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Treatment of landfill leachate by continuously reused ferric oxyhydroxide sludge-activated hydrogen peroxide

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HIGHLIGHTS

- Proposed sludge-activated Fenton-based system operating in sequencing batch mode.
- Combined sludge/Fe^{2+} as an effective activator for the Fenton-based process.
- Observed effective organic load removal in the H_2O_2/sludge/Fe^{2+} system.
- Complete sludge reuse for up to ten Fenton-based treatment cycles.
- Verified improvement in reused ferric sludge properties and reduction in quantity.

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ABSTRACT

The ferric oxyhydroxide sludge-activated Fenton-based oxidation and its application for landfill leachate treatment were studied. The mechanism of iron dissolution form the surface of ferric oxyhydroxides was proposed. The impact of humic substances, corresponding to 11% of COD, on the iron dissolution and the subsequent hydrogen peroxide activation was assessed. An innovative H_2O_2/sludge system with the addition of ferrous iron, which was operated in sequencing batch mode, was determined to be a promising technique for the effective degradation of an organic load and for the reduction of the produced residual ferric waste. The observed results indicated the effective removal of COD, DOC, BOD_7 and total phenols (TPh) in the H_2O_2/sludge/Fe^{2+} system at a $H_2O_2/[O]_{COD}$ and H_2O_2/Fe^{2+} molar ratio of 1.5/1 and 50/1, respectively, during ten sludge reuse cycles in a sequencing batch reactor (SBR). Accordingly, the removal of the organic contaminants after the 1st/10th reuse cycle was 63/55% (COD), 51/44% (DOC), and 79/79% (TPh). Moreover, a rough estimation of the biodegradability of the SBR effluent is given as the BOD_7/COD ratio, which indicated the potential use of a biological post-treatment to improve the overall quality of the effluent. The sludge-activated Fenton-based treatment also resulted in more effective thickening of the ferric oxyhydroxide sludge and in a lower content of adsorbed organic compounds in the solid residue compared with the sludge formed after a single Fenton treatment.

1. Introduction

Nowadays, the disposal of solid wastes in sanitary landfills is considered as the most common method of municipal waste management [1]. However, rainwater percolation through the landfilled wastes, washing out organic and mineral contaminants along with their decomposition products, inevitably leads to the generation of hazardous landfill leachate [1,2]. As a result, to prevent potential undesirable infiltration into the soil and subsequent percolation into the groundwater aquifers, the landfill leachate needs to be collected and properly treated.

The effective destruction of persistent, bio-refractory and toxic organic pollutants in different types of wastewaters, including landfill leachate, via the hydroxyl radical-based Fenton process has been extensively studied [3–5]. The generally accepted mechanism of classical Fenton oxidation consists of a sequence of reactions in which hydroxyl radicals ($HO^{\cdot}$) are produced according to Eq. (1) and the oxidised activator (Fe^{3+}) is regenerated via Eqs. (2) and (4) or through the reaction with organic radicals ($R^{\cdot}$), as shown in Eq. (6) [3,6,7]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + HO^{-} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^{+} \quad (2)$$

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$$HO^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \quad (3)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + H^+ + O_2 \quad (4)$$

$$HO^{\cdot} + RH \rightarrow H_2O + R^{\cdot} \quad (5)$$

$$Fe^{3+} + R^{\cdot} \rightarrow Fe^{2+} + R^+ \quad (6)$$

The main advantage of this advanced oxidation technique over other HO·-based technologies is the simplicity of installation and the practical application; however, there is also an important limitation that hinders the widespread industrial use of the Fenton process for processing effluents and manufacturing wastewater treatment. To terminate the homogeneous Fenton oxidation, the pH of the system is usually raised to alkaline values to promote the settling of amorphous ferric oxyhydroxides. Thus, a large volume of solid iron-containing hazardous sludge that requires proper treatment and special disposal is produced [8].

To reduce the ferric oxyhydroxide sludge formation, the use of heterogeneous solid iron-bearing activators, such as zeolites [9,10], clays [11,12], activated carbon support [13,14], iron oxides [15–17], minerals [18] and zero-valent iron [19,20], and the reuse of the iron-rich sludge [21–27] have been considered. The application of the former techniques provides high performance oxidation over a longer period as the iron is immobilised within the interlayer space of heterogeneous activators. Moreover, these solids can be easily separated from the treated wastewater and subsequently reused. However, the repetitive use of a heterogeneous activator usually diminishes its properties due to leaching of the active iron [29] and decaying of the active sites on the surface of the catalytic agent [30]. Notably, during the Fenton treatment of wastewater, the coagulation with subsequent sedimentation (hereinafter both processes are referred to as the coagulation step) of ferric oxyhydroxides advances the removal of the organic compounds. Thus, the elimination of this treatment step may lead to the reduction of the overall purification efficacy. Therefore, the application of Fenton treatment modifications that result in a lower sludge production than traditional treatment processes could be more advantageous and practicable than eliminating the coagulation step. The Fenton-based treatment and the reuse of the ferric oxyhydroxide sludge inherently involve a coagulation step to support organic contaminant elimination. Thus, this approach can minimise the hazardous waste production and may be considered as a promising and more preferable method. According to the available literature, the reuse of the ferric oxyhydroxide sludge as an iron source for the Fenton-based process has been studied mainly after its regeneration using high temperature treatments [21,22], reducing agents [23] or electrochemical reduction [24,25]. Alternatively, the ferric sludge could be reused as an additive to enhance pre-coagulation of wastewater prior the Fenton treatment [28]. Conversely, the application of the non-regenerated ferric sludge was found to be effective for the degradation of phenol in aqueous solution by the Fenton-based process over nine reuse cycles [27]. Moreover, in our recent study [26], it was confirmed that the separated and partially dewatered non-regenerated ferric oxyhydroxide sludge could be effectively reused several times as an activator for the Fenton-based treatment of municipal waste landfill leachate, hazardous waste landfill leachate and hardwood soaking basin effluent. However, the mechanism of iron dissolution from the surface of ferric oxyhydroxides and the subsequent hydrogen peroxide activation was not considered in details. Conversely, the results of previous studies strongly suggested that the oxidation of organic contaminants by the Fe^{3+}-activated hydrogen peroxide system could be effectively promoted using organic reducing agents [31–33] and complexing ligands [34–37] that are potentially present in complex industrial wastewater matrices and/or the partial addition of supplementary ferrous ions (Fe^{2+}) to the reaction system [32]. Therefore, to overcome or to alleviate the problems associated with waste ferric solid utilisation and to minimise the overall cost of the treatment, the continuous reuse of ferric oxyhydroxide sludge as an iron source in the oxidation step of the Fenton-based treatment of municipal landfill leachate is proposed here. Landfill leachate is known to be a complex mixture of high-strength organic and inorganic contaminants usually containing elevated fractions of humic substances (HS, mainly humic and fulvic acids) [1,2], which could substantially improve the efficacy of Fe^{3+}-activated hydrogen peroxide system due to strong complexing properties of these amorphous biopolymers [38,39].

The main purpose of this study was to evaluate the efficacy of the ferric oxyhydroxide sludge continuous reuse in the Fenton-based treatment of landfill leachate in a sequencing batch reactor with and without the addition of supplementary ferrous iron. The sequencing batch mode that was applied in the proposed schemes presumes the complete reuse of the non-regenerated and non-processed ferric sludge. Thus, the industrial scale implementation of this modification of the Fenton process may be performed with few sludge-associated concerns. The novelty of the study is the consideration of the mechanism of the ferric oxyhydroxide sludge-activated hydrogen peroxide oxidation in the presence of strong complexing and reducing agents. To the best of our knowledge, this the first study on the continuous reuse of the ferric sludge in the Fenton-based treatment of any aqueous matrix. Therefore, the results of this study may provide fundamental knowledge for the practical and cost-effective application of ferric oxyhydroxide sludge-activated Fenton-based processes for industrial wastewaters and especially effluents containing elevated fractions of substances with complexing and reducing properties treatment.

2. Experimental

2.1. Chemicals and materials

Hydrogen peroxide (PERDROGEN™, H_2O_2, ⩾30%) and ferrous sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$, ⩾99%) were purchased from Sigma-Aldrich Co. (USA). All of the other chemicals were of analytical grade and used without further purification. Stock solutions were prepared in ultrapure water (Millipore Simplicity® UV System, Merck, Germany).

The municipal landfill leachate sample was obtained from a municipal non-hazardous waste landfill that began operating in 2003. The leachate production rate varies between 500 and 2500 m^3 per month depending on the season. The collected leachate sample was stored at 4 °C. The properties of the leachate sample that was obtained from the landfill in November 2014 are presented in Table 1.

Table 1
Chemical composition and properties of the leachate sample.

Parameter	Unit	Value
COD	mg/L	6650 ± 170
BOD_7	mg/L	4210 ± 140
BOD_7/COD		0.63
DOC	mg/L	2260 ± 18
DN	mg/L	1920 ± 10
HS	mg/L	728 ± 4
TPh	mg/L	24 ± 0.85
Conductivity	mS/cm	8.7
pH	–	7.03
TFS (600 °C)	mg/L	568 ± 11
TSS (105 °C)	mg/L	3195 ± 14
Alkalinity	mg$CaCO_3$/L	2900 ± 125