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Radical assisted iron impregnation on preparing sewage sludge derived Fe/carbon as highly stable catalyst for heterogeneous Fenton reaction

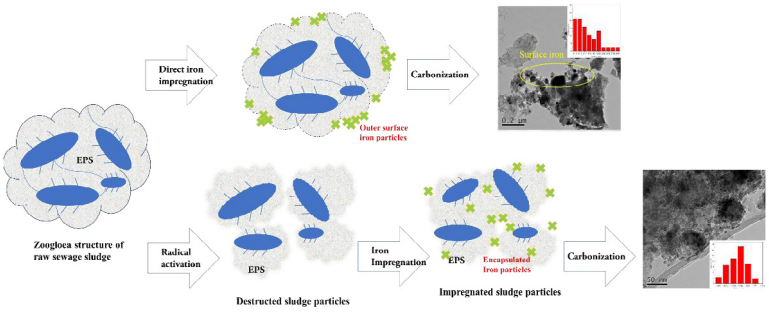
Haifeng Wen[a,1], Lin Gu[a,b,1,*], Haixiang Yu[a], Xingbo Qiao[a], Daofang Zhang[a], Jianfeng Ye[c,*]

[a] School of Environment and Architecture, University of Shanghai for Science and Technology, Shanghai 200093, PR China
[b] China United Northwest Institute for Engineering Design & Research Co., Ltd, Xi'an 710077, PR China
[c] Shanghai Academy of Environmental Science, Shanghai 200233, PR China

HIGHLIGHTS

- Radical assisted iron impregnation was used to prepare sludge precursors.
- Radical oxidation promoted enhanced Fe^{3+} interaction with disintegrated sludge flocs.
- The resulted catalyst had Fe NPs uniformly encapsulated in carbon matrix.
- The resulted catalyst had much improved stability and activity.
- Fe NPs distributed in pores facilitate the polar interaction with organic acids.

GRAPHICAL ABSTRACT



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ABSTRACT

Radical induced sewage sludge pretreatment has been developed to enhance sludge stabilization and dewaterability. Except for anaerobic digestion, the reutilization of the oxidized sludge residuals is still a challenging issue for wastewater treatment plant. In the view of favorable role in sludge disintegration, the pretreated sludge precursors, which was obtained by sequential radical oxidation and iron impregnation, was carbonized to prepare the carbon encapsulated Fe nanoparticles (Fe NPs), which could then behave as highly stable and active heterogeneous Fenton-like catalyst to degrade Black-T. By contrast, the carbonized products derived from direct iron impregnation were also prepared as a control method. The effect of H_2O_2/Fe^{2+} on zeta potential, particle size, morphology and texture structure of the pretreated sludge precursors and their corresponding influence on the carbonized materials were systematically evaluated. Results showed that radicals' activation could facilitate the iron impregnation on sewage sludge by rupturing the microbial aggregate and making them more accessible to subsequent microbial fragments. Compared to direct iron impregnation, the carbonized products featured much higher iron insertion rate and the uniformly dispersed Fe NPs encapsulated into porous carbons, which in turn enables catalysts exhibiting more efficient catalytic activity in continuous heterogeneous Fenton-like degradation and resistance to metal leaching.

* Corresponding authors at: School of Environment and Architecture, University of Shanghai for Science and Technology, Shanghai 200093, PR China.
E-mail address: lin_gu@hotmail.com (L. Gu).
[1] The first author and second author contributed equally to this article.

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1. Introduction

Sewage sludge (SS), which is the by-product originating from the municipal wastewater treatment plant, consists of a wide range of organic and inorganic species including carbonaceous materials such as bacterial cells, bio-macromolecules and ashes such as silica, alumina, calcium, ferric oxides [1,2]. It attracted much more concern due to its huge production amount and the increasingly stringent regulations imposed on them. Therefore, the common way such as incineration and landfill dumping are no long acceptable.

Recent researches on SS thermal conversion to multifunctional carbon materials, such as adsorbent, catalyst and capacitors have gained noticeable interest [3–5]. Depending on their physiochemical properties, the carbon materials are widely used in various environmental remediation process, including Catalytic Wet Air Oxidation (CWAO) [6], Electro-Fenton oxidation [7], Photo-Fenton oxidation [8], catalytic ozone oxidation [9], and mostly in the fields of Catalytic Wet Peroxide Oxidation (CWPO) [4,10,11]. The existence of diverse components such as SiO_2 and Al_2O_3 exerts catalysts the extra catalytic performance. Regarding the patterns of sludge catalysts reported so far, iron immobilized sludge carbon accounts for a great proportion for its low cost and naturally abundance [12]. For example, Tu et al. [4] synthesized the SS-supported iron materials and studied the respective role of Fe_2O_3, SiO_2 and Al_2O_3 as heterogeneous Fenton-like catalyst. Bedia et al., [3] prepared iron supported sludge carbon by solid mixing of dry SS with Fe salt and found much improved catalytic stability when being used in CWPO degradation of antipyrine.

The general procedure for sludge carbon supported Fe preparation follows the way of sludge carbonization and Fe impregnation. However, the process normally need extra sludge activator (e.g., KOH, $ZnCl_2$, H_3PO_4) to promote the pore development and avoid Fe NPs agglomeration [13]. The decorating of iron species directly onto carbon also had the defects of low affinity between Fe and sludge precursors. In respect to the process of solid sludge/iron mixing prior to carbonization, it always needs large proportions of Fe salts, making the process economic infeasible [3]. Recent reports on facile wetness impregnation of Fe salts onto raw sludge particles provided an insight into efficient synthesis of sludge carbon supported iron catalyst [14]. However, the low insertion rate of Fe ions and the agglomeration of sludge surface-bonded Fe particles notably affected the catalytic behavior of the prepared catalyst.

Radicals induced sludge oxidation, as an advanced sludge pretreatment that lyses the microbial cells and destruct the particles, has been widely used to improve the sewage sludge dewaterability [15]. Among them, Fenton's reagent (H_2O_2 + Fe^{2+}), which produces highly oxidative species, such as hydroxyl radicals ($^{\cdot}OH$), can effectively destroy the zoogloea structure of sludge particles, and cause the release of metal cations into aqueous solutions [16]. Our previous research on sludge carbonization also found that radicals induced volatile release could act as an efficient activator for pore formation [17]. Since Fe^{2+} behaves as both catalyst and coagulant in the process of Fenton's conditioning of sewage sludge, the way it worked on sludge must be different from the direct Fe^{2+} impregnation. The enhanced interactions are therefore expected to promote the activity and stability of the resulted catalyst.

Thus, in this study, the comparative experiments on sewage sludge pretreatment by radical assisted iron impregnation was conducted. The effectiveness of radical activation on preparing the stable and active carbon encapsulated iron catalyst was evaluated in terms of both sludge precursor and catalysts' physiochemical properties. The effect of H_2O_2/Fe^{2+} ratio on the characteristics of resulting materials was also investigated. Heterogeneous Fenton-like reactions in batch mode were carried out to degrade a typical azo dye contaminate Black-T and the mechanism for radicals' assisted on synthesizing iron immobilized sludge carbon catalyst was proposed. Black-T is a typical naphthalene dye intermediates that is being widely used in dyeing and textile production. It exists largely in water and soil and pose potential threat to wildlife and human beings. The delocalization-conjugated bond composed of ten carbon atoms is quite stable and hardly decomposed by traditional biological treatment.

2. Experimental

2.1. Materials and methods

The sewage sludge used in this study was sampled from the secondary sentimental tank of Songshen municipal wastewater treatment plant, Shanghai. Atypical operating/weather conditions (e.g., raining, the unstable influent flux) was excluded to ensure the uniform characteristics of the used samples. The raw sludge was saved at 4 °C prior to use. The basic properties of the sampled sewage sludge solution are as follows: pH 6.71, Total Solids 18.7 g/L, Volatile Solids 12.7 g/L, TCOD 1.18 g/L. 30% H_2O_2, $FeSO_4{\cdot}7H_2O$ and 98% H_2SO_4 were purchased from Shanghai Chemical Reagent Co., China. Black-T were provided by Sinopharm, China.

2.2. Sludge activation

Prior to carbonization, sample of 500 mL raw sludge was hold in a 2 L plastic beaker equipped with a mechanical mixer of variable rotational speed (50–250 rpm). The reactor was placed at room temperature and stirred with the droplet addition of 1.0 M H_2SO_4 until a desired pH (2.5–3) was reached. The activation was initialed by adding 22.8 mM/(g VS) (equals to volume ratio of 2.25%) H_2O_2, the amount of which is determined to ensure the destroy of the zoogloea structure of sludge particles and the destruction of cell membrane [16]. Then $FeSO_4{\cdot}7H_2O$ with a determined molar ratio of Fe^{2+}/H_2O_2 (0.1, 0.2 and 0.4) was added into the solution, which was based on the optimal ratio for Fenton reactions. In traditional Fenton reaction for sludge dewatering and stabilizing, the molar ratio of Fe^{2+}/H_2O_2 was less than 1 and Fe^{2+} only serves as catalyst [16]. The mixer was stirred at 120 rpm for 120 min. The obtained precursors were then denoted as RS-F-*x*, where x represented the molar ratio of Fe^{2+} to H_2O_2.

For comparison, the direct Fe impregnation was also conducted by a facial incipient wetness impregnation. The given mass of $Fe_2(SO_4)_3{\cdot}9H_2O$ was dissolved into 500 mL raw sewage sludge solutions and stirred at 120 rpm for 120 min. The impregnated samples were denoted as RS-I-*x*, where *x* equals to 0.1, 0.2 and 0.4, representing the identical iron dosage to Fenton's activation process.

2.3. Catalyst preparation

The pretreated mixture was immediately filtrated with 0.45 μm membrane and dried at 105 °C to a constant weight. Finally, the samples were carbonized at 600 °C under a heating rate of 10 °C/min and a high purity N_2 flow of 130 mL/min with a horizontal furnace equipped with a quartz tube. The cooled products were repeatedly washed by distilled water until constant pH was reached. The catalyst prepared from radical assisted impregnation and direct impregnation were denoted as SC-F-*x* and SC-I-*x* respectively.

2.4. Heterogeneous Fenton degradation of Black-T

The batch catalytic degradation experiments were performed in 50 mL brown glass reactor under stirring at 200 rpm. 1 mM Black-T solution was introduced into the reactor and then pre-heated to maintain a constant temperature by water bath shaker for 20 min, the amount of which is determined by consideration that the dye concentration in most polluted surface waters is in tiny amount. Catalysts (1*g*/L), which had been previously immersed in solution with 1 mM Black-T to reach adsorption-desorption equilibrium, was transferred into the reactor. The solution pH was adjusted to 3 with 0.1 M H_2SO_4