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Effects of Chlorine Disinfection on Toxicity Formation in Reclaimed Water

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Wastewater reclamation and reuse is an effective way to alleviate the shortage of water (Asano and Levine 1996). However, the safety of reclaimed water is one of the critical areas that must be addressed because there are more chemicals and pathogens in wastewater than in drinking water (Barker and Stuckey 1999). In general, most harmful pollutants and pathogens in drinking water can be removed by conventional treatment processes, but, for wastewater, due to the complex composition and unpredictable water characteristics [e.g. ammonia nitrogen (NH_3-N), dissolved organic carbon (DOC)], there are challenges in developing adequate design and operational parameters for wastewater reclamation.

Among wastewater treatment processes, disinfection is a key but complex process. In addition to being an effective disinfectant, chlorine can react with certain residual organic compounds to form disinfection by-products (DBPs), which could bring adverse effects on ecosystem and human health (Ashbolt 2004). Free chlorine can also react with NH_3-N in water to form combined chlorine, which greatly decreases its disinfection capability. Therefore, learning how to effectively use disinfectants for reducing pathogenic harm without producing DBPs is needed (Monarca et al. 2000).

With current physicochemical analyses, it is impossible to detect all chemicals one by one, not only in undisinfected water, but also in disinfected water due to their complex composition (Weinberg 1997). However, toxicity tests can measure biological effects of pollutants as a whole (Monarca et al. 2004). In this study, the photobacterium bioassay was used to: (1) screen the toxicity of water samples; (2) reflect the formation of toxic DBPs during chlorination; (3) study the effects of chlorine dosage on toxicity formation during wastewater disinfection; (4) explore the relationships of toxicity formation with chlorine dosage and water characteristics (NH_3-N, UV absorbance at 254nm UV_{254} etc.); and (5) provide scientific recommendations for further studies and ultimately for optimizing the reclamation processes.

MATERIALS AND METHODS

All samples of wastewater effluent prior to disinfection were collected from

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several municipal wastewater reclamation plants in the vicinity of Beijing, China, in which activated sludge (AS), biological filtration (BF), membrane bioreactor (MB) and anaerobic-anoxic-oxic process (A^2O) were used as the main treatment processes. Within 24h after sampling, chlorination disinfection of 600mL samples was conducted in triplicate at pH 7.0±0.2 under a series of dosages of available chlorine for 30 min at 20°C. Then the residual chlorine was removed with Na_2SO_3, and the toxicity was measured with the standard photobacterium bioassay after a 15-min exposure (SEPA 1995). The test instrument (toxicity analyzer DXY -2) and test bacteria (*Photobacterium phosphoreum*, freeze-dried powder) were provided by the Institute of Soil Science, CAS, Nanjing PRC.

The luminescence inhibition of water samples to *Photobacterium phosphoreum* was measured, and no inhibition was observed prior to chlorination disinfection. However, chlorination significantly increased the toxicities of water samples even after dechlorination with Na_2SO_3. It was noted in the beginning of the study that the toxicities of some samples were exceedingly high after chlorination / dechlorination. Therefore, in order to obtain meaningful data, the samples were diluted before toxicity tests. Moreover, to conveniently compare the toxicity increase of a water sample before and after disinfection, a concurrent Zn^{2+} reference toxicant sample was run with each water sample test. Due to the advantages of Zn^{2+} as a reference toxicant (Wang et al. 2004), in this study the inhibition percentage of luminescence was standardized as an equivalent concentration of Zn^{2+}.

Water quality parameters (NH_3-N, DOC, UV_{254}) and concentrations of residual chlorine in water samples were measured according to standard methods (APHA 1995). All of the chemical reagents used in this study were of analytical purity.

RESULTS AND DISCUSSION

Chlorine disinfection can be classified into three phases according to the forms of residual chlorine in the system [Figure 1] (Palin 1974): PHASE I (before peak-point, mass ratio $Cl_2 : N < 5 : 1$), residual chlorine is mainly the combined form monochloramine (NH_2Cl); PHASE II (between peak-point and breakpoint, $5 : 1 < Cl_2 : N < 7.6 : 1$), residual chlorine is mainly as monochloramine (NH_2Cl) and dichloramine ($NHCl_2$); and PHASE III (after breakpoint, $Cl_2 : N > 7.6 : 1$), residual chlorine is mainly the free form. Because the reactivity of free chlorine is greater than that of combined chlorine (Nissinen et al. 2002), the forms of residual chlorine should be taken into account when investigating the effect of chlorine dosage on toxicity formation during disinfection, due to the wide variability of NH_3-N in wastewater.

Table 1 lists the characteristics of the six wastewater samples used in the study. The samples were dosed with 0 - 50 mg/L free chlorine. After 30 min of contact time, concentrations of residual free chlorine and combined chlorine were measured. Toxicities of disinfected water samples were determined after dechlorination. All results are presented in Table 2.

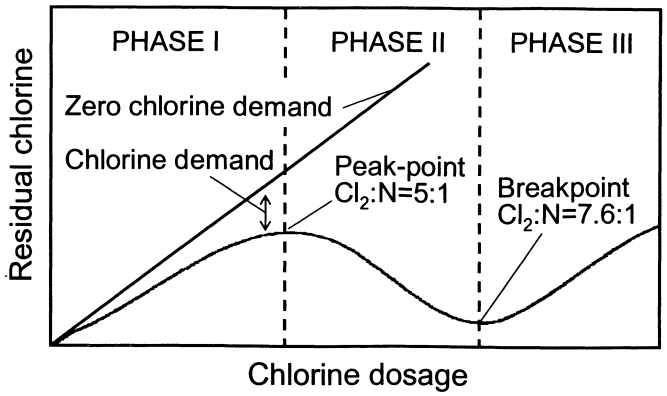

Figure 1. Chlorine demand curve.

Table 1. Characteristics of the wastewater samples.

Sample	DOC(mg/L)	NH_3-N (mg/L)	UV_{254}(1/m)
A1 (BF)	5.1	<0.2	5.0
A2 (BF+MB)	14.6	2.0	8.4
A3 (MB)	1.5	14.0	5.5
A4 (AS)	10.6	0.5	12.6
A5 (AS+$(NH_4)_2SO_4$)	12.9	2.0	12.8
A6 (AS+$(NH_4)_2SO_4$)	12.8	14.0	12.8

Table 2. Residual chlorine and toxicity formation after disinfection of wastewater.

Sample	Added dosage of free chlorine (mg/L)	0 [a] / 0 [b]	1.54 [a] / 2.0 [b]	2.30 [a] / 5.0 [b]	2.50 [a] / 10.0 [b]	3.07 [a] / 20.0 [b]	5.76 [a] / 30.0 [b]	9.22 [a] / 50.0 [b]
A1	FC [c] (mg/L)	0	0.17	0.63	0.71	1.15	2.76	5.50
	CC [d] (mg/L)	0	0.09	0.02	0.02	0.32	0.62	1.35
	Toxicity [e]	0.56	0.92	1.65	1.61	1.56	1.56	1.61
A2	FC (mg/L)	0	0	0	0	0.06	4.06	15.8
	CC (mg/L)	0	0.76	2.10	3.80	1.14	3.94	12.3
	Toxicity	0.56	0.73	1.39	1.55	1.68	1.67	1.64
A3	FC (mg/L)	0	0	0	0	0	0	0
	CC (mg/L)	0	1.43	2.67	6.70	9.20	10.3	19.6
	Toxicity	0.56	0.75	0.89	0.96	1.16	1.45	1.55
A4	FC (mg/L)	0	0.01	0.04	2.11	9.29	14.4	29.3
	CC (mg/L)	0	0.55	0.99	2.51	6.11	9.24	17.2
	Toxicity	0.56	0.68	1.25	1.65	1.51	1.44	1.42
A5	FC (mg/L)	0	0	0	0	0.12	5.82	16.6
	CC (mg/L)	0	1.38	3.30	6.55	1.98	6.28	13.6
	Toxicity	0.56	0.99	1.22	1.60	1.73	1.65	1.63
A6	FC (mg/L)	0	0	0	0	0	0	0
	CC (mg/L)	0	1.78	3.02	6.15	12.4	16.5	30.2
	Toxicity	0.56	0.76	1.04	1.25	1.39	1.55	1.58

[a]: Chlorine dosage for wastewater A1, [b]: Chlorine dosage for wastewater A2-A6.
[c]: Residual free chlorine, [d]: Residual combined chlorine.
[e]: Toxicity unit is mg-Zn^{2+}/L

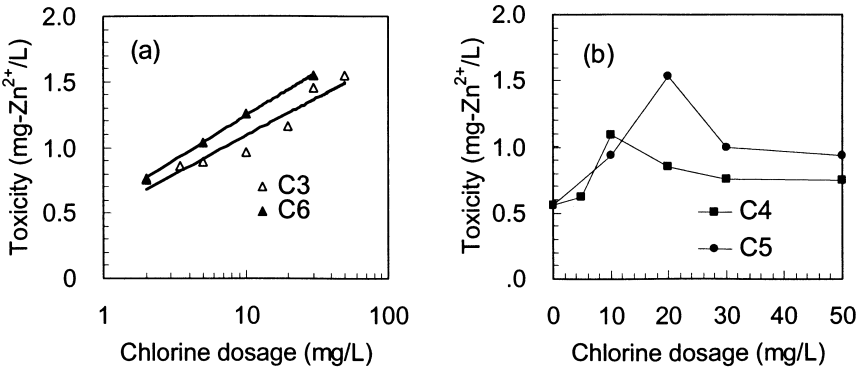

Figure 2. Effects of residual chlorine forms on toxicity of disinfected water.

It can be seen from Table 2, that the forms and concentrations of residual chlorine in the disinfection system heavily depend on NH_3-N concentrations in wastewater. In the presence of low NH_3-N, the residual chlorine was mainly the free form even with a low dosage of chlorine; whereas in high NH_3-N, it was mainly the combined form, even with a high dosage of chlorine. Regarding toxicity, it was apparent that the toxic effect [expressed as the equivalent of a given amount of Zn^{2+} (mg/L)] increased with increase in chlorine dosage; however, after reaching a certain dosage point, the effect became stabilized. The strong toxicity after chlorination implies the formation of toxic by-products, which is most likely to be attributed to the reactions of chlorine disinfectant with organic chemicals. Toxicity values of disinfected water depended on the water characteristics and chlorine dosage (Nikolaou et al. 2004; Sadiq and Rodriguez 2004). As shown in Figure 2(a), when residual chlorine was mainly the combined form, e.g. samples A3 and A6, the toxicity increased continuously with increasing chlorine dosage, and the relationship was linear. However, when residual chlorine was mainly in the free form [e.g. samples A4 and A5, in which the toxicities were conducted after fivefold dilution due to their strong inhibition], it was noted the toxicity declined slightly after reaching a peak level [Figure 2(b)]. This pattern clearly indicates that the reactivity of free chlorine was higher than that of combined chlorine; however, the complex reactions, the intrinsic mechanisms, and the analyses of the species of DBPs formed in the samples upon chlorine disinfection require further studies.

Besides the effects of NH_3-N on toxicity formation during chlorination, organic compounds play an important role as well. As an important parameter of aromatic organics, UV_{254} has been widely used to reflect the amount of organic precursors in the study of drinking water disinfection (Amy et al. 1987), and has been reported to be linearly correlative with total trihalomethanes (TTHMs) and formation potentials of haloacetic acids (HAAFP) for surface water (White et al. 2003). In order to express the effect of NH_3-N and UV_{254} on toxicity formation during chlorination of wastewater, a term "half inhibitory chlorine dosage" was defined as the chlorine dosage that caused 50% inhibition of bacterial luminescence. The higher the 'half inhibitory chlorine dosage', the lower is the toxicity of disinfected wastewater. Figure 3 shows that the 'half inhibitory

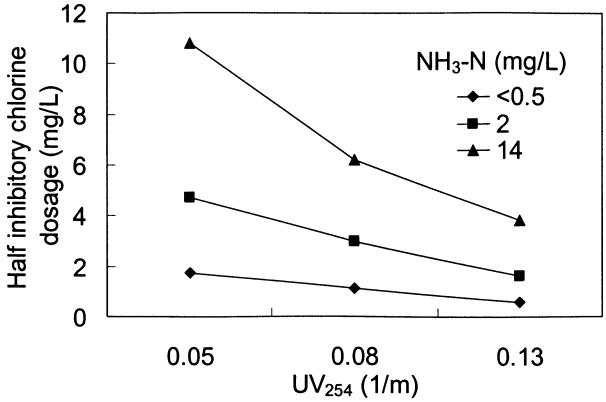

Figure 3. 'Half inhibitory chlorine dosage' for samples with different NH_3-N and UV_{254}.

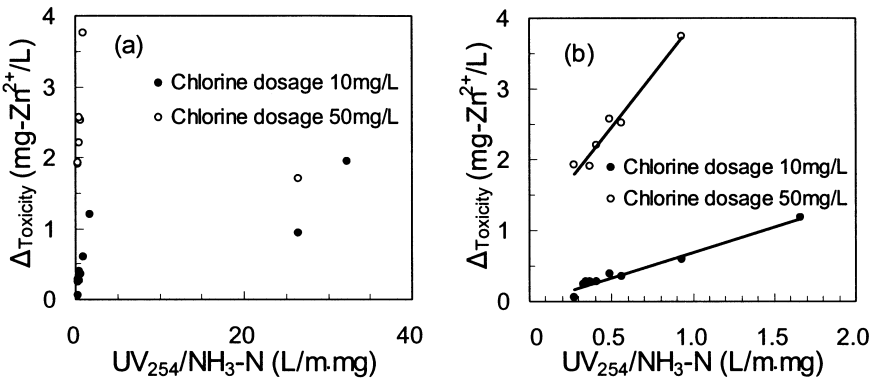

Figure 4. Relationship of toxicity formation with UV_{254}/NH_3-N ratio.

chlorine dosage' decreases with increasing UV_{254} and increases with increasing NH_3-N, which suggests that both lower UV_{254} and higher NH_3-N would result in lower toxicity during the disinfection of wastewater.

In order to quantitatively determine the relationship between the characteristics of wastewater and toxicity formation during chlorination disinfection, eleven wastewater samples were tested. The samples were disinfected with two chlorine dosages: 10mg/L and 50mg/L, and their toxicities were measured after dechlorination. Water quality parameters DOC, NH_3-N and UV_{254} are shown in Table 3. The disinfection phase of each water sample was determined according to the mass ratio of Cl_2 to N, which are included in Table 3 as well. A new parameter UV_{254}/NH_3-N ratio was defined because NH_3-N had a negative effect on toxicity formation and UV_{254} had a positive effect. The relationship between the toxicity formation and UV_{254}/NH_3-N ratio was evaluated, and the results were plotted in Figure 4(a). It can be seen that there are three distinct points located further away from y-axis in Figure 4(a). They corresponded to three wastewaters with very low

Table 3. Characteristics and toxicity after chlorination of wastewater samples.

Samples	DOC (mg/L)	NH_3-N (mg/L)	UV_{254} (1/m)	Chlorine dosage 10mg/L		Chlorine dosage 50mg/L	
				PHASE[a]	Toxicity[b]	PHASE[a]	Toxicity[b]
B1 (AS)	15.43	44.7	16.60	I	0.28	I	1.90
B2 (AS)	17.60	8.0	13.32	I	1.19	II	3.51
B3 (AS)	15.60	23.8	13.31	I	0.36	I	2.52
B4 (AS)	5.26	32.9	8.86	I	0.06	I	1.93
B5 (AS)	14.78	38.7	12.60	I	0.25	I	—
B6 (AS)	10.80	16.0	14.90	I	0.59	I	3.75
B7 (AS)	13.83	31.9	11.11	I	0.28	I	—
B8 (MB)	22.14	32.5	15.90	I	0.39	I	2.57
B9 (MB)	6.76	30.4	12.40	I	0.27	I	2.20
B10(MB)	3.91	0.1	3.23	III	1.95	III	—
B11(A^2O)	6.38	0.4	10.60	III	0.93	III	1.70

[a]: Disinfection phase, [b]: Toxicity unit is mg-Zn^{2+}/L

NH_3-N concentrations and the disinfection PHASE was not I, but II or III. However, by considering only wastewater samples with disinfection PHASE I, it was noted that there were linear relationships between toxicity formation and UV_{254}/NH_3-N ratios [Figure 4(b)]. This suggested that the toxicity of disinfected wastewater could strongly be dependent upon disinfection phase. Since the disinfection for most practical processes is PHASE I, the UV_{254}/NH_3-N ratio might be an important parameter to predict toxicity formation of wastewater chlorination.

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