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Pyrolytic temperature dependent conversion of sewage sludge to carbon catalyst and their performance in persulfate degradation of 2-Naphthol

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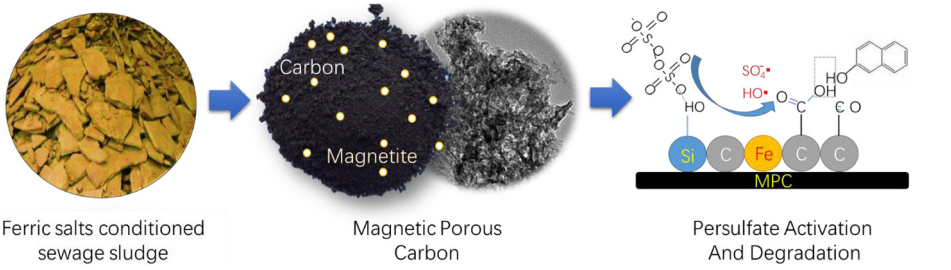
HIGHLIGHTS

- Sewage sludge conditioned by ferric salts can be successfully converted to magnetic porous carbon.
- The simultaneously produced $SO_4^{\cdot-}$ and $HO^{\cdot}$ can degrade 2-Naphthol in heterogeneous MPC/PS system.
- Correlation between catalyst properties and carbonization temperature and their subsequent catalytic behavior was discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

The evolution of oxygen-functioning groups in sewage sludge based carbon is influenced by minerals presented in the raw sludge. In this study, the $FeCl_3$ and polyacrylamide conditioned sludge in real wastewater treatment plant and demineralized sludge were carbonized in the temperature range of 300 °C–800 °C to investigate the roles of temperature and ash components on the interactions between surface groups conversion and crystalline structure evolution. The temperature-dependent ash effect on the conversion of oxygen containing groups was found by using XPS, Boehm titration, XRD and TPR characterization. The phase transfer of hematite to magnetite promoted the formation of hydrophilic organic groups at 600 °C, which may play a significant role on carbon's adsorptive and catalytic behavior. To gain an in-depth knowledge and understanding, the as-prepared carbon was used as heterogeneous catalyst in persulfate degradation of a model pollutant 2-Naphthol. The use of carbon obtained at 600 °C (MC600) can achieve 88.7% and 47% of 2-Naphthol and TOC removal respectively at neutral pH, far higher than that of MC prepared at 300 and 800 °C. Further research revealed a strong correlation between adsorptive and catalytic efficiency of MC and its mineral structure, surface functional groups as well as operating pH. The formed hydrophilic oxygen-containing groups at higher temperature of MC600 are responsible for 2-Naphthol retention and the hydrogen bonds in siloxane bridges can easily adsorb persulfate. The pH effect on degradation in the presence of persulfate verified the broad pH operation, which is apparently superior than conducting with traditional heterogeneous Fenton process. The quenching experiments and EPR spectrum were further used to detect the oxidative species $SO_4^{\cdot-}$ and $HO^{\cdot}$, and confirmed the catalytic role of MC.

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1. Introduction

Sewage sludge (SS), which is the residual being produced from wastewater treatment plants (WWTPs), has recently caused much more attention due to their increased continuously annual generation [1]. It is estimated that the amount of dewatered sewage in China can reach 30 million tons a year. Due to the complex composition and increasing production of SS, the SS disposal has currently becoming a hot issue. Conventional treatment practices for SS follows the route of sludge sedimentation, sludge stabilization, sludge dewatering and subsequent final disposal including incineration and landfill [2]. By sludge dewatering, the concentrated sludge seems normally much easier to handle and dispose. In order to enhance the effectiveness of SS dewaterability, a whole range of chemicals were added [3], among which, iron salts and organic surfactants are widely used in China, making the dewatered sludge consisting of high concentration of minerals and difficult for stabilization [4]. Recently, sludge pyrolysis, which appears to be more efficient and less polluting, has received noticeable attention because it can considerably reduce SS volume and in the same time produce value-added carbonaceous materials for further applications such as catalyst, energy storage and pollutants adsorbents [5].

Due to the carbonaceous nature of SS and the composition of wide variety of inorganic components, such as Fe, Si, Al and Ti, the carbon based functional materials have served as a stable and efficient catalyst for environment remediation, especially in the systems of catalytic wet air oxidation (CWAO) [6], catalytic heterogeneous peroxide oxidation (CWPO) [7,8], electro-Fenton's oxidation [9], photo-Fenton's oxidation [10,11] and catalytic ozone oxidation [12]. It is found that the treatment and reuse of SS as value-added practice has led to considerable research interest. Our previous study on converting SS to a multifunctional porous carbon had proved its capability to catalyze H_2O_2 producing high reactive species HO· [13].

Given the heterogeneity of SS itself and the diversity of the pyrolytic products, the catalytic behavior of sludge derived carbon are highly complex. Recent research on catalytic role of SS carbon catalyst has confirmed the influence of chars crystalline structures and surface functional groups. Yu et al., found that acids modified char surface with more oxygen-containing groups has positive effect on CWPO catalytic adsorption and degradation [8]. Xin et al., mentioned that the ferric-activated carbon showed higher O/C which can significantly improve the hydrophilicity of adsorbent [14]. Our previous report on utilization of SS as Fenton-like catalyst has demonstrated the great impact of mineral structure on char's catalytic role [15]. And Silva et al., found that increasing the pyrolytic temperature promoted the increase of surface acidity [16]. Although some effects are well presented in literatures, the mechanism for how mineral mater, which exists in large quantities in raw sludge, affects surface chemistry under different pyrolytic temperatures is highly inadequate. It is speculated that iron and some minerals in dewatered sludge would undergo series of reactions with carbon basal, which may in turn affect the crystal structure transformation, surface functional groups evolution and porosity development. However, until now, few studies have addressed its effect and its influence on catalytic behavior.

Until now, the effectiveness of SS based catalyst have been well demonstrated in various systems [17], most of which are relying on produced hydroxyl radicals. However, the high pressure applied in CWAO and the rigid pH requirement in Fenton-like systems limited its use. For example, Tu et al. [18] conducted Fenton-like experiments at pH 4 to degrade Orange II and Bedia et al. [19] adjusted initial pH to 3 to carry out the experiment on Fenton-like elimination of antipyrine. Therefore, an oxidative system which would function over wide pH range is needed, among which the process based on SS carbon catalyzed persulfate oxidation is rarely reported so far. Notably, sulfate radicals are more selective than hydroxyl radicals for pollutants oxidation and could achieve much better mineralization [20,21]. Fang et al., has elucidated the persistent free radicals formed in biochar could successfully activate persulfate to produce sulfate radicals [22]. The proven SS utilization as an efficient catalyst in various oxidation medium make it justifiable to think that SS based carbon catalyst would either serve as a desirable candidate for PS activation.

Therefore, in this study, a SS converted magnetic carbon (MC) was prepared and used as adsorbent and catalyst to eliminate a naphthalene pollutant 2-Naphthol in the presence of persulfate. 2-Naphthol is widely used as a starting material for synthesizing a whole range of synthetic dyes [23]. It exists largely in water and soil and pose potential threat to wildlife and human beings [24]. The choose of 2-Napthol as model compound in this study is primarily based on the consideration that the hydroxyl bond on molecules may well interact with hydrophilic sites on carbons.

2. Experimental section

2.1. Chemicals and materials

The sewage sludge was sampled from Songjiang municipal wastewater treatment plant (WWTP) in Shanghai, China. The influent of the selected facility is mainly of domestic origin. The secondary sludge with water content > 99% was conditioned by successive addition of $FeCl_3$ and polyacrylamide to improve their dewaterability. The dewatered raw sludge was stored in a plastic container at 4 °C prior to use and its composition was listed in Table S1.

Fe_3O_4 MNPs, HNO_3, KOH and 30% (w/w) H_2O_2 were provided by Shanghai Reagent CO., Ltd (Shanghai, China). 2-Naphthol was provided by Sanfeng chemical CO., Ltd (Zhejiang, China), Sodium persulfate were bought from Merck, Taiwan. The spin-trapping agent 5,5-dimethyl-pyrroline-N-oxide (DMPO) was purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). All chemicals were analytical grade reagents and were used as received without further purification. Synthetic wastewater containing 1.0 mM 2-Napthol was dissolved with high-purity water and then pH-adjusted with 0.2 N NaOH or 0.2 N H_2SO_4 solutions. All chemicals were prepared using high-purity water from a Millipore system with a resistivity of 18.2 MΩ cm.

2.2. Preparation of catalysts

Magnetic porous carbon derived from sewage sludge was prepared following the procedure by microwave digestion and pyrolysis [15]: the pre-dried sludge was impregnated into 10% HNO_3 solutions under microwave digestion at room temperature for 2 h, which was used to facilitate the dissolution of inorganic species. The digested sludge was then further stirred for 30 min in a temperature-controlled cabin at 50 °C for 20 h with the dropwise addition of 1.0 M KOH solution until the pH reached 11. After being cooled, the precipitate was filtered and dried at 105 °C. Finally, the dried samples was carbonized in N_2 (130 mL min^{-1}), in a quartz tube into a horizontal furnace at a heating rate of 10 °C min^{-1} for 2 h. The obtained samples were ground to fine powders and filtrated through 200 mesh sieve then washed by soaking (24 h) into successive portions of distilled water until constant pH was obtained. For comparison, the MC thermal treated at 300, 600 and 800 °C were prepared and named as MC300, MC600 and MC800 respectively. The Fe_3O_4 MNPS was synthesized in situ by reverse impregnation method with a known mass of $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3$, as described elsewhere [25,26].