

Review

Integrated treatment scheme for rubber thread wastewater: Sulfide precipitation and biological processes

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Abstract

In this study, acidic latex wastewater containing high average zinc and acetic contents of 816 mg L^{-1} and $20,862 \text{ mg COD L}^{-1}$, respectively, was treated successfully by a series of chemical and biological processes without any addition of acid or base for pH adjustment. Total dissolved solids of the treated effluent increased by only 1.1-fold on average for sulfide precipitation as compared to 2.8-fold for the hydroxide strategy. The oxidation–reduction potential (ORP) value of 0 mV was used successfully as an indicator for optimum sulfide addition which consistently provided an appreciable reduction in effluent concentrations to less than 1 and 2 mg L^{-1} for zinc and residual sulfide, respectively. The anaerobic filter was very stable in handling the chemically treated wastewater up to the organic loading rate of $11.8 \text{ g COD L}^{-1} \text{ day}^{-1}$ with an average efficiency of 92%. Methane production and biomass yield were $0.32 \text{ L (g COD}_{\text{removed}})^{-1}$ and $0.014 \text{ g VSS (g COD}_{\text{removed}})^{-1}$, respectively. For the activated sludge process, the optimum sludge age and hydraulic retention time were 30 and 0.8 days, respectively, which are equivalent to the organic loading rates of $2.50 \text{ g COD L}^{-1} \text{ day}^{-1}$ or $2.13 \text{ g BOD L}^{-1} \text{ day}^{-1}$. Under these optimum conditions, average removal efficiencies for COD and BOD were 96.6 and 99.4%. Average soluble COD, BOD and suspended solids in the effluent were 71, 11 and 38 mg L^{-1} , respectively. This integrated treatment scheme was proven to be an effective approach for highly polluted and toxic rubber thread wastewater.

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Keywords: Rubber thread wastewater; Sulfide precipitation; Zinc; Anaerobic filter; Activated sludge

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1. Introduction

Rubber thread production processes produce two major wastewater streams. The first stream is latex wastewater generated from the latex preparation step. It is a neutral to basic low strength wastewater and can be simply treated by acidic skimming to recover rubber particles followed by an ordinary biological treatment facility. The second stream of concern in this study is from the threading step and contains very concentrated acetic acid and zinc. The pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD) and zinc are about 3–4, 10,000–30,000, 7500–18,000 and 350–1500 mg L⁻¹, respectively. This high zinc-content wastewater is very hazardous and toxic, so it is not able to be directly treated by biological treatment processes unless zinc has been removed from the liquid phase. Several separation methods such as adsorption, membrane separation and precipitation have been used to remove heavy metals from waste streams [1]. Among these technologies, zinc precipitation using hydroxide is the most widely used treatment scheme in Thailand due to its easy operation and low cost. However, regarding the potential formation of zinc–organic ligand complexes, zinc hydroxide precipitation in highly organic-polluted wastewaters like rubber thread wastewater may face some problems [2]. Fortunately, several kinds of microorganisms existing in anaerobic and aerobic biological processes can absorb inorganic matter including zinc from wastewater to some extent [3,4]; thus, they can reduce the final zinc effluent within the standard of 5 mg L⁻¹ set by the Department of Industrial Works, Ministry of Industry. It was found that the COD and BOD of the effluent from a rubber thread factory located approximately 70 km south of Bangkok were consistently above the standard values of 120 and 20 mg L⁻¹, respectively. This was due to the tremendous excess of suspended solids (SS) which was always higher than the standard value of 50 mg L⁻¹ regardless of the sludge age. From microscopic observation of the sludge taken from the aeration tank of the activated sludge system of this rubber thread factory, the biomass contained neither protozoa such as swimming and stalked ciliates nor rotifers which are typical indicators of high-quality and effective activated sludge. In addition, with sludge age of 5–30 days, the bioflocs appeared to be fragile and not tightly aggregated. Solid precipitates which were not in the form of zinc hydroxide were also found throughout the sludge as

shown in Fig. 1 even though the pH of the mixed liquor in the aeration tank was neutral. Further analyses indicated very high total dissolved solids (TDS) of above 20,000 mg L⁻¹ in the mixed liquor which was likely due to acid and alkaline addition for pH adjustment during the hydroxide precipitation process. Consequently, this high TDS somehow inhibits the microbial flocculation under aerobic conditions. At present, in order to comply with effluent standards, this rubber thread factory and several others employing similar treatment strategies have to use coagulation and filtration processes as their tertiary treatment to remove excess solids before final discharge, which significantly increases their treatment and disposal costs.

To overcome this problem, the TDS has to be reduced to a level that does not inhibit or interfere with aerobic microbial aggregation. Apart from the hydroxide process, sulfide precipitation is another alternative for heavy metal removal. In this process, the working pH is theoretically close to neutral which is also appropriate for microbial growth. In addition to a low dissolved solid increment, the removal efficiency of sulfide precipitation is typically superior to the hydroxide approach [5], making it to be a more promising alternative than the current practice. Kim et al. [2] compared the performance of hydroxide and sulfide precipitation for removing heavy metals from automotive wastewater and found zinc sulfide precipitation to be far superior to the hydroxide method, particularly at neutral pH even in the presence of 2 mg L⁻¹ EDTA. One of the disadvantages of the sulfide scheme is the control of optimal dosage. Unlike the hydroxide precipitation scheme which can simply use pH control, optimization of sulfide addition in the field with frequent variation in zinc concentration is a more difficult task particularly in a continuous operation scenario. Insufficient sulfide can lead to high zinc content in the effluent while over dosage can result in excessive residual sulfide and a malodor problem. Hence, there is also a need to search for an appropriate parameter for sulfide-addition control which is simple and inexpensive.

The aim of this study is to investigate an integrated treatment scheme for rubber thread wastewater using sulfide precipitation followed by anaerobic and aerobic processes. Moreover, this study also examined the possibility of using oxidation–reduction potential (ORP) as an indicator for optimizing sulfide dosage, which represents the relative capacity of a solution to oxidize or reduce.

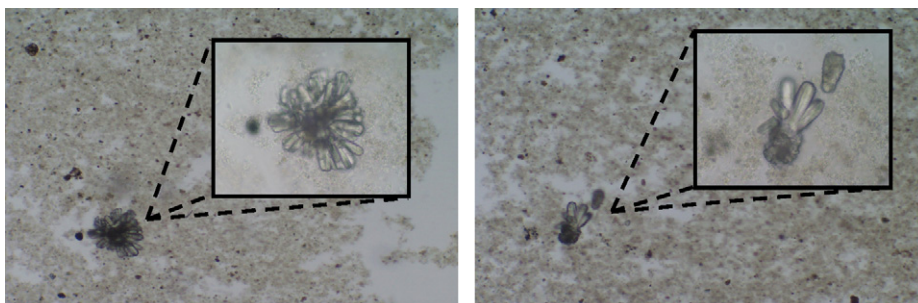


Fig. 1. Solid crystallization in the activated sludge following the zinc hydroxide precipitation scheme.

2. Materials and methods

2.1. Sulfide precipitation experiments

Chemical experiments were performed in both a lab-scale unit (using a Jar Test apparatus (Flocculator SW1, Stuart Scientific, UK)) and a bench-scale reactor (using a 200-L cylindrical polyethylene reactor with a stainless mixer). Wastewater was regularly collected from a rubber thread factory, stored at 4 °C, and allowed to reach room temperature before being used. The chemical experiments were carried out in batch mode. The 6N H₂SO₄ and NaOH were used to neutralize the solution pH as necessary, but in later experiments the wastewater was treated without any pH adjustment. A commercial 62% sodium sulfide hydrate (Tessenderlo Group, Belgium) was used as a sulfide source since Kim et al. [2] revealed no significant difference in heavy metal removal efficiency as compared to other more expensive sulfur-containing precipitants. Samples were filtered through GF/C filter papers and analyzed by a Z9000 Atomic Absorption Spectrophotometer (Hitachi, Japan) for zinc and by an iodometric method for sulfide [6]. The pH and ORP were monitored throughout the experiments by Sension 2 pH/mV Meters (Hach Company, USA). Supernatant was withdrawn from the reactor into polyethylene containers and kept at 4 °C for the biological study which was carried out in a continuous manner. Wastewater before and after treatment were analyzed for pH, BOD, COD, Zn, SS, TDS, total Kjeldahl nitrogen (TKN) and total phosphorus (TP) according to the APHA [6].

2.2. Anaerobic experiments

An acrylic anaerobic filter with 30 cm in diameter and 100 cm high was used as an anaerobic digestion vessel (Fig. 2). Six sampling ports along the filter height were provided for the profile study. The 75 cm high filter compartment was packed with 919

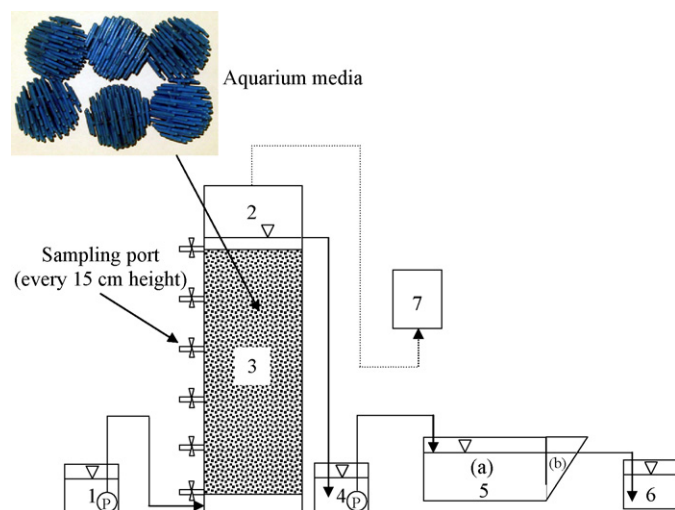


Fig. 2. Experimental setup. (1) Feeding tank; (2) anaerobic filter; (3) packed media; (4) anaerobic effluent tank; (5) activated sludge vessel: (a) aerobic chamber and (b) settling chamber; (6) aerobic effluent tank; (7) gas correction and measuring unit; P: pump.

aquarium media with a specific surface area of 104.55 cm² per piece (Fig. 2). Seed sludge with mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) of 11,376 and 3105 mg L⁻¹, respectively, was from an anaerobic pond of a fruit-processing factory. The seed sludge was initially acclimatized with the latex wastewater after zinc removal at the organic loading rate (OLR) of 0.25 g COD L⁻¹ day⁻¹ and was sequentially increased to 0.50, 0.75, 1.00, 1.25 and 1.50 g COD L⁻¹ day⁻¹ when the COD removal reached 80% or higher. Since the nitrogen was in excess compared to the COD, phosphorus from Na₃PO₄ (Merck, Germany) was added to increase the phosphorus content to an appropriate COD:P ratio of 100:0.6 for anaerobic digestion. This acclimation period took about 15 days. After acclimatization, film fixation was performed for a period of 45 days by circulating the mixed liquor through the tank containing the aquarium media at the constant OLR of 1.50 g COD L⁻¹ day⁻¹. Microbial fixed-film media were then transferred to the anaerobic filter vessel. The aim of this step was to ensure that the majority of initial biomass in the filter was fixed-film growth. Then, the reactor was fed upwardly and continuously with the chemically treated supernatant. Due to the variation in wastewater strength of each sampling, it was more convenient to use hydraulic retention time (HRT) as a control parameter than OLR. An initial HRT of 10 days was used, corresponding to the OLR of 1.5 g COD L⁻¹ day⁻¹, and was gradually decreased stepwise to 2.5 days over a 14-month period. Influent and effluent COD was frequently analyzed to determine system performance. Gas production and carbon balance were also performed to characterize the filter's behavior. Generated biogas was collected from the top of the filter which was connected to a volume-measuring device and further analyzed for methane and carbon dioxide by a GC-8A Gas Chromatograph (Shimadzu, Japan). Total organic carbon (TOC) was analyzed by a TOC-V_{CPH} Analyzer (Shimadzu, Japan). At steady state, COD, BOD, SS, volatile suspended solids (VSS), TKN and TP were analyzed [6]. Effluent from the anaerobic filter was kept at 4 °C for using in the succeeding aerobic treatment study. If it contained COD over 2500 mg L⁻¹, which seldom occurred, then less-concentrated stock anaerobic effluent was used to dilute the COD strength in order to ensure that the aerobic system was not overloaded.

2.3. Aerobic experiments

Three identical acrylic vessels with 10 and 2.5 L aeration and sedimentation compartments, respectively, were used as complete-mixed activated sludge systems. The aeration and sedimentation compartments were separated by an inclined plate with a 3 cm gap at the bottom to allow passage of mixed liquor and settled sludge between the aerated compartment and the sedimentation compartment. Anaerobic filter effluent was allowed to reach room temperature prior to being fed continuously into the aeration compartment. Excess sludge from a textile factory was used as seed for the start up of the activated sludge process. In each unit, air was vigorously supplied through a diffuser system by an aquarium air pump in order to maintain the dissolved oxygen over 2 mg L⁻¹ and

provide adequate mixing conditions. Whenever necessary, external phosphorus from NaH_2PO_4 (Merck) was added to the influent to increase the BOD:P ratio to 100:1, which is appropriate for aerobic growth. The HRT and sludge age were varied from 10 to 0.8 and 10 to 30 days, respectively. Water characteristics were analyzed according to APHA [6].

3. Results and discussion

3.1. Sulfide precipitation performance

In general, sulfide precipitation should be performed at neutral pH in order to avoid the formation of H_2S gas which has a rotten egg smell. The $\text{p}K_{\text{A}1}$ of 7.1 implies that dissolution of Na_2S at pH below 7.1 will lead to the generation of H_2S as the principal species and cause an odor problem. Preliminary tests revealed that a large amount of NaOH had to be added to raise the pH to a neutral range since the wastewater contained very concentrated acetic acid. By doing this, the TDS was substantially increased, so the ionic problem faced in the hydroxide precipitation scheme was not completely solved. Although several researchers successfully removed zinc by sulfide precipitation in a neutral pH range [7–9], no previous study has been found to work directly on very acidic wastewater with pH as low as 4.2 as in this study. As a consequence, certain experiments were conducted without pH control with two wastewater samples and the results were shown in Fig. 3. These results show that sulfide can precipitate zinc effectively even at very low pH. In addition, there was no noticeable odor from the mixtures until zinc was completely removed, which implies that the formation of ZnS was so rapid that it immediately shifted the equilibrium of the sulfide system. Un-ionized H_2S as the principal species at $\text{pH} < 7$ simultaneously dissociated to HS^- and then to S^{2-} , so very little free H_2S remained in the solution to produce a rotten-egg smell. Dashed lines in the figure represent the remaining

zinc calculated from the stoichiometric equation of zinc sulfide precipitation:



In Fig. 3(a), the calculated and analyzed values are comparable, while they were quite dissimilar in Fig. 3(b). This implies that the constituents in these two samples were very different in terms of metal content. This diversity led to the variation in the optimum pH of hydroxide precipitation causing zinc to sporadically leak with the treated effluent. However, for sulfide precipitation, this characteristic variation caused no negative impact on removal efficiency providing that sulfide is added in a sufficient amount. A problem arose as to how the optimum dose of sulfide could be simply determined to avoid complexity in field operation. In this study, the ORP was monitored as a function of sulfide addition. Raw wastewater had a positive ORP value, representing an oxidative environment, but as the amount of sulfide increased, the ORP gradually dropped and finally became negative (Fig. 3), implying a reductive environment. It is interesting to observe that most of the zinc had been completely precipitated out when the ORP approached zero. Further addition of sulfide after this point started to cause a noticeable rotten egg smell although soluble zinc was still minimal. This implies that the formation of soluble zinc sulfide complexes ($\text{Zn}(\text{HS})^+$ and $\text{Zn}(\text{HS})_2^0$) had not yet occurred in significant amounts under the study conditions. As a result, the zero ORP can effectively serve as an indicator for optimizing sulfide addition for zinc precipitation regardless of wastewater characteristics. In fact, this finding from the Jar Test experiments was successfully applied to precipitate zinc in a 200-L reactor for over 400 days and 19 batches, which strongly verified the reliability of the sulfide precipitation performance. Further mass balance analysis revealed that one-third of the dry sludge weight was derived from metal sulfide species other than zinc sulfide, but no further attempt was made to identify these solids.

Regardless of wastewater characteristics, as ORP was between 0 and -30 mV, the remaining zinc was consistently less than 1 mg L^{-1} , which had no significant impact on anaerobic biodegradation. Lin and Chen [10] reported the zinc concentrations which inhibit 50% of acetic acid degradation by methanogens to be $53\text{--}182 \text{ mg L}^{-1}$, far over the values obtained in this study. In addition, zinc entering the aerobic stage should be even lower due to biosorption, so it should not pose any harmful effects on the activated sludge process either. Sulfide residuals from the chemical precipitation process were constantly less than 2 mg L^{-1} , which is much lower than the reported EC_{50} for methanogens of $60\text{--}240 \text{ mg L}^{-1}$ [11]. In addition, Maillacheruvu et al. [12], who studied the effect of sulfide on anaerobic filters fed with acetate and propionate, found no inhibition of methanogen activity up to approximately 200 mg L^{-1} of H_2S . With the use of ORP control, the sulfide supplement is so accurate that little residual sulfide is present in the treated effluent. Hence, it neither causes an odor problem nor requires further treatment such as air stripping for residual sulfide removal prior to the biological process. Furthermore, the TDS of the treated effluent only increased slightly from the initial amount, approxi-

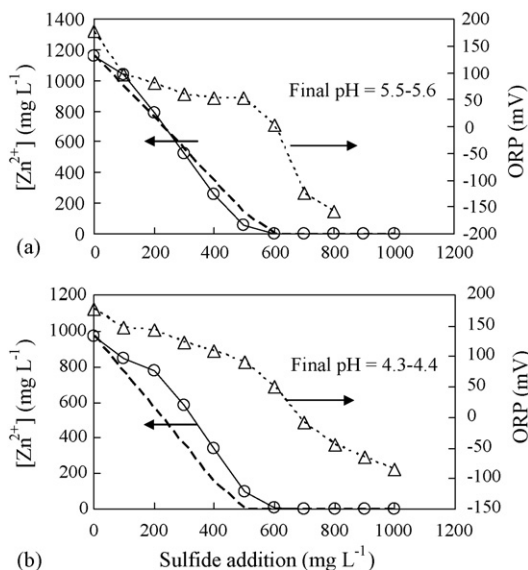


Fig. 3. Effect of sulfide on zinc solubility and solution ORP (dash lines are the stoichiometric calculation).

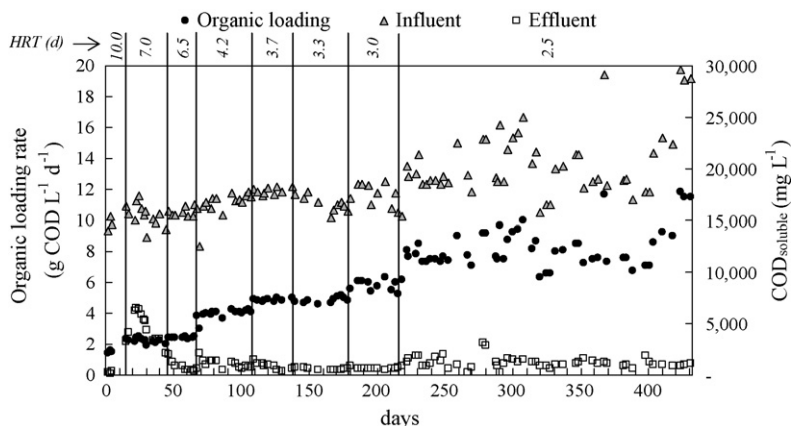


Fig. 4. Organic loading and influent and effluent COD of anaerobic filter.

mately 1.1-fold on average, as compared to 2.8-fold in the case of hydroxide precipitation using NaOH and HCl. Supernatant was withdrawn after 4 h of settling and filled into storage containers and kept at 4 °C for the biological study. In conclusion, with treatment reliability and less sensitivity to wastewater characteristics, sulfide precipitation should be a better alternative than the hydroxide mode when applied to full-scale treatment.

3.2. Anaerobic degradation of organic pollutants

After it was allowed to reach room temperature, the supernatant from chemical treatment was continuously fed into the acclimated anaerobic filter without pH adjustment. Even though the pH after sulfide precipitation was around 4.2–5.6, it was found not to be harmful to the anaerobic microbes in the reactor. Except for some points particularly in the beginning stage, the COD removal efficiency was higher than 90% as seen from Fig. 4, and the pH of the treated effluent increased to a neutral range. This is because most of the acidity was derived from acetic acid which is biodegradable, so the acidity was reduced as the acetic acid was consumed. The OLR was gradually increased from less than 2 to over 11 g COD L⁻¹ day⁻¹ so that the methanogens could build up their mass rapidly enough to handle the incoming organic load. In fact, should mineral base be used to neutralize the wastewater, the pH would increase tremendously inside the filter as the acetic acid is taken up and metabolized by the microbes. This would ultimately lead to the failure of the anaerobic system due to an excessively basic environment. Average influent and effluent COD and removal efficiency were 18,219 and 1400 mg L⁻¹ and 92%, respectively. Effluent COD during the HRT of 2.5 days was still steady even under organic loading fluctuations caused by deviations in the influent COD from days 215 to 430 as shown in Fig. 4. This implies that the anaerobic filter has a high capability to stabilize its effluent quality. Maximum OLR achieved during the study period was 11.8 g COD L⁻¹ day⁻¹. Significant variation in OLR within the same HRT was solely due to the difference in raw wastewater COD. As the HRT was reduced from 10 to 2.5 days, wastewater samples had to be collected at a more frequent interval, causing greater variation in wastewater characteristics.

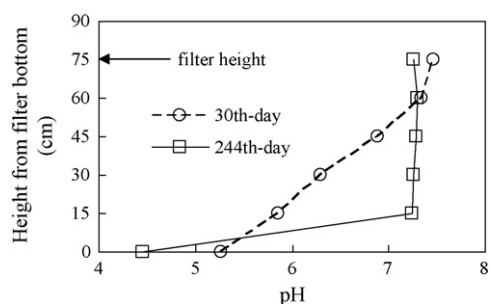


Fig. 5. pH profile of the anaerobic filter.

Nonetheless, this situation represents the actual field conditions and the obtained performance should be more realistic for field application.

Water temperature varied seasonally from 24 to 33 °C, which is in the mesophilic range. The pH profiles in Fig. 5 show a very impressive neutralization ability of the filter. The pH gradually increased as it passed through the filter on day 30 with an OLR of 1.9 g COD L⁻¹ day⁻¹ whereas it sharply increased within only 15 cm of the filter height on day 244 at an OLR of 9.0 g COD L⁻¹ day⁻¹. The difference was due to the accumulation of methanogens within the column which increased over time. As the methanogens amplified, acetic acid was consumed more rapidly as the wastewater traveled upward through the column, resulting in an increase in pH toward the neutral range. The COD profile at day 30 as shown in Fig. 6 indicates a rapid degradation of organic matter within the bottom zone

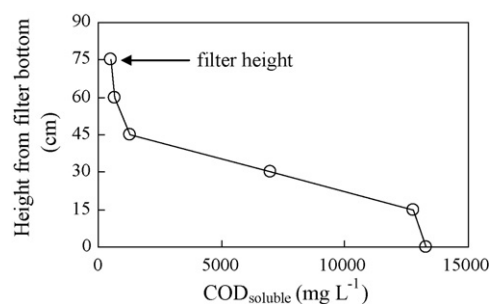


Fig. 6. COD profile of the anaerobic filter on day 30.

of the packed filter which corresponded very well with its pH profile. Biogas production measured on the 381st day at 28 °C was 230 L day⁻¹ which contained 52 and 46% of CH₄ and CO₂, respectively. This was equivalent to the methane generation rate of 0.32 L (g COD_{removed})⁻¹ which is in a good agreement with the value of 0.39 L (g COD_{removed})⁻¹ calculated stoichiometrically from the methanogenesis equation of acetic acid [11]. Slight differences are likely due to other organic pollutants contaminating the rubber thread wastewater. Results from the carbon balance of the final stage at the HRT of 2.5 days indicated that of the 9.24 mol of carbon consumed daily, 52.4, 46.3 and 1.3% were converted to CH₄, CO₂ and biomass, respectively. As a result, biomass accumulation in the packed column was very low, so no clogging problem occurred throughout the experimental period of more than 400 days. After the anaerobic filter was terminated, total biomass in the reactor was quantified. Since the initial biomass in the filter and that lost with the effluent were known, the biomass production throughout the experimental period could be estimated. By accumulating the COD removed during the study period, the biomass yield could be calculated and was found to be 0.014 g VSS (g COD)⁻¹, in good agreement with the reported range of 0.010–0.054 g VSS (g COD)⁻¹ for acetoclastic methanogenesis [11]. Apparent methanogenic activity of the anaerobic filter was estimated to be 0.28 g COD (g VSS)⁻¹ day⁻¹, much lower than 2.6–11.6 g COD (g VSS)⁻¹ day⁻¹ as reported by Speece [11]. However, this value was an average figure for the whole filter in which most of the COD removal occurred at the bottom part, so intrinsic activity of the methanogens in the anaerobic filter should be higher.

3.3. Aerobic degradation of organic pollutant

Treated effluent from the anaerobic filter with pH, COD, BOD, TKN and TP of 6.5–8.0, 829–2182, 340–1870, 130–158 and 22–25 mg L⁻¹, respectively, was fed continuously into the completely mixed aeration compartment. Considering the COD removal efficiency as shown in Fig. 7, it was found that the typical 10 days sludge age might not be appropriate for rubber thread wastewater, since only 55% on average of the total COD was removed in 5 days of HRT. As sludge age was increased to 20 and 30 days, the removal efficiency increased comparably to greater than 75% on average, but the system with a sludge age of 30 days provided a slightly lower COD and clearer effluent. No solid precipitate was found in microscopic observations of the biomass, which was much different from observations of the zinc hydroxide precipitation scenario as shown in Fig. 1. This was expected since the TDS after zinc removal was much lower in the case of sulfide than the hydroxide process, so inorganic salts were present at concentrations less than their solubility products (K_{sp}). In addition, it was found that the stalked ciliates dominated the system with 10 days of sludge age whereas rotifers, a higher life-form, were predominant at 20 and 30 days of sludge age. Variations in microbial consortia due to sludge age relied mainly on wastewater characteristics, metabolism kinetics and reproduction rate. This implies that the sludge with 20 and 30 days of retention time was more stable than at 10 days. Based

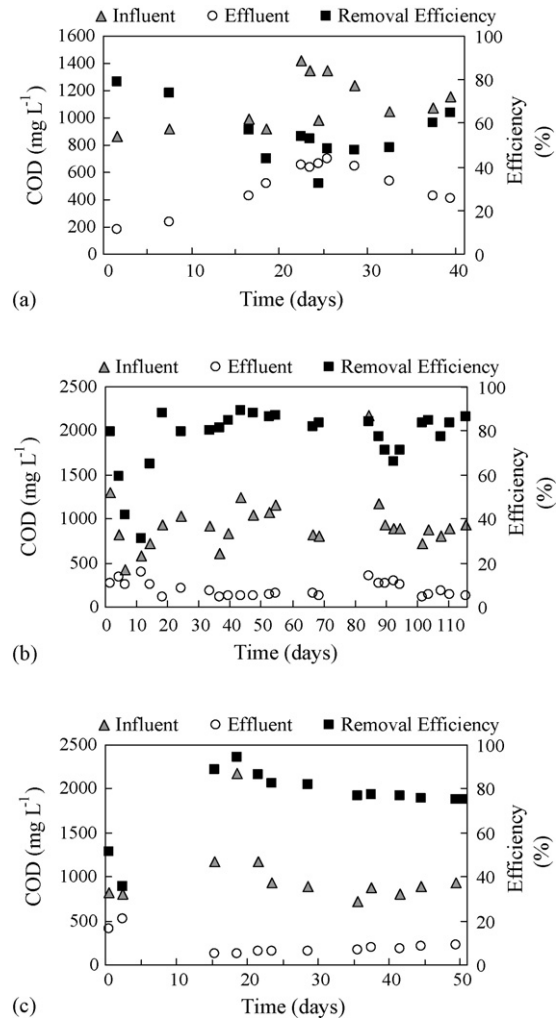


Fig. 7. Effect of sludge age on COD removal by the activated sludge process at a hydraulic retention time of 5 days: (a) 10 days of sludge age; (b) 20 days of sludge age; (c) 30 days of sludge age.

on these results, 30 days is the most appropriate sludge age for an activated sludge process receiving rubber thread wastewater.

By controlling the sludge age of 30 days and sequentially varying the HRT from 10 to 0.8 days, equivalent to the OLR of 0.21–2.50 g COD L⁻¹ day⁻¹ or 0.18–2.13 g BOD L⁻¹ day⁻¹, it was found that the removal efficiency in terms of COD and BOD was quite steady above 90% as shown in Fig. 8. It is

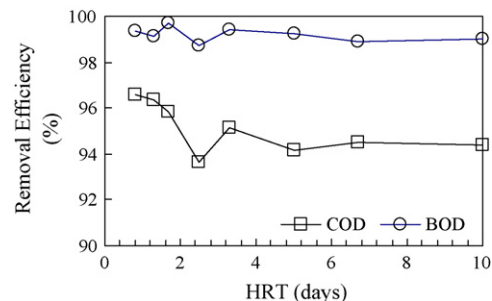


Fig. 8. Effect of HRT on the efficiency of the activated sludge process with 30 days of sludge age.

important to note that slightly better efficiencies at low HRT derived from wastewater characteristics which change from time to time. Average soluble COD and BOD in the activated sludge effluent were 71 and 11 mg L⁻¹, respectively. Suspended solids were also low with an average of 38 mg L⁻¹. The MLVSS at steady state built up notably from 590 to 2200 mg L⁻¹ as the OLR increased from 0.18 to 2.13 g BOD L⁻¹ day⁻¹. Filamentous microorganisms were also found to be more present as loading increased, though they never caused a bulking problem in this study. Nonetheless, in field practice, operators should be aware of these nuisance microorganisms and take actions to prevent sludge bulking if the system is operated under high rate conditions.

4. Conclusions

In this work, an integrated treatment scheme for rubber thread wastewater has been thoroughly investigated. Sulfide precipitation for zinc removal was found to be superior to the conventional hydroxide mode and was less dependent on wastewater characteristics due to its higher efficiency and reliability. Optimal addition of sulfide salt could be easily achieved by controlling the solution ORP around 0 mV at which soluble zinc and residual sulfide were constant at less than 1 and 2 mg L⁻¹, respectively. Further treatment by an anaerobic filter effectively reduced COD with an average efficiency of 92% at the OLR of 11.8 g COD L⁻¹ day⁻¹. Methane production, biomass yield and apparent methanogenic activity were 0.32 L (g COD_{removed})⁻¹, 0.014 g VSS (g COD_{removed})⁻¹ and 0.28 g COD (g VSS)⁻¹ day⁻¹, respectively. With final treatment by an activated sludge process with 30 days sludge age and 0.8 day HRT, average soluble COD, BOD and SS in the effluent were 71, 11 and 38 mg L⁻¹, respectively, corresponding to organic removal efficiencies of 96.6 and 99.4% in terms of COD and BOD, respectively. In addition, as a result of the TDS control by sulfide precipitation scheme, no solid precipitate was found in the activated sludge and the protozoa and metazoans were abundant, indicating a very healthy sludge. This integrated

treatment strategy has proven to be an effective treatment for highly polluted and toxic rubber thread wastewater.

Acknowledgements

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