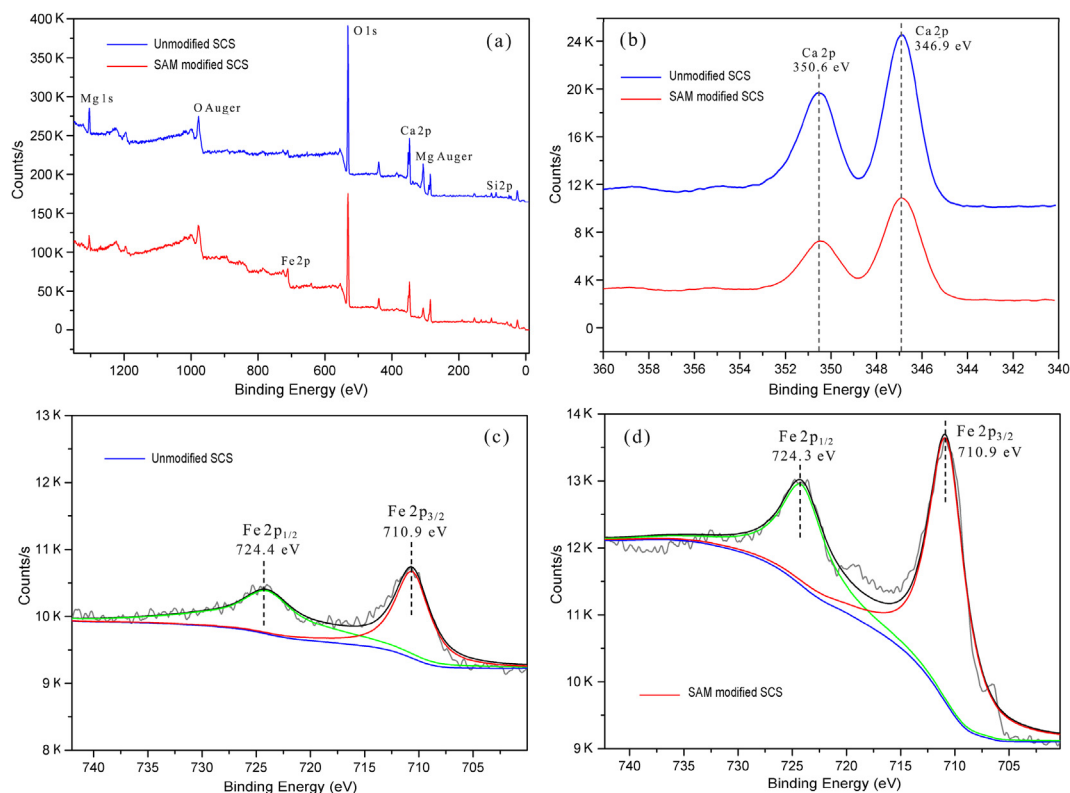


Fig. 4. XPS survey spectra (a) and high-resolution XPS spectra of Ca 2p (b), Fe 2p (c, d).

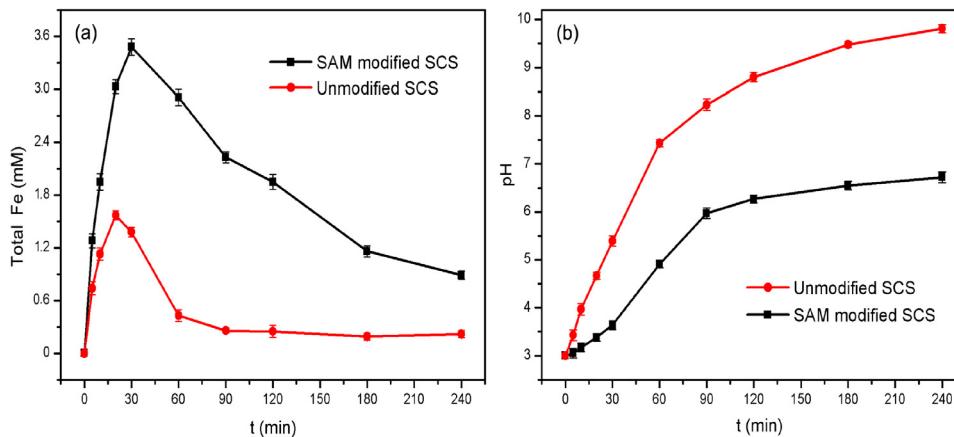


Fig. 5. Variation of total iron ions concentrations (a) and pH values (b) in the different heterogeneous Fenton systems. Alachlor: 0 mM, SCS/SAM-modified SCS: 5 g/L, H_2O_2 : 120 mM, initial pH: 3.0, T: 20 °C.

3.4.2. The effect of initial pH of alachlor solution

The influence of initial pH value on the degradation performance of alachlor in the SAM-modified SCS/ H_2O_2 system was then investigated (Fig. 7b). The experiments were performed by changing the initial pH of the alachlor solutions. We found that the alachlor concentration at initial pH value of 6.0 only decreased 45.4% within 240 min (Fig. 7b). The decrease of initial pH value from 6.0 to lower values led to a prominent increase in the degradation efficiency of alachlor. At initial pH value of 2.0, the complete removal of alachlor was achieved in 180 min. This result is due to the fact that higher efficiencies of iron oxides dissociation and Fenton-like reaction would occur at the lower pH [8,43]. We found the solution pH in the pH = 2.0 system could maintain <4 for about

2 h (Fig. S4). Therefore, much higher degradation rate of alachlor was observed in the pH = 2.0 system.

3.4.3. The effect of temperature

The effect of temperature on the degradation was examined by performing the experiments at 10 °C, 20 °C, 30 °C and 40 °C. As shown in Fig. 7c, the degradation efficiencies of alachlor increased along with the increase of temperature from 10 °C to 40 °C. The complete disappearance of alachlor took more than 240 min at 10 °C, while it took only 120 min at 30 °C and 40 °C (Fig. 7c). This is because the increase of temperature can increase the energies of the reactants and the mass transfer rates of species, which lead to the higher reaction rates [48–50].

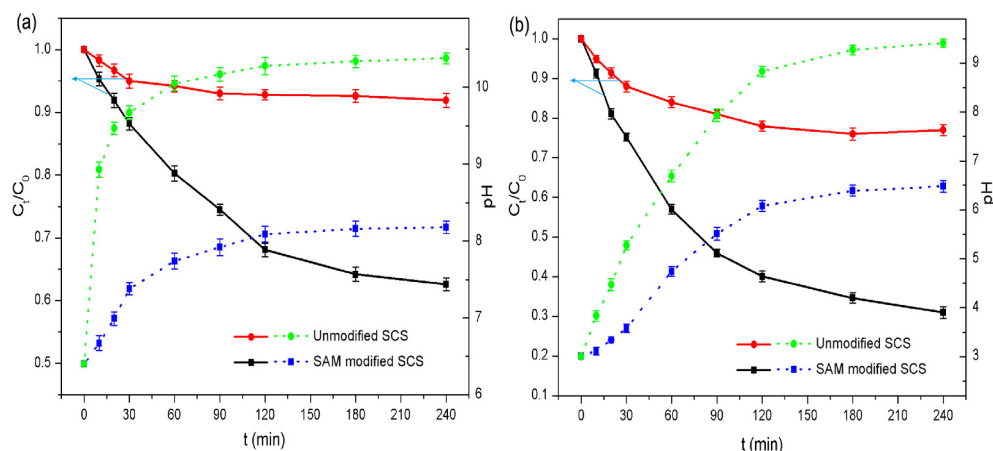


Fig. 6. Variation of alachlor concentrations (solid lines) and pH values (dotted lines) in the different heterogeneous Fenton systems. Alachlor: 0.15 mM, SCS/SAM-modified SCS: 5 g/L, H_2O_2 : 120 mM, initial pH: 6.4 (a) and 3.0 (b), T: 20 °C.

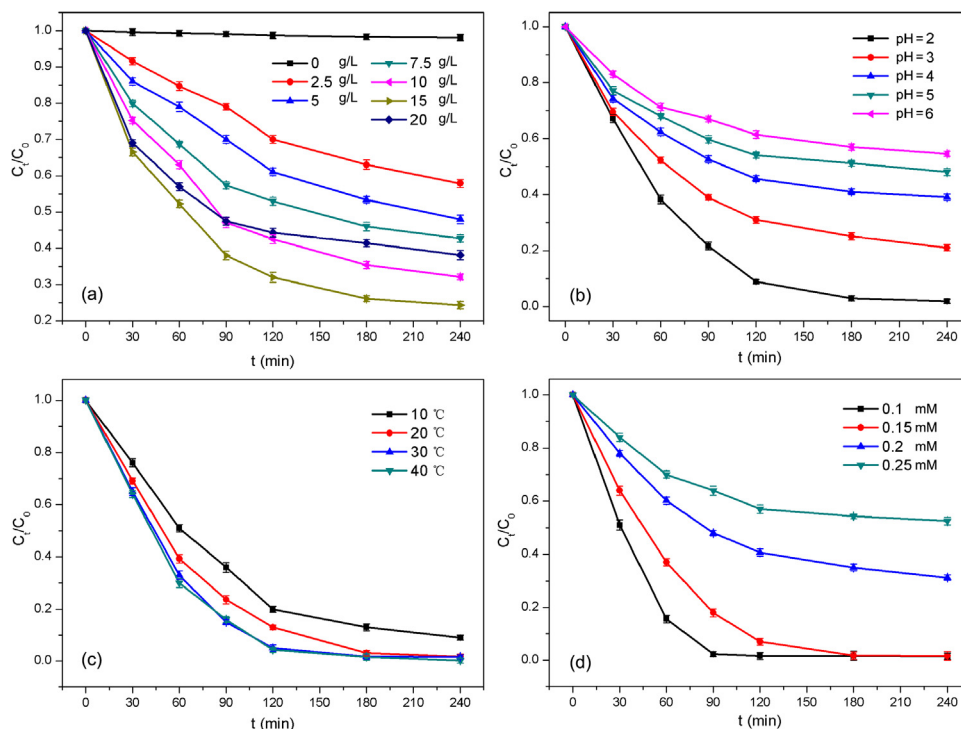


Fig. 7. The effect of the amount of catalysts (a, alachlor: 0.15 mM, H_2O_2 : 120 mM, initial pH: 3.0, T: 20 °C), initial pH (b, alachlor: 0.15 mM, SAM-modified SCS: 15 g/L, H_2O_2 : 120 mM, T: 20 °C), temperature (c, alachlor: 0.15 mM, SAM-modified SCS: 15 g/L, H_2O_2 : 120 mM, initial pH: 2.0) and initial alachlor concentrations (d, SAM-modified SCS: 15 g/L, H_2O_2 : 120 mM, initial pH: 2.0, T: 20 °C) on the degradation rates of alachlor during the heterogeneous Fenton treatment.

3.4.4. The effect of initial concentration of alachlor

Finally, the effect of initial concentration of alachlor was tested. As can be seen in Fig. 7d, degradation efficiencies of alachlor gradually decreased when increasing the initial concentration of alachlor from 0.1 mM to 0.25 mM. It is mainly because the production rate of $\cdot OH$ at the studied conditions is constant [51]. Therefore, increasing the initial concentration of alachlor would lead to lower contact rates between $\cdot OH$ and alachlor molecules.

3.5. Mineralization of alachlor

TOC analysis was employed to detect the fates of alachlor in the SAM-modified SCS/ H_2O_2 system. As shown in Fig. 8, only 11.8% of alachlor in the system was mineralized in 30 min, but the TOC val-

ues continued to decline with prolonging the process time. About 52.7% of alachlor could be mineralized within 240 min, suggesting the simultaneous mineralization of alachlor in the SAM-modified SCS/ H_2O_2 system. Further, the concentration changes of short-chain carboxylic acids ($HCOOH$, CH_3COOH and $HOOCCH_2COOH$) during the treatment were measured (Fig. 8). The concentrations of the three tested carboxylic acids were very small within 30 min, but increased quickly after that. This was in accordance with the results in a previous study, in which the mineralization pathway of alachlor by Fenton systems was thoroughly investigated by using Gas chromatography–mass spectrometry (GC–MS) and HPLC [31]. It was suggested in the degradation process, $\cdot OH$ preferentially attacks C–N bond to form N-dealkylation degradation products, therefore small amount of carboxylic acids would be

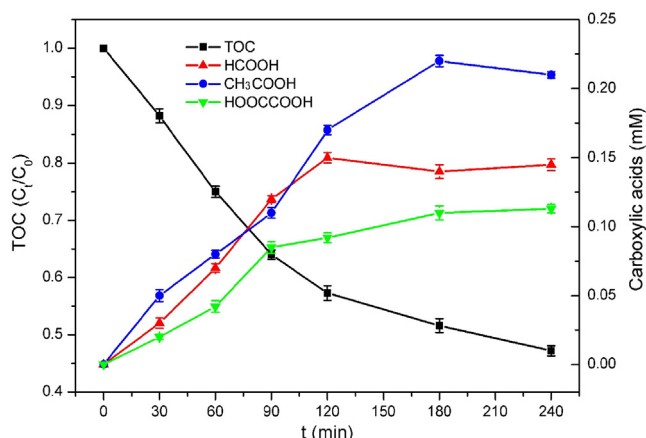


Fig. 8. Variation of TOC and carboxylic acids concentrations in the different heterogeneous Fenton systems. Alachlor: 0.15 mM, SAM-modified SCS: 15 g/L, H_2O_2 : 120 mM, initial pH: 2.0, T: 20 °C.

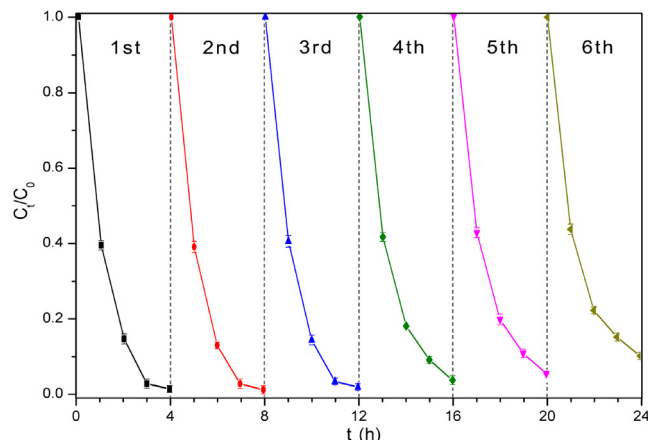


Fig. 10. Cycling runs of SAM-modified SCS for alachlor degradation. Alachlor: 0.15 mM, SAM-modified SCS: 15 g/L, H_2O_2 : 120 mM, initial pH: 2.0, T: 20 °C.

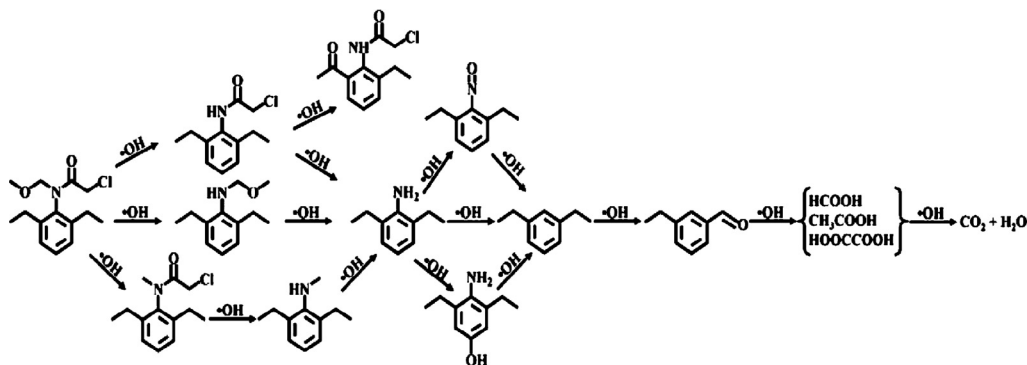


Fig. 9. Possible alachlor degradation pathway in the Fenton/Fenton-like processes. Adapted with permission from Ref. [31]. Copyright 2015 American Chemical Society.

generated in the early stage. A significant increase was found in the concentration of the short-chain carboxylic acids up to 120 min. This is likely due to the benzene ring in alachlor was cleaved under the attack of $\cdot\text{OH}$, leading to the formation of short-chain carboxylic acids (Fig. 9) [31].

3.6. Environmental implications

Different from the ferric salts used in traditional homogeneous Fenton processes, SCS is one of the final wastes of iron-making industries and thus is of more economical benignity. In China, the wholesale price of grinded SCS is extremely low ($\sim\text{US\$ } 150 \text{ t}^{-1}$) since massive amounts of SCS (~ 100 million tons) is generated every year [24]. The versatility of this SAM-modified SCS/ H_2O_2 system is also enhanced by the fact that this process did not reduce but increase the solution pH to near neutral, which can reduce the environmental risk caused by the acidic solution. More importantly, this catalyst shows high recyclability. An insignificant loss (2.1%) was observed in the catalytic activity of SAM-modified SCS after four-time successive degradation experiments (Fig. 10). And the catalyst can be recovered by a simple settling and separation process that enables the reuse of the catalyst. If the studied Fenton-like process can be put into practical application, it will provide a feasible way to reuse SCS and also achieve good environmental benefit.

4. Conclusions

This is the premier study reporting the preparation of SAM-modified SCS and application in heterogeneous catalytic oxidation

of the organic pollutant. The characterization (BET, SEM, EDS, XRD, FT-IR, XPS) of SCS and SAM-modified SCS indicated that calcium silicate minerals in SCS surface were selectively removed by SAM modification. The degradation experiments showed alachlor removal rates of SAM-modified SCS/ H_2O_2 system at initial pH of 3.0 and 6.4 were 462% and 307% of those of SCS/ H_2O_2 system, respectively. The big enhancement is mainly because SAM modification can 1) provide more solid–liquid interfaces for the heterogeneous Fenton-like reaction, 2) promote the release of iron from SCS, and 3) prevent the rapid increase in solution pH. Further studies showed that this heterogeneous Fenton-like process can be operated over a wide range of temperatures (20–40 °C) and was most suitable to be operated at initial pH = 2.0. The prepared SAM-modified SCS catalyst shows high recyclability being reused 4 times without noticeable losses in activity. Due to its low cost and high catalytic performances, SAM-modified SCS/ H_2O_2 Fenton-like system may be an important technology for practical application at a large scale.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2017.06.153>.

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