



Reuse of ferric sludge as an iron source for the Fenton-based process in wastewater treatment

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HIGHLIGHTS

- Reused ferric sludge as an effective catalyst for the Fenton-based process.
- Observed a similar Fenton-based treatment efficacy for up to 4 ferric sludge reuses.
- Revealed the effective catalytic properties of ferric-sludge without any prior regeneration.
- Displayed a similar treatment efficiency using dissolved iron or ferric sludge in the catalysed Fenton process.

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ABSTRACT

A mature municipal landfill leachate (S1), a wood soaking basin effluent from a plywood manufacturing plant (S2), and a leachate collected from a semicoke landfill area of an oil-shale thermal treatment plant (S3) were subjected to the Fenton/Fenton-based treatment ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$, $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ and $\text{H}_2\text{O}_2/\text{sludge}$ systems). The results of ferric coagulation trials indicated a high efficacy in S2; thus, only pre-coagulated samples (cS2) were further treated by the $\text{H}_2\text{O}_2/\text{iron}$ systems. Irrespective of reaction duration, S1 was more recalcitrant to oxidation than cS2 and S3. The optimal $\text{COD}/\text{H}_2\text{O}_2$ weight ratio for cS2 and S3 was 1:1 with respective 21(35) and 36(45)% residual COD(DOC). In the case of S1, the $\text{COD}/\text{H}_2\text{O}_2$ w/w of 1:3.45 proved the most efficient with 30 and 35% residual COD and DOC, respectively. The results also indicated an increase in BOD_7/COD ratio and a reduction in the acute toxicity to *Daphnia magna* of the studied wastewater samples after the Fenton/Fenton-based treatment. The application of the Fenton-based process catalysed with iron-containing sludge exhibited efficacies similar to classical Fenton treatment over four reuse cycles. The reuse of ferric sludge without any regeneration as an iron source in the Fenton-based process was displayed as a feasible solution to minimise the production of hazardous ferric waste and reduce the overall cost of the treatment process.

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1. Introduction

The Fenton process has been extensively studied and successfully used for the treatment of a wide range of different wastewaters. For example, the Fenton process can be used to treat highly loaded, refractory, toxic and coloured wastewaters which cannot be biologically treated [1–3]. However, the practical application of the Fenton process is limited mainly because of the large amount of ferric sludge produced during neutralisation after oxidation. The solid waste sludge, which is potentially hazardous because of residual organics adsorbed from treated wastewater,

requires proper treatment and disposal to specific sites. This resultant sludge is therefore the main obstacle preventing the application of the full-scale Fenton process in industrial wastewater treatment [1].

The iron-containing sludge could be reused as a coagulant for water/wastewater pre-treatment prior the Fenton process, resulting in up to 50% reduction in the required coagulant [4]. However, the ferric sludge could be effectively utilised only once in this type of reuse system. To minimise the above-mentioned sludge formation, two approaches have been investigated: the use of heterogeneous catalysts and the reuse of the iron-containing sludge. The application of a heterogeneous catalyst, such as naturally occurring minerals [5], iron-containing clays [6,7], iron immobilised on a solid support [8,9], and zero-valent iron [10–12], in the Fenton

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process reduces the amount of ferric sludge formed, results in extended periods of catalyst use without regeneration or replacement and efficiently removes the catalyst from the treated wastewater by sedimentation or filtration. The majority of heterogeneous catalysts studied to initiate the Fenton/Fenton-based reaction resulted in additional homogeneous hydrogen peroxide catalysis because of the leaching of ferrous ions into the surrounding solution, notably in acidic condition [5,10].

During the Fenton treatment of wastewater, the oxidation and coagulation of ferric-hydroxy complexes both contribute to the removal of the organic compounds; therefore, the complete elimination of the coagulation step may be undesirable when a high overall process efficacy is desired. Accordingly, the sludge recycling/reusing methods resulting in a lower sludge production than traditional treatment processes could be more preferable than those eliminating the coagulation step. The use of iron-containing sludge as a catalyst for the Fenton process has been performed mainly after thermal regeneration and subsequent re-dissolution of iron-containing solids by acid [13,14], chemical regeneration with reducing agent [15] and electrochemical reduction [16,17]. All mentioned techniques functioned well, but increased the overall cost of wastewater treatment because of the additional sludge regeneration step.

The main objective of this study was to minimise the production of iron-containing sludge by completely reusing it as an iron source in the oxidation part of the Fenton-based treatment. The alternative without any regeneration is proposed to reduce the overall cost of the process without eliminating the coagulation step in the Fenton treatment, which contributes to the overall treatment efficacy of the process.

2. Experimental

2.1. Chemicals and materials

Hydrogen peroxide (PERDROGEN™, ≥30%) and ferrous sulphate heptahydrate (FeSO₄·7H₂O, ≥99%) were purchased from Sigma–Aldrich, ferric sulphate hydrate (Fe₂(SO₄)₃·xH₂O, Fe 21–23%) was obtained from Riedel-de Häen. All other chemicals were of analytical grade and used without further purification. Stock solutions were prepared in ultrapure water (Millipore Simplicity® UV System). Sodium hydroxide and sulphuric acid aqueous solutions were used to adjust the pH.

The studied wastewater samples were comprised of: (i) Sample 1 (S1) – a mature municipal landfill leachate (the landfill has operated for more than 10 years) (October, 2013), (ii) Sample 2 (S2) – a wood soaking basin effluent from a plywood manufacturing plant (the wastewater is rich in lignin, water-soluble wood, mechanical particles, and extractives such as terpenes, resin acids, triglycerides, fatty acids, and phenolic compounds) (April, 2013), and (iii) Sample 3 (S3) – a leachate collected from a semicoke (hazardous waste rich in phenols such as phenol, p-cresol, dimethylphenols, resorcinol, 5-methylresorcinol and 2,5-dimethylresorcinol) landfill area of an oil-shale thermal treatment plant (March, 2013). The collected wastewater samples were stored at 4 °C. The main properties of wastewater samples are presented in Table 1.

2.2. Experimental procedure

The coagulation with ferric sulphate (KEMIRA PIX-322, Fe_{total} 12.5 ± 0.3%) was performed in a jar test apparatus (Kemira, Finland). The wastewater volume in each jar was 0.6 L. The coagulant doses (Fe_{total}) varied in the range of 100–1000 mg L⁻¹. The operating conditions were as follows: 1 min of fast mixing at 400 rpm ($G = 956 \text{ s}^{-1}$), 30 min of slow mixing at 40 rpm

Table 1
General chemical properties of the wastewater samples.

Parameter	S1	S2	S3
COD, mg L ⁻¹	5928 ± 280	5145 ± 213	2100 ± 190
BOD ₇ , mg L ⁻¹	3160 ± 190	1607 ± 126	375 ± 11
BOD ₇ /COD	0.53	0.31	0.18
DOC, mg L ⁻¹	2002 ± 12	1260 ± 11	493 ± 1
TN, mg L ⁻¹	480 ± 2.3	11.5 ± 0.3	15.5 ± 1.5
Conductivity, μS cm ⁻¹	7.2	973	9000
pH	7.32	4.75	7.9
TS (105 °C), mg L ⁻¹	6770 ± 70	2549 ± 34	8650 ± 10
TFS (600 °C), mg L ⁻¹	3010 ± 230	516 ± 6	7639 ± 17
TSS (105 °C), mg L ⁻¹	1900 ± 180	912 ± 140	21 ± 7
F ⁻ , mg L ⁻¹	23.5 ± 1.7	62	1
Cl ⁻ , mg L ⁻¹	2280 ± 10	557	6146
PO ₄ ³⁻ , mg L ⁻¹	–	66	42
SO ₄ ²⁻ , mg L ⁻¹	114 ± 3	161	1510
Total phenols, mg L ⁻¹	–	51	6
<i>Daphnia magna</i> EC ₅₀ , %	7.9 ± 1.7	15.3 ± 2.2	19.5 ± 2.9
Lignin and tannins, mg L ⁻¹	–	560 ± 10	–

($G = 30 \text{ s}^{-1}$), and 24 h of sedimentation. Afterward, the supernatant was collected for further analysis.

The H₂O₂/Fe²⁺(Fe³⁺) and H₂O₂/sludge systems with neutralisation/sedimentation step are hereinafter referred to as the Fenton and Fenton-based treatment, respectively. All the Fenton/Fenton-based process trials were performed in batch mode and in non-buffered solutions. Half-litre wastewater samples were treated in 1 L cylindrical glass reactor with a permanent agitation speed (400 rpm) for a period of 1–24 h. The catalyst (FeSO₄·7H₂O or Fe₂(SO₄)₃·xH₂O) was added, and after complete dissolution of the catalyst, the Fenton reaction was initiated by adding H₂O₂. The pH of the wastewater samples was not adjusted in the subsequent treatment, if not specified otherwise. The weight ratio of H₂O₂/Fe²⁺(Fe³⁺) was maintained at 5:1, which is optimal [18]. The oxidation was halted by neutralising the treated samples with NaOH (10 M) to a pH approximately 9 under mechanical stirring. Neutralisation led to the iron precipitating as ferric-hydroxy complexes. This process was followed by an iron sludge settling period of 24 h (for effective thickening of the sludge). Finally, the supernatant was collected for further analysis. During the sludge reuse trials, the additional solid–liquid separation of ferric-hydroxy complexes from the solution was performed by centrifugation (10 min, 4000 rpm). The concentrated sludge was used as an iron source for the Fenton-based oxidation (pH 3) without any chemical or thermal pre-regeneration. The scheme for the ferric sludge reuse in the Fenton-based treatment of wastewater samples is presented in Fig. 1.

The experiments on wastewater oxidation with non-catalysed hydrogen peroxide were conducted in identical reactors and treatment conditions for the respective Fenton treatment trials.

All experiments were duplicated and the data on the initial parameters of wastewater samples were verified with at least three replicates. The results of the analysis are presented as the mean with a standard deviation below 4% in all cases. The experiments were performed at ambient room temperature (22 ± 1 °C).

2.3. Analytical methods

The chemical oxygen demand (COD) was determined with a closed reflux colorimetric method [19]. The correction for the hydrogen peroxide interference on COD test was performed by the correlation equation reported by Kang et al. [20]. The total suspended solids (TSS), total solids (TS), total fixed solids (TFS), and a 7-day biochemical oxygen demand (BOD₇) were determined according to APHA [19]. The acute toxicity of the initial and treated samples to *Daphnia magna* (*Cladocera*, *Crustacea*) was measured

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