Reduction of dissolved organic matter in terms of DOC, UV-254, SUVA and THMFP in industrial estate wastewater treated by stabilization ponds

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Abstract The aim of this research was to monitor the influent and effluent water quality of the aeration, facultative and oxidation water treatment ponds of an industrial estate. This industrial estate, the largest in northern Thailand, has proposed to utilization of reclaimed treated wastewater in their raw water supply so as to cope with the yearly water shortage during the dry season. Water samples were collected four times from four sampling points and evaluated for their dissolved organic matter (DOM) content in terms of dissolved organic carbon (DOC), ultraviolet light absorbance at 254 nm (UV-254), specific ultraviolet absorption (SUVA), trihalomethane formation potential (THMFP) and trihalomethane (THM) species. Average values of DOC, UV-254, SUVA and THMFP in the influent wastewater of 12.9 mg L^{-1} , 0.165 cm⁻¹, 1.29 L mg⁻¹m⁻¹ and 1.24 mg L⁻¹, respectively, were observed. The aeration ponds produced the best results: a 54% reduction of DOC, a 33% reduction of UV-254, and a 57% reduction of THMFP. However, SUVA in

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S. Wattanachira (🖂) Department of Environmental Engineering /NRC-EHWM, Chiang Mai University, Chiang Mai 50200, Thailand e-mail: suraphong@eng.cmu.ac.th the aeration pond effluent showed a moderate increase. The facultative ponds and oxidation ponds did not take part in the reduction of DOC, UV-254, SUVA and THMFP. Average DOC, UV-254, SUVA and THMFP value of the treated wastewater were 5.8 mg L⁻¹, 0.107 cm⁻¹, 1.85 L mg⁻¹m⁻¹ and 468 μ g L⁻¹, respectively. Chloroform, at 72.6% of total THMFP, was found to be the predominant THM species.

Keywords DOC · Industrial estate wastewater · SUVA · Stabilization ponds · THMFP · UV-254

Introduction

The selected industrial estate in this study utilizes a considerably high quantity of approximately 14,000 m³ of water per day. During the dry season (late Februaryearly June), water shortage is a serious concern. The industrial estate, therefore, initiated a plan to draw about 12,000 m³d⁻¹ of stabilization pond treated wastewater, into their raw water supply reservoir. While relieving one problem, this may induce another. The dissolved organic matter (DOM) in the treated effluent could react with the chlorine used in the disinfection process of water treatment plant and form disinfection by-products (DBPs), such as haloacetic acids (HAAs) and trihalomethanes (THMs) (Janhom et al. 2005; Musikavong et al. 2005). Due to their potentially carcinogenic property (Bellar et al. 1974; Rook 1974), THMs could adversely affect the workforce of the industrial estate, who utilizes the water as a drinking water source.

Conclusive results from past research have shown that the major surrogate parameters for representing the level of DOM in water and wastewater are dissolved organic carbon (DOC), ultraviolet light absorbance at 254 nm (UV-254), specific ultraviolet absorption (SUVA), and trihalomethane formation potential (THMFP). The amount of DOM in the treated wastewater mainly depends upon the quantity of DOM in the influent wastewater and the performance capability of the wastewater treatment plant. The aim of this research, therefore, was to evaluate the quantities of DOM in terms of DOC, UV-254, SUVA and THMFP, and their reductions by stabilization ponds of the studied industrial estate.

Materials and methods

Study site

Figure 1 shows the study site of this research: the central wastewater treatment plant of the largest industrial estate in the North of Thailand. The total area of this industrial estate is approximately 286 ha and contains 76 factories specializing in electronics, machinery parts and equipment, agricultural products, leatherwear, food products, wooden products, jewelry and accessories, construction, etc.

The stabilization pond system consists of two aeration ponds, two facultative ponds, and two oxidation ponds. Effluent from the oxidation ponds and rainwater from the receiving area within the industrial estate (about 286 ha in size) directly flows into a detention pond. The total area of the central wastewater treatment plant is 12 ha and the total detention time for the wastewater is 22 days. After treatment, the treated effluent from the detention pond is discharged downstream into the Mae-Kuang River. Due to the water shortage during the dry season, the treated wastewater in the detention pond will be treated by a reclamation process prior to being stored in the raw water supply reservoirs and used as raw water for water supply plant.

Water sample and analytical methods

Water samples were collected from four sampling locations, (1) (2) (3) (4), as shown in Fig. 1. They were



Fig. 1 Diagram of stabilization pond system of the central wastewater treatment plant of studied industrial estate

taken in September 2004, October 2004, February 2005 and July 2005. The treatment system was designed such that most rainwater was directed towards the final detention pond; therefore, each of the prior treatment ponds only receives the rain that falls directly onto its surface. This amount of rainwater was estimated to be less than 5% of the total water in each pond; and therefore, the effect of dilution was considered to be minimal. Since the final detention pond was affected by the larger amount of rainwater, it was excluded from this investigation. The effluent from the oxidation ponds was deliberately classified as the treated wastewater from the stabilization ponds.

A total of 16 water samples were filtered through a pre-combusted (550°C for 2 h) Whatman GF/F filter (nominal pore size 0.7 μ m) prior to storage at 4°C until analysis. DOC, UV-254, SUVA and THMFP measurements were taken in all water samples.

DOCs were analyzed in accordance with Standard Method 5310D (Standard Methods for the Examination of Water and Wastewater 1995) using a TOC analyzer (O.I. analytical, College Station, Texas, USA). Milli-Q water (ELGA, Lane End, High Wycomebe, UK) was used to clean the TOC analyzer prior to its use on every sample.

UV-254 was analyzed in accordance with Standard Method 5910B (Standard Methods for the Examination of Water and Wastewater 1995) using a UV/VIS spectrometer, Jasco V-350 spectrophotometer (Jasco Corporation, Tokyo, Japan) at 253.7 nm, with matched quartz cells, that provided a path length of 10 mm. H_2SO_4 and NaOH were used on all water samples to adjust the pH to 7 by prior to the UV-254 analysis.

THMFP measurements were carried out according to Standard Method 5710B (Standard Methods for the Examination of Water and Wastewater 1995). The neutralized solution was buffered by a phosphate solution before incubation at $25\pm2^{\circ}$ C in amber bottles with PTFE liners. At the end of the 7-day reaction period, samples had a remaining free chlorine residual of between 3 and 5 mg L⁻¹. THMs were extracted with pentane in accordance with Standard Method 6232B (Standard Methods for the Examination of Water and Wastewater 1995). Agilent Gas Chromatography-6890 with an electron capture detector (ECD) (Agilent



Fig. 2 Average values of DOC, UV-254 and SUVA (with standard deviation ranges) of the influent and effluent of the aeration, facultative, and oxidation ponds

technologies Inc., Wilmington, Delaware, USA) and chromatographic column (J&W Science DB-624, DE, USA), 0.2-mm X 25 m 1.12 μ m film were used to analyze THMs. At least two replications of DOC, UV-254 and THMFP measurements were performed.

Residual chlorine was measured according to the procedures mentioned in Standard Method 4500-Cl G (Standard Methods for the Examination of Water and Wastewater 1995), the *N*,*N*-dechthyl-p-phenylenediamine colorimetric method. The level of chlorine was then recorded by light absorbance at 515 nm using a UV/VIS spectrometer (Jasco V-350 spectrophotometer with matched quartz cells that provided a path length of 10 mm). It must be noted that Milli-Q water was used for all dilutions, sample and chemical preparations, and final glassware cleaning.

Results and discussion

Reductions of DOC, UV-254 and SUVA

DOC and UV-254 are commonly utilized as surrogate parameters for DOM in water and wastewater. These parameters are capable of providing significantly different information on DOM properties. DOC could be used to represent the level of organic carbon in water, whereas UV-254 represents the aromatic character of humic and fulvic acids. Figure 2 illustrates the average values of DOC, UV-254 and SUVA (with standard deviation ranges) in the influent and effluent samples of the aeration, facultative, and oxidation ponds. The samples were collected in September 2004, October 2004, February 2005 and July 2005.

An average value of DOC of 12.9 mg L^{-1} was observed in the influent wastewater. Table 1 depicts the reduction efficiency of each pond on DOC, UV-254 and SUVA and the accumulated reduction efficiency of the ponds based on these parameters. It was found that the aeration ponds could remove DOC by 54%, and the average value of DOC in the aeration pond effluent was 5.9 mg L^{-1} . The facultative ponds did not seem to further treat DOC. The average concentration of DOC in the facultative pond effluent of 6.0 mg L^{-1} was slightly higher then the average DOC concentration in the influent. This small increase of DOC in the effluent from the facultative ponds may have been due to the effect of algae growth (or the growth of other microorganisms) within the ponds. The oxidation ponds did not further enhance DOC removal. The average DOC concentration in the oxidation pond effluent was 5.8 mg L^{-1} . The difference between the DOC observed in the facultative pond effluent and in the oxidation pond effluent was utterly due to the inadvertent analytical deviation.

With regard to UV-254, the average value of UV-254 of influent wastewater was 0.165 cm⁻¹. The aeration ponds reduced UV-254 by 33%. The average value of UV-254 in the aeration pond effluent was 0.110 cm⁻¹. However, UV-254 could not be reduced by the facultative ponds and oxidation ponds. An average value of UV-254 of 0.112 cm⁻¹ was observed in the effluent water from the facultative ponds; the average value of UV-254 of oxidation ponds effluent was similar.

Tambo (1989) classified organic substances in DOCs on the basis of their ability to adsorb light in the UV range. He divided them into two fractions: UV-sensitive and UV-insensitive. McKnight et al. (1994) proposed that UV-sensitive fraction was mostly

| Parameters | Reduction efficiency ^a | | | Accumulated reduction efficiency ^b | | | |
|------------|-----------------------------------|-------------------|-----------------|---|-------------------|-----------------|--|
| | Aeration ponds | Facultative ponds | Oxidation ponds | Aeration ponds | Facultative ponds | Oxidation ponds | |
| DOC | 54 | (-2) | 3 | 54 | 53 | 55 | |
| UV-254 | 33 | (-2) | 4 | 33 | 32 | 33 | |
| SUVA | (-45) | 1 | 0 | (-45) | (-43) | (-43) | |

Table 1 Reduction efficiency and accumulated reduction efficiency of the stabilization pond process on DOC, UV-254 and SUVA

Remark: a DOC reduction efficiency = [(Average DOC_{influent water to pond} - Average DOC_{effluent water from pond})/

(Average DOC_{effluent water to pond})] $\times 100$

^bAccumulated DOC reduction efficiency = $[(Average DOC_{influent wastewater} - Average DOC_{effluent water from pond})/(Average DOC_{influent wastewater})] × 100$

The reduction efficiency and accumulated reduction efficiency of the stabilization pond process on UV-254 and SUVA were calculated using the mentioned equations.

hydrophobic or aromatic in nature. According to the UV-254 reduction results in Table 1, the stabilization ponds had moderate difficulty removing UV-sensitive organic fraction with aromatic characteristics when compared with the overall reduction of DOC.

In general, SUVA could be utilized to provide the relative index of humic content of the DOC in water (AWWA 1993). An average SUVA value of 1.29 L mg^{-1} m⁻¹ was observed in the influent wastewater. The SUVA value in the aeration pond effluent increased moderately to 1.87 L mg⁻¹ m⁻¹. It was suspected that the biological process in the aeration ponds easily removed the UV-insensitive fraction from the influent wastewater; therefore, the remaining dissolved organic matter in the treated wastewater was mainly composed of more UV-sensitive fractions that provided a high relative index of DOC humic content. Fukushima et al. (1996) reported that the SUVA of total DOM increased as the lake water, influenced by pedogenic DOC, was allowed to further stabilize through biodegradation over a long period of time. Imai et al. (2002) reported that since a biological treatment had been employed in the sewage treatment plants, the SUVA value for its effluent should have been higher than that of its influent. It was noted that further treatment in the facultative ponds did not reduce SUVA and the SUVA of the effluent was observed to be 1.85 L mg⁻¹ m⁻¹, which was close to the inlet level. Similarly, no further reduction in SUVA was achieved by the oxidation ponds.

Based on the DOC and UV-254 reduction results, it can be stated that the aeration pond was the main course of action that reduced DOC and UV-254. The reduction of dissolved organic matter at the central wastewater treatment plant relied primarily on the efficiency of the aeration ponds. In terms of the overall efficiency of the system, the stabilization ponds were able to reduce DOC and UV-254 by 55 and 33% respectively; however, they did not reduce SUVA.

Reductions of THMFP and THM species

In general, THMs refer to the concentration of THMs measured in the water at the time of the sampling. This value represents the amount of THMs that could adversely affect the consumers who utilize the water. THMs have recently been put under regulation in the USEPA Disinfectant/Disinfection By-Products

(D/DBPs) Rule (United States Environmental Protection Agency or USEPA 1998). The current drinking water maximum contaminant level for four THMs, namely chloroform (CHCl₃), dichlorobromoform (CHCl₂Br), dibromochloroform (CHClBr₂) and bromoform (CHBr₃), is set at 40 μ g L⁻¹. The World Health Organization (World Health Organization 1996) has set the health related guideline values (GV) of 200, 60, 100 and 100 μ g L⁻¹ for CHCl₃, CHCl₂Br, CHClBr₂ and CHBr₃, respectively.

In order to gain a better understanding of THMs formation due to the reaction of DOM in water sources with chlorine, the THMFP has been commonly utilized to determine the THMs at the completion of the reaction condition between DOM and the excess amount of chlorine. Water with a high THMFP value could potentially form a high level of THMs. In addition, the reduction of the THMFP by water treatment processes can be used to represent the reduction of DOM, which has an active ability of forming THMs. THMFP, therefore, was deemed to be an appropriate indicator and was utilized to monitor the highest possible concentrations of THMs in the water. The THMFP was determined from the summation of the chloroform formation potential (CHCl₃-FP), dichlorobromoform formation potential (CHCl₂Br-FP), dibromochloroform formation potential (CHClBr₂-FP) and bromoform formation potential (CHBr₃-FP).

The average THMFP and THM species values (with standard deviation ranges) for the influent and effluent samples taken from the aeration, facultative, and oxidation ponds in September 2004, October 2004, February 2005 and July 2005 are illustrated in Fig. 3. Percent distributions of CHCl₃-FP, CHCl₂Br-FP, CHClBr₂-FP and CHBr₃-FP in the influent wastewater and effluent water from the ponds are depicted in Fig. 4. An average THMFP value of 1.24 mg L^{-1} was observed in the influent wastewater. This value came from the summation of the CHCl₃-FP at 1.10 mg L⁻¹, CHCl₂Br-FP at 114 µg L⁻¹, CHClBr₂-FP at 21.3 μ g L⁻¹ and CHBr₃-FP at 4.0 μ g L⁻¹. CHCl₃, therefore, was the major THMs species in the influent wastewater and made up about 88.8% of the total THMFP; while the percentages of CHCl₂Br, CHClBr₂ and CHBr₃ were 9.2, 1.7 and 0.3%, respectively.

As can be seen from Table 2, there was as much as a 57% reduction in THMFP due to the action of the aeration pond. At a 66% reduction, CHCl₃ was the

Fig. 3 Average values (with standard deviation ranges) of THMFP, CHCl₃-FP, CHCl₂Br-FP, CHClBr₂-FP and CHBr₃-FP in the influent and effluent of the aeration, facultative, and oxidation ponds



major THMs species reduced in the aeration ponds; on the other hand, CHCl₂Br, CHClBr₂ and CHBr₃ were not reduced by the aeration ponds. The average THMFP value of the aeration pond effluent was 529 μ g L⁻¹. This value came from the summation of the CHCl₃-FP of 376 μ g L⁻¹, CHCl₂Br-FP of 113 μ g L⁻¹, CHClBr₂-FP of 36.0 μ g L⁻¹ and CHBr₃-FP of 3.7 μ g L⁻¹. The facultative ponds did not reduce the THMFP; similarly, they did not remove THM species. The average THMFP value of the facultative pond effluent was 517 µg L⁻¹ (CHCl₃-FP of 371 µg L⁻¹, CHCl₂Br-FP of 110 µg L⁻¹, CHClBr₂-FP of 32.6 µg L⁻¹, and CHBr₃-FP of 3.3 µg L⁻¹). The oxidation ponds neither reduced the THMFP nor removed THM species. An average THMFP value of 468 µg L⁻¹ in the oxidation pond effluent was observed (CHCl₃-FP of 340 µg L⁻¹, CHCl₂Br-FP of 103 µg L⁻¹, CHClBr₂-FP of



Fig. 4 Percent distributions of CHCl₃-FP, CHCl₂Br-FP, CHClBr₂FP and CHBr₃-FP in the influent and effluent of the aeration, facultative, and oxidation ponds

| Parameters | Reduction efficiency ^a | | | Accumulated reduction efficiency ^b | | | |
|-------------------------|-----------------------------------|-------------------|-----------------|---|-------------------|-----------------|--|
| | Aeration ponds | Facultative ponds | Oxidation ponds | Aeration ponds | Facultative ponds | Oxidation ponds | |
| THMFP | 57 | 2 | 9 | 57 | 58 | 62 | |
| CHCl3-FP | 66 | 1 | 8 | 66 | 66 | 69 | |
| CHCl ₂ Br-FP | 1 | 3 | 6 | 1 | 4 | 10 | |
| CHClBr ₂ -FP | (-69) | 9 | 34 | (-69) | (-53) | (-1) | |
| CHBr ₃ -FP | 8 | 11 | (-6) | 8 | 18 | 13 | |

Table 2 Reduction efficiency and accumulated reduction efficiency of the stabilization pond process on THMFP, CHCl₃-FP, CHCl₂Br-FP, CHCl₃-FP and CHBr₃-FP

Remark: ^a THMFP Reduction efficiency = $[(Average THMFP_{influent water to pond} - Average THMFP_{effluent water from pond})/((Average THMFP_{influent water to pond})] × 100$

^b Accumulated THMFP Reduction efficiency = [(Average THMFP_{influent wastewater} - Average THMFP_{effluent water from pond})/(Average THMFP_{influent wastewater})] × 100

The reduction efficiency and accumulated reduction efficiency of the stabilization pond process on the THMs species were calculated using the mentioned equations.

21.5 μ g L⁻¹ and CHBr₃-FP of 3.5 μ g L⁻¹). CHCl₃, therefore, was the major THMs species in the oxidation pond effluent, as it accounted for about 72.6% of total THMFP. The percentages of CHCl₂Br, CHClBr₂ and CHBr₃ were approximately 22.0, 4.6 and 0.7%, respectively. The difference between the THMFP and THMs species observed in the facultative pond effluent and that of in the oxidation pond effluent was entirely due to the inevitable analytical deviation. The THMFP of the treated wastewater obtained in this study was compared with other raw water supply sources in Thailand (as shown in Table 3). It was found that the THMFP values of the treated wastewater in this study were considerably higher than those of other raw water supply sources in

Thailand, e.g. the Chao Phraya River, Bangkok; Aung-Keaw Reservoir, Chiang Mai; Mae-Kuang Reservoir, Chiang Mai; and Bhumibol Dam Reservoir, Tak. Based on this finding, the DOM in the treated effluent must be more effectively removed by the reclamation process prior to the reuse of such water in the water supply plant.

When considering the presence of THM species, it was found that CHCl₃ was the major THM species in the treated effluent of treatment plant in this study and all other water supply sources in Thailand. This observation also corresponded well with the results of previous research. Rodriguez et al. (2003) found that, at about 80%, CHCl₃ was the predominant THM compound in treated water from the two major

Table 3 THMFP and THMs species in the treated effluent of this study compared with the values from other raw water supply sources in Thailand

| Water source | Sampling times | $\begin{array}{c} \text{THMFP} \\ (\mu g \ L^{-1}) \end{array}$ | CHCl3-FP $(\mu g L^{-1})$ |
|--|------------------|---|---------------------------|---------------------------|---------------------------|---------------------------|
| The Chao Phraya River Bangkok, Thailand (Panyapinyopol et al. 2005) | August 2003 | 313 | 262 (84%) ^a | 43.8 (14%) | 6.9 (2%) | ND ^b |
| Aung-Keaw Reservoir, Chiang Mai, Thailand (Homklin 2004) | November 2004 | 403 | 372 (92%) | 20.3 (5%) | 11.1 (3%) | ND |
| Mae-Kuang Reservoir, Chiang Mai, Thailand (Homklin 2004) | December 2004 | 236 | 214 (90%) | 15.4 (7%) | 6.9 (3%) | ND |
| Mae-Sa River, Chiang Mai, Thailand (Homklin 2004) | February 2005 | 113 | 94 (83%) | 11.7 (10%) | 7.0 (7%) | ND |
| Bhumibol Dam Reservoir, Tak, Thailand (Panyapinyopol et al. 2005) | April 2005 | 318 | 292 (92%) | 25.6 (8%) | ND | ND |
| Treated effluent from this study | _ | 468 | 340 | 103 | 21.5 | 3.5 |

Remark: ^a()=percent distribution and ^bND=Not detected

drinking water utilities of the greater area of Quěbec City, Canada, namely Lěvis, and Sainte-Foy. In addition, CHCl₃ levels of approximately 90% were found in treated water from three other major drinking water utilities of the greater area of Quěbec City (i.e. Beauport, Charlesbourg and Quěbec City). Thacker et al. (2002) reported that CHCl₃ was the major THMFP species found in the treated water of the Panjrapur, Bhanup, Tulsi and Vehar treatment plants in India.

Based on the obtained results, it could be remarked that the aeration ponds were the main process capable of reducing THMFP and THM species. Therefore, this plant relied on the efficiency of its aeration ponds for reducing the THMFP in the water. In terms of overall efficiency, the stabilization ponds could reduce the THMFP by 62%. CHCl₃, which was reduced by 69%, was the major THM species that was reduced.

The THMFP of 468 μ g L⁻¹ of the oxidation pond effluent was extremely high when compared with the maximum contamination level of 40 μ g L⁻¹ for drinking water (USEPA 1998). According to the report of the World Health Organization (1994), the maximum acceptable levels of CHCl₃ and CHCl₂Br are 200 and 60 μ g L⁻¹, respectively. In terms of toxicity, CHCl₂Br, is therefore more hazardous than CHCl₃. However, CHCl₃ was present at much higher concentrations than the other THM species, and therefore it was considered to carry a higher level of human-health concern. In this study, 340 μ g L⁻¹ of CHCl₃ and 103 μ g L⁻¹ of CHCl₂Br were found in the oxidation pond effluent. It can be stated that the DOM in the treated wastewater has a high potential of forming THMs at levels that exceed the maximum acceptable level recommended by the WHO.

Conclusions

The water samples came from the influent wastewater and treated effluent of the aeration, facultative and oxidation ponds of the central wastewater treatment plant of the selected industrial estate in northern Thailand. The amounts of DOC, UV-254, SUVA, THMFP and THM species were taken and analyzed to determine the efficacy of the stabilization ponds. Moderately high values of DOC and THMFP in the influent wastewater were detected. CHCl₃ was found to be the major THM species in the influent wastewater. The aeration pond was the main process capable of reducing DOC, UV-254 and THMFP. However, the SUVA value showed a moderate increase in the aeration pond effluent. The facultative ponds and oxidation ponds did not reduce the DOC, UV-254, SUVA and THMFP in the water. The average THMFP values of the treated effluent were considerably high in comparison to the THMFP values of raw water for other raw water supply sources in Thailand. In addition, CHCl₃ and CHCl₂Br in the treated effluent were found at levels that exceeded the maximum acceptable level recommended by the WHO. Due to this finding, the treated effluent would not be able to be drawn directly into the raw water supply reservoir for reuse by the water supply plant. The DOM in the treated effluent should be sufficiently removed through a reclamation process in order to lower the level of potentially carcinogenic substances that might occur in the produced water supply. Future work should endeavor to discover a water treatment process capable of lowering the DOM in wastewater to an acceptable level for reuse as a part of a raw water supply.

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