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Mystery of the high chlorine consumption in disinfecting a chemically enhanced primary saline sewage

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ABSTRACT

Stonecutters Island Sewage Treatment Works is one of the largest sewage treatment plants in the world and consists mainly of a chemically enhanced primary treatment (CEPT) unit and a disinfection unit. It has long been realized that most of the dosed chlorine (15 mg/L) is lost at the beginning part of the disinfection unit during disinfection of the CEPT effluent. Lab-scale tests were therefore conducted in this study to determine the causes. Because ferric chloride is used in CEPT, ferrous iron in the CEPT effluent (from the reduction of ferric iron) was initially thought to be the main chlorine consumer. However, the chlorine consumption by ferrous iron was found to be 1.2 mg/L at most. Suspended solids and sulfide also did not contribute significantly to the chlorine consumption. Batch tests were therefore conducted to evaluate the effects of mixing condition and chlorine stock solution concentration on the chlorine consumption. Less chlorine was consumed upon increased mixing. Using a high-concentration chlorine stock solution (25000 mg/L) resulted in a 3-times-higher chlorine consumption in the absence of mixing than using a low-concentration chlorine stock solution (2500 mg/L). By correlating the losses of ammonia and total nitrogen with the chlorine consumption, we hypothesized that the use of a high-concentration chlorine stock solution under poor mixing leads to a localized high ratio of chlorine to ammonia, resulting in breakpoint chlorination and an unusually excessive chlorine consumption. A novel apparatus was developed to quantify the nitrogen gas generated during chlorination of a simulated wastewater, and the mass balance of nitrogen-containing species (i.e., ammonia, nitrogen gas, nitrite and nitrate) during the chlorination was inspected. The good fit between the measured chlorine consumption and that back-calculated from nitrogen-containing species verified our hypothesis. Finally, it needs mentioning that the high chlorine consumption and the breakpoint chlorination may occur during chlorine disinfection of any sewage effluents with relatively high ammonia levels; thus it is suggested that either not-too-high concentrations of chlorine stock solutions or sufficient mixing should be applied during disinfection of the sewage effluents.

1. Introduction

Chemically enhanced primary treatment (CEPT) is a wastewater treatment process in which wastewater is dosed with chemicals to enhance gravitational settling for the removal of pollutants at the primary stage (Chagnon and Harleman, 2002). The chemicals used in CEPT are mainly metal salts (e.g., ferric chloride, ferric sulfate, and alum) (Chagnon and Harleman, 2002). CEPT consists of coagulation, flocculation and sedimentation processes, which promote the assembly of small suspended particles into larger particles which settle more easily. CEPT is more efficient than conventional primary treatment processes in removing organic matters, nutrients, and suspended solids (Mahmoud, 2009; Xu et al., 2009). Moreover, because of the faster settling of particles and pollutants, the residence time is considerably reduced in CEPT and thus the process can sustain much higher flow rates than other primary treatment processes (Haydar and Aziz, 2009). Due to its high effectiveness and large treatment capacity, CEPT has become increasingly popular and is considered as an excellent alternative to traditional wastewater treatment processes, especially for densely populated cities (Murugesan et al., 2014). After CEPT, the effluent is usually disinfected before it is discharged into the receiving water

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body (Harleman et al., 2002). Among various disinfection methods, chlorination is the most commonly used, due to its technical maturity and cost-effectiveness (Shannon et al., 2008; Drinan and Spellman, 2012; Lee and von Gunten, 2010; Gong and Zhang, 2015; Li et al., 2016; Cai et al., 2016; Li et al., 2017).

Hong Kong is a coastal city with more than 40 swimming beaches open to the public. Back to 2003, several beaches were forced to close temporarily due to the discharge of undisinfected sewage from local wastewater treatment plants into the sea (Chan et al., 2013). To prevent deteriorating the coastal water quality again and to protect swimmers from pathogenic infection, disinfection was introduced in the wastewater treatment plants. Stonecutters Island Sewage Treatment Works (SCISTW) is a local wastewater treatment plant that applies disinfection after CEPT. It is one of the largest wastewater treatment plants in the world with a treatment capacity of 1.9 million m^3/d. Ferric chloride (15 mg/L as Fe) is used for coagulation and sulfide oxidation during CEPT, and chlorination is provided to disinfect the CEPT effluent (HKDSD, 2015). During disinfection, a high-concentration chlorine stock solution (10% sodium hypochlorite) is applied to the CEPT effluent at a target dose of 15 mg/L as Cl_2 with a 12-min contact time. Surprisingly, the residual chlorine is barely detectable in the flow distribution chamber, which is the beginning part of the disinfection unit. In other words, more than 80% of chlorine is consumed before performing its intended function of inactivating bacteria, resulting in a poor disinfection efficiency (Lee et al., 2017). However, in the lab-scale disinfection test, only 3 mg/L as Cl_2 (20%) is consumed after 12-min disinfection of the CEPT effluent with an initial dose of 15 mg/L as Cl_2 under strong mixing condition. This is in conflict with the observation in SCISTW. The reason for this unusually high chlorine demand (accompanied with the poor disinfection efficiency) during the disinfection in SCISTW has long been a mystery. Accordingly, there is a critical need to disclose the mystery of the high chlorine consumption during chlorine disinfection of the primary effluent.

This study was designed to investigate the reasons for the high chlorine consumption in disinfecting the CEPT effluent from SCISTW. We initially hypothesized that, because ferric chloride is used in CEPT, ferrous iron in the CEPT effluent (from the reduction of ferric iron) could be the main chlorine consumer; Also, the suspended solids and sulfide in the effluent could contribute to the chlorine consumption. Later, we realized that because the concentration of the 10% chlorine stock solution used in the wastewater treatment plant was approximately 120000 mg/L as Cl_2; To achieve the target dose of 15 mg/L, the chlorine stock solution needs to be diluted by 8000 times; Such a high dilution requirement made mixing a critical factor during the disinfection. Therefore, the objectives were to identify the main consumers of chlorine and to verify the proposed pathways of chlorine consumption by checking mass balances between reactants and products.

2. Materials and methods

2.1. Chemicals and reagents

An original chlorine stock solution (15% sodium hypochlorite) was prepared in the laboratory to ensure the purity. The experimental set-up for preparing this stock solution (Zhang and Minear, 2006) is shown in Fig. S1 in the Supplementary Information. The concentration of the original chlorine stock solution was determined using the N,N-diethyl-p-phenylenediamine (DPD) ferrous titrimetric method (APHA et al., 2012). A series of chlorine stock solutions were prepared at different concentrations (i.e., 100000, 50000, 25000, 10000, 5000, and 2500 mg/L as Cl_2) by diluting the original chlorine stock solution. All other chemical solutions were prepared by dissolving chemicals of analytical grade or higher (Fisher Scientific or Sigma-Aldrich) in ultrapure water (18.2 MΩ cm), which was supplied by a water purification system (Cascada, US). All glassware used in the experiments was rinsed with ultrapure water and baked at 550 °C for 3 h before use.

2.2. Collection, characterization and storage of the CEPT effluent

To identify the potential chlorine consumers, the collected CEPT effluent was firstly characterized. Undisinfected 24-h composite CEPT effluent samples were collected from SCISTW without headspace. The samples were delivered to the lab immediately after collection and characterized on the same day. The turbidity and pH of the samples were measured with a portable turbidimeter (2100P, HACH) and a pH meter (Thermo Orion), respectively. The alkalinity was determined by titrating the sample with a 0.1 M HCl solution to pH 4.5 (APHA et al., 2012). The samples were filtered with a 0.45-μm membrane filter and measured for their dissolved organic carbon (DOC) content with a TOC analyzer (TOC-VCSH, Shimadzu). Bromide and ammonia concentrations were determined with an ion chromatograph equipped with an anionic column (ICE-ASI, Dionex) and a flow injection analyzer system (QuikChem 8500, Lachat), respectively. The UV_{254} value was obtained using a UV–Vis spectrophotometer (Lambda 25, Perkin Elmer Inc.) with a quartz cuvette with a light path of 1 cm.

Table 1 shows the parameters of the samples collected on December 8 and 22, 2015. Because the effluent varied slightly from day to day, we took the mean values of the parameters, which are shown in Table 1: turbidity 46.2 NTU, specific density 1.03, pH 7.12, alkalinity 155 mg/L as $CaCO_3$, DOC 21.7 mg/L as C, UV_{254} 0.222 cm^{-1}, NH_4^+ 24.8 mg/L as N, Br^- 27.9 mg/L as Br, total ferrous iron 7.12 mg/L as Fe, dissolved Fe^{2+} 0.95 mg/L as Fe, S^{2-} < 0.1 mg/L as S. Since the characteristics of the CEPT effluents collected on different dates were basically identical, the effluent sample collected on December 22, 2015 was thus chosen to use for investigation in the later experiments. The remaining sample that was not used on the

Table 1
Characterization of CEPT effluent samples from SCISTW.

Parameters	Collected on Dec. 8, 2015	Collected on Dec. 22, 2015	Mean value
pH	7.10	7.14	7.12
Turbidity (NTU)	48.1	44.3	46.2
Density (kg/L)	1.03	1.03	1.03
Alkalinity (mg/L as $CaCO_3$)	153	157	155
DOC (mg/L as C)	20.2	23.1	21.7
UV_{254} (1/cm)	0.217	0.226	0.222
NH_4^+ (mg/L as N)	25.2	24.3	24.8
Br^- (mg/L as Br)	27.2	28.6	27.9
Total iron (II) (mg/L as Fe)	7.63	6.60	7.12
Dissolved Fe^{2+} (mg/L as Fe)	0.86	1.04	0.95
S^{2-} (mg/L as S)	<0.1	<0.1	<0.1