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

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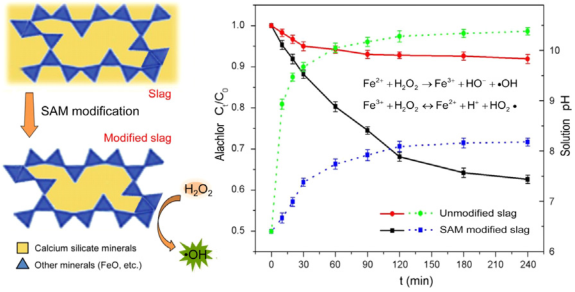
## HIGHLIGHTS

- 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/$H_2O_2$ system was 3.07 times of that in SCS/$H_2O_2$ 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.

## 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, **.**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 resent 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 ($C_{14}H_{20}ClNO_2$, standard grade) was obtained from Sigma-Aldrich (Missouri, USA). Hydrogen peroxide ($H_2O_2$, 30% in water), methanol (chromatographic grade) and salicylic acid ($C_7H_6O_3$, analytical grade) were obtained from Sinopharm Chemical Reagent (Beijing, China). Ultrapure water (18.3 MΩ•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 μm 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, TRISTAR3020, 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 with a D/max-2500 X-ray diffractometer (XRD; Rigaku, Japan) using in the region of $2\theta$ from 5° to 80°. X-ray photoelectron spectrum (XPS) of the samples was obtained by using Al $K\alpha$ radiation ($h\nu = 1486.6$ 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 ± 0.5 °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, 0.1g 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-