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Organic matter removal from biologically treated sewage effluent by flocculation and oxidation coupled with flocculation

Shanthini Saminathan[a], Hong Liu[b], Tien Vinh Nguyen[c], Saravanamuthu Vigneswaran[c]*

[a]*Faculty of Applied Science, Vavuniya Campus of the University of Jaffna, Sri Lanka*
[b]*Department of Resource and Environment Engineering, Wuhan University of Science and Technology, Wuhan , Hubei 430081, PR China*
[c]*Faculty of Engineering and IT, University of Technology, Sydney (UTS), PO Box 123, Broadway, NSW 2007 Australia*
Tel. +61 (2) 95142614; Fax +61 (2) 95142633; email: s.vigneswaran@uts.uts.au,

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ABSTRACT

Flocculation alone and flocculation coupled with oxidation process were used for removing organic matter from biologically treated sewage effluent. The performances of different flocculants such as ferric sulphate, ferric nitrate, ferric chloride, and aluminium sulphate were experimentally evaluated. Among the flocculants tested, ferric chloride was selected because of its highest dissolved organic carbon (DOC) removal efficiency (67%) and the large size of the floc (mean size $d_{(0.5)}$ = 53.04 μm). The optimum dosage of $FeCl_3$ was determined as 16 mg (Fe^{3+})/L. Different fractionation of organic matter before and after the flocculation process was analyzed. It was observed that $FeCl_3$ could remove 90% of hydrophobic compounds and 61% of hydrophilic compounds. Oxidation process by Fenton reagent coupled with flocculation was also trialed. It is observed that DOC removal efficiency of Fenton reagent coupled with flocculation could reach 86%. The combination of flocculation and Fenton reagent increased the hydrophilic removal to 85%.

Keywords: Effluent organic matter; Fenton; Flocculation; Oxidation; Wastewater treatment

1. Introduction

Effective treatment or appropriate disposal of industrial and domestic wastewaters is necessary to preserve waterways. Although after the secondary and tertiary treatments, the wastewater can be discharged into waterways but without further treatment, this effluent cannot be reused [1].

Membrane processes are recognized as an important method in the wastewater treatment for reuse. However, one of the major problems of membrane processes is membrane fouling, especially when membrane is used to treat wastewater contained a high amount of effluent organic matter (EfOM). The EfOM fouling can have strong effects on membrane performance including permeability and EfOM rejection [2]. Therefore, there is a pressing need to minimise the membrane fouling and pretreatment is a well-liked method to minimize the membrane fouling.

A number of researches on different technologies for removing organic matter have been reported in the literature. Some of these technologies are flocculation and advanced oxidation with fenton process [3–7].

Aguiar et al. [3] studied the organic matter removal from highly colored impoundment and river waters by coagulation with ferric iron. They found that Total organic carbon (TOC) removal by coagulation with Fe(III) at pH

* Corresponding author.

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of 5.5 ranged between 60 and 80% and the optimal dose of coagulant was 2.1 ± 0.2 mg Fe/mg of TOC.

Friedler et al. [4] used ferric chloride as pretreatment for "light" greywater that had TOC and turbidity were 24.9 mg/L and 34 NTU respectively. Their results showed that with a dose of 50 mg/L, the UF flux decline rate reduced by 43%. With this dose, 94% of the turbidity and 60% of the TOC were removed from the greywater.

Calcium chloride was used as coagulant agent for secondary effluent of the wastewater treatment plant at Staoueli (Algeria) [5]. The coagulation test with 50 mg/L of $CaCl_2$ showed that the chemical oxygen demand reduced from 46 mg/L to 12 mg/L and turbidity reduced from 16 to 3 NTU.

Al-Malack and Anderson [6] evaluated the effect of alum and lime as coagulants on the performance of cross-flow microfiltration for secondary effluent from wastewater treatment plant. They found an improvement in flux values with the increase in alum dose from 20 to 120 mg/L. However, lime was found not to be a suitable coagulant.

Badawy and Ali [7] found that using 400 mg/L $FeCl_3$ as coagulant could remove 63% chemical oxygen demand (COD) and 44% color from combined industrial and domestic wastewater (COD and total suspended solid were 2284 and 372.0 mg/L respectively). The removal could be increased to more than 90% of COD when Fenton process (pH 3.0 ± 0.2, Fe^{2+} dose = 400 mg/L and H_2O_2 = 550 mg/L) was applied.

The main objective of this research was to evaluate the removal of organic matter from biologically treated sewage effluent by different flocculants. The combination of oxidation with flocculation was also trialed for improving the organic matter removal efficiency. In this study, the effects of a number of process conditions such as pH, oxidant doses were experimentally investigated.

2. Material and methods

2.1. Material

2.1.1. Wastewater

The synthetic wastewater was used in this study. This synthetic wastewater represents the biologically treated sewage effluent as it consisted of organic substances such as humic acid, tannic acid, lignin, arabic acid and other high molecular weight (MW) carbohydrates. The dissolved organic carbon (DOC), pH and turbidity of synthetic wastewater are around 10 mg/L, 7.3, and 3.9 NTU respectively. This synthetic wastewater was first used by Seo et al. [8] and the composition of synthetic wastewater is presented in Table 1. Synthetic wastewater was made in the laboratory on the same day of experiment that was carried out.

The results from Shon et al. [2] showed that the MW of the synthetic wastewater varied from 291 to 34118 Da with the weight-averaged MW of 29532 Da.

Table 1
Constituents of the synthetic wastewater

Compounds	Weight (mg/L)
Beef extract	1.8
Peptone	2.7
Humic acid	4.2
Tannic acid	4.2
(Sodium) lignin sulfonate	2.4
Sodium lauryle sulphate	0.94
Acacia gum powder	4.7
Arabic acid (polysaccharide)	5.0
$(NH_4)_2SO_4$	7.1
KH_2PO_4	7.0
NH_4HCO_3	19.8
$MgSO_4.3H_2O$	0.71

2.2. Flocculation

In this study, ferric sulphate, ferric nitrate, ferric chloride, aluminium sulphate and polyaluminium chloride (PAC) were used as flocculants. These flocculants were selected as they have different ferric and aluminous cations as well as different chloride, nitrate and sulfate anions. The synthetic wastewater was placed in 1 L beakers, where known amounts of flocculants were added in. The samples were then stirred for 10 min at 120 rpm, followed by 10 min of slow mixing at 30 rpm, and 30 min of settling. The supernatants were taken, filtered through 0.45 micron filter and analyzed for dissolved organic matter and organic fractions to determine the effects of the flocculants in the removal of organic matter from the wastewater.

2.3. Oxidation process

Firstly, pH of synthetic wastewater was adjusted to predetermined values by adjusting with diluted HCl. After that, $FeCl_3$ or $FeCl_2$ of 16 mg/L (in terms of Fe^{3+} or Fe^{2+}) and different amount of H_2O_2 (2, 5, 10, and 32 mg/L) were added and mixed at 120 rpm for 15 min before pH was adjusted back to a neutral value with 1% NaOH. Synthetic wastewater was then mixed for 2 min followed by a slow mixing at 30 rpm for 10 min and then the content was allowed to settle for 30 min. The supernatants were taken and analyzed for dissolved organic matter and organic fractions.

2.4. Measurement

Dissolved organic carbon (DOC) was measured using Multi N/C2000 TOC analyser after filtering samples through 0.45 micron filter. Multi N/C2000 TOC analyser measures total organic carbon (TOC) by the difference method, i.e. by measuring the total carbon (TC) and total inorganic carbon (TIC), the difference is calculated to obtain TOC value.

The floc size was measured after the floc growth by Mastersizer 2000.

Organic fractions presented in wastewater before and after treatment were also measured by DOC-LABOR liquid chromatography – organic carbon detector (LC-OCD). This system uses size-exclusion chromatography to separate classes of dissolved organic materials (organic acids, bases and neutral species) before measuring by a catalysed UV oxidation.

3. Results and discussion

3.1. DOC removal by flocculants

Fig. 1 shows the variation of DOC removal efficiency as a function of concentrations of $Fe_2(SO_4)_3$ and $FeCl_3$. It can be seen that the DOC removal efficiency increased with the increase in flocculant concentrations and DOC removal efficiency reached its highest rate at a flocculant dose of 16 mg/L (in terms of Fe^{3+}) for both $Fe_2(SO_4)_3$ and $FeCl_3$. However, when continued increasing the concentrations of flocculants to more than 16 mg/L, the DOC removal efficiency decreased due to the restabilisation of the colloidal particles.

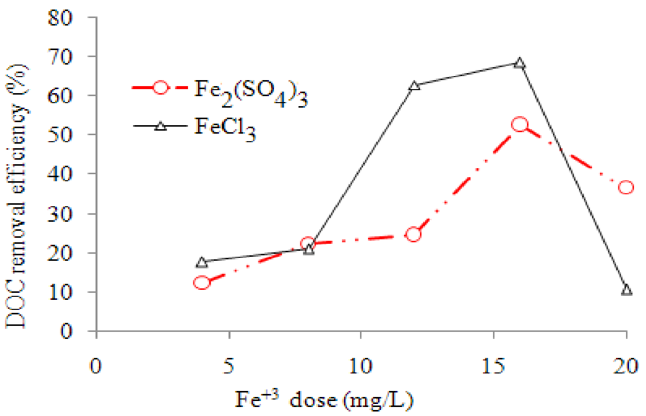

Fig. 1. DOC removal efficiency as a function of concentrations of $Fe_2(SO_4)_3$, $FeCl_3$.

The comparison of performance of 5 flocculants (concentration of 16 mg/L in terms of Fe^{3+} or Al^{3+}) with synthetic wastewater is presented in Table 2. The result shows that at the same dose DOC removal efficiency with $FeCl_3$ was higher than that of other flocculants. In the flocculation, Fe^{3+} combines with some natural organic matters, such as tannin to form sediment or another substance.

$FeCl_3$ was preferred over $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ as the DOC removal efficiency of $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ was found to be lower than that of $FeCl_3$ and SO_4^{2-} also could produce repulsion to organics in wastewater.

The results show that although the floc size with PAC and $Fe(NO_3)_3$ were higher than that with $FeCl_3$, DOC removal efficiencies by them were still lower than that by $FeCl_3$. Another disadvantage of PAC over the $FeCl_3$ is the problem of toxicity of residual aluminum. $FeCl_3$ was also found to be a better flocculant than $Fe(NO_3)_3$ not only because of higher DOC removal efficiency but also NO_3^- is one of the factors that leads to algae bloom in water.

Thus, among the flocculant studied, $FeCl_3$ with an optimum dose of 16 mg/L was chosen in the subsequent experiments.

Liquid chromatography–organic carbon detection (LC–OCD) was used to find the organic fraction removed by the different flocculants. Removal efficiency of different fractionation of organic matter by flocculation analysed by LC-OCD is presented in Table 3.

The results also show that $FeCl_3$ was the best flocculant among those studied. It could remove a majority of hydrophobic compounds (90%) and a significant amount of hydrophillic compounds (61%). The hydrophilic compounds and hydrophobic compounds in the synthetic wastewater before treatment was 80% and 20% respectively. The removal efficiencies of biopolymer (MW < 20,000), humic substances (MW ≈ 1,000), low molecular weight of neutrals (MW < 350) were also high with 90%, 55% and 56% respectively. However, the removal efficiency of building blocks (MW 300~500) by $FeCl_3$ was only 13%.

3.2. DOC removal by oxidation coupled with flocculation

Fenton is a process in which hydroxyl radical (•OH) is produced from reaction between hydrogen peroxide

Table 2
Comparison of performance of different flocculants with synthetic wastewater

Flocculants	$FeCl_3$	$Fe(NO_3)_3$	$Fe_2(SO_4)_3$	$Al_2(SO_4)_3$	PAC
pH	5.17	5.12	4.76	5.45	6.86
Turbidity, NTU	1.1	2	1.7	2.6	0.4
DOC removal efficiency, %	67	48	20	55	38
Floc size, μm	53.04	56.3	47.66	17.6	84.27

Table 3
Removal efficiency of different fractions of organic matter by flocculations

	DOC (%)	Hydrophobic (%)	Hydrophilic (%)	Biopolymer (%)	Humic (%)	Building blocks (%)	Neutrals (%)
$Fe_2(SO_4)_3$	20	8	28	—	40	50	—
$Fe(NO_3)_3$	48	25	56	95	72	4	—
PAC	38	15	56	96	44	13	11
$FeCl_3$	67	90	61	90	55	13	56

(H_2O_2) and iron catalyst. This process can be used to oxidize various contaminants in wastewater due to the strong oxidation of $^{\bullet}OH$ radical. The H_2O_2 concentration in the wastewater has a significant effect on the performance of the Fenton reaction. In this study, the effect of H_2O_2 on DOC removal efficiency was evaluated and the result is presented in Table 4.

In the first experiment, pH of synthetic wastewater was firstly adjusted to 3 and then 16 mg/L (as Fe^{2+}) of $FeCl_2$ and different dosages of 30% H_2O_2 were added in each beaker. After fast stirring 15 min, pH was adjusted again to about 7 and synthetic wastewater was continued fast stirring for 2 min and slow stirring 10 min.

The results show that the increase of H_2O_2 concentration led to the increase of DOC removal efficiency. The removal efficiency was up to 58% at a dose of 10 mg/L of H_2O_2. However, a further increase in H_2O_2 dose led to a decrease in the removal efficiency. When the concentration of H_2O_2 continued increase to 32 mg/L, the removal efficiency decreased due to the $^{\bullet}OH$ scavenging effect of H_2O_2 [Eqs. (1) and (2)] and the recombination of $^{\bullet}OH$ [Eq. (3)]. This trend is similar to the previous studies by Hsueh et al. [9] and Guo et al. [10]. Thus, the dose of 10 mg/L was chosen as optimum for H_2O_2.

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \qquad (1)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow O_2 + H_2O \qquad (2)$$

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \qquad (3)$$

The pH value plays an important role in the Fenton reaction and normally the optimum pH value for Fenton reaction is about 2.5–4. Kang and Hwang [11] reported that COD removal efficiency decreased at pH higher than 5 due to the decomposition of H_2O_2 as well as deactivation of the ferrous catalyst.

In this study, $FeCl_3$ was also used as a source of iron catalyst in the Fenton process. In the experiment, pH value of the synthetic wastewater was adjusted to different values from 2.5 to 7.9 and then 16 mg/L of $FeCl_3$ and 10 mg/L of H_2O_2 were added in. Fig. 2 shows the effect of pH on the DOC removal efficiencies.

As expected, the DOC removal efficiency is significantly influenced by the pH. Similar to observation of Kang and Hwang [11], the DOC removal efficiencies at pH more than 5 was only 63–66%, lower than 78% at pH 4.4 and 86% at pH 2.5. The removal at pH more than 5 was nearly the same as flocculation by $FeCl_3$ only. This means that at pH more than 5, only flocculation was take placed.

The removal efficiency of different fractionation of organic matter by oxidation coupled with flocculation is presented in Table 5.

The results show that oxidation coupled with flocculation could improve the hydrophilic removal. The hydrophilic removal increased from 60% with flocculation alone to 85% when H_2O_2 was added in. $^{\bullet}OH$ could help in oxidizing hydrophilic parts and therefore more than 54% of all hydrophilic compounds was removed (Table 5). The results also show that DOC removal efficiency by using $FeCl_3$ as iron catalyst had much better than that of $FeCl_2$

Table 4
Effect of H_2O_2 on DOC removal efficiency

Dose of H_2O_2 (mg/L)	Turbidity	DOC removal efficiency (%)
0	1.19	41
2	0.79	47
5	0.57	39
10	0.55	58
32	0.66	50

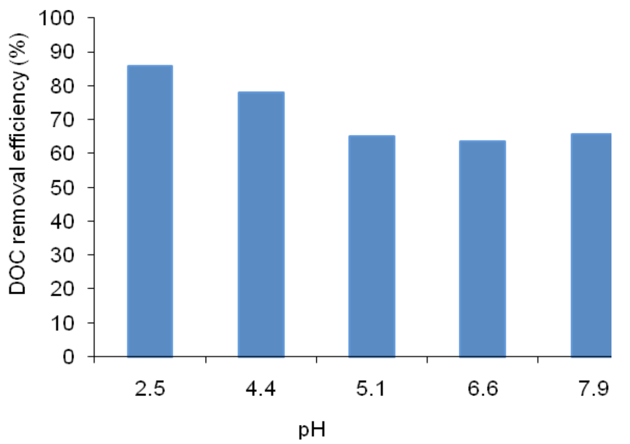

Fig. 2. The effect of pH on the DOC removal efficiencies.

Table 5
Removal efficiency of different fractions of organic matter by oxidation coupled with flocculation

	DOC (%)	Hydrophobic (%)	Hydrophilic (%)	Bio-polymer (%)	Humic (%)	Building blocks (%)	Neutrals (%)
$FeCl_2$ (16 mg/L as Fe^{2+}) + H_2O_2 (10 mg/L), pH =3	58	68	57	99	97	89	79
$FeCl_3$ (16 mg/L as Fe^{3+}) + H_2O_2 (10 mg/L), pH 2.5	86	91	85	94	97	83	54

as $FeCl_3$ not only play a role as a catalyst of oxidation but also as a flocculant.

4. Conclusion

$FeCl_3$ was found to be the best flocculant for removal of organic matter from synthetic wastewater (similar to biologically treated sewage effluent). It could remove up to 67% of DOC. A majority of hydrophobic compounds (90%) and a significant amount of hydrophillic compounds (61%) were removed at a $FeCl_3$ concentration of 16 mg/L. The removal efficiency could be improved to 86% when oxidation was coupled with flocculation. $FeCl_3$ was observed to be a better iron catalyst than $FeCl_2$ in the Fenton reaction.

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