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The analysis of melamine and the removal efficiencies in the advanced oxidation process (AOP) and granular activated carbon (GAC) processes

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ABSTRACT

Melamine is an important organic chemical and is widely used in industry. So, outflow of melamine into the environment has increased. However, research on melamine has been limited to research on food. In this study, to measure the concentration of melamine present in the environment, melamine and its by-products, Ammeline, Ammelide and Cyanuric acid, were simultaneously analyzed using gas chromatography time of flight. Also, for the removal of melamine and its by-products, the removal efficiencies were investigated via absorption experiments using the granular activated carbon (GAC) process and advanced oxidation process (AOP). Looking at the removal by each substance at ozone concentration, 10 mg/L Cyanuric acid was approximately examined using ozone and ozone/peroxide as advanced treatment processes. The concentration of ozone was from the minimum of 0.5 mg/L to the maximum of 10 mg/L and the degree of removal was checked by making the concentrations of 11 kinds react with each other for 20 min. The highest efficiency was shown at 0.5 mg/L of peroxide dose when the concentration of ozone is 0.5 mg/L and good efficiency was shown at 1 mg/L of peroxide dose when the concentration of ozone is 2 mg/L. At last, the best efficiency was shown at 2 mg/L of peroxide dose when the concentration of ozone is 5 mg/L. In the process of using ozone and peroxide, the best efficiency was shown when the ratio of ozone and peroxide is 1:0.5. And, if GAC process is added to the latter part of AOP process, melamine and by-products which are present in water can be removed more effectively.

Keywords: Melamine; By-products of melamine; GC-TOF; GAC process; Cyanuric acid; Ammeline; Ammelide

1. Introduction

Melamine (CAS 108-78-1, $C_3H_6N_6$) was first prepared, from the fusion of potassium thiocyanate with ammonium chloride, and described in 1834 by Justus von Liebig, with its molecular structure published by A.W. Von Hoffmann in 1885 [1]. The first commercial plants for the production of melamine was started in the late 1930s [2], with melamine now having become an increasingly important chemical commodity. In 1970, the world capacity of melamine

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was estimated at 200,000 t, with current production estimated to be 1,400,000 t.

Melamine has various uses, such as in resins, flame retardants, adhesives, and laminates. Since one melamine molecule contains six nitrogen elements, it has a nitrogen mass ratio of 66%, and therefore obtained a patent as a non-protein nitrogen feed in 1958 [3], but was banned for use as a feed in 1978 because of its incomplete hydrolysis in livestock, which is also slower than other protein sources such as urea [4], and many countries in the world and Codex Alimentarius Commission do not allow the use of melamine in food. Also, the Globally Harmonized System of Classification and Labelling of Chemicals European Union safety guidelines have classified melamine as causing cancer. However, some immoral milk processing companies have added melamine to milk or dairy products to artificially increase the measured protein concentration contained in milk, as this is examined via the nitrogen content, which will be elevated due to the high nitrogen content of melamine. However, studies on the toxicities of melamine and its by-products are still ongoing, but they have been shown to increase when melamine is present with by-products than alone. The most critical research related to the toxicity of melamine was that of Dobson et al. in 2008, where the by-products of melamine, Ammeline and Ammelide (10–100 ppm) and melamine/Cyanuric acid mixtures and elamine/Ammeline/Ammelide/Cyanuric acid mixtures (400/400 mg/kg/day) were orally administered to Sprague-Dawley rat. It was reported that Ammeline and Ammelide when individually administered did not cause disorder in the kidneys, but the mixtures showed significant renal toxicity [5,6]. Recently, reported cases of renal stones and acute renal failure have been increasing among Chinese children who were fed infant formula contaminated with melamine. According to a 2008 World Health Organization (WHO) report, 294,000 babies showed symptoms, 51,900 hospitalized, and six died from renal failure [7]. The symptoms reported to the Chinese Ministry of Health (MoH) during the melamine dry milk crisis are shown in Table 1.

Table 1
Symptoms caused by the administration of melamine

Signs/symptoms (issued by MoH, China)
• Unexplained crying in infants, especially when urinating, possible vomiting
• Naked eye visible or microscopic hematuria
• Acute obstructive renal failure (Oliguria or anuria)
• Stones discharged while passing urine
• High blood pressure, edema, painful when knocked on kidney area

Between 2004 and 2007, pet food containing melamine was associated with numerous deaths among cats and dogs in North America. In the case of Dichloro-Diphenyl-Trichloroethane, the use of which is currently banned due to its harmful effects, during the early stage of its development, was called "cheap and effective dream technology" and in the 1950s, the WHO actively recommended its use to prevent malaria. Previously, little information was available on the harmful effects of synthetic chemical substances, which were openly sold and used even though they may be fatal to humans. However, it is difficult to completely verify the harmful effects of all chemicals. Countless chemicals are produced, processed, and used globally, but the actual harmful effects of only certain products have been identified, with casual relationships identified when a certain amount of a substance is used for a considerable period; therefore, accurately judging the harmful effects of all chemicals is not straightforward. Studies on the harmful effects of melamine to the human body are also insufficient and in addition to the danger of melamine itself, the cocktail effect of chemicals, i.e. their unexpected harmful effects, can be shown by mixing with other substances. Even now the production and use of melamine is increasing with relatively high possibility of water contamination. However, in reality, studies on the degree of melamine pollution of rivers are insufficient. In this study, melamine and its by-products, Ammeline, Ammelide, and Cyanuric acid, were simultaneously analyzed using gas chromatography time of flight (GC/TOF). Also, for the removal of melamine and its by-products [8], the removal efficiencies were investigated via absorption experiments using the granular activated carbon (GAC) process and removal characteristics were also examined using ozone and ozone/peroxide, as advanced treatment processes.

2. Materials and methods

2.1. Sampling points

We collected three same samples at the suburbs of Paldang Dam located in the relative upstream in Han River and Ttukseom amusement park in the downstream region and collected samples equally at the Hongreung stream, Wangsuk stream, and Cheonggye stream among streams flowing into Han River and then measured melamine concentration after purification. Fig. 1 shows the points where the samples were collected and they are Cheonggye stream, Ttukseom amusement park, Wangsuk stream, Hongreung stream, and the suburbs of Paldang Dam from the left.

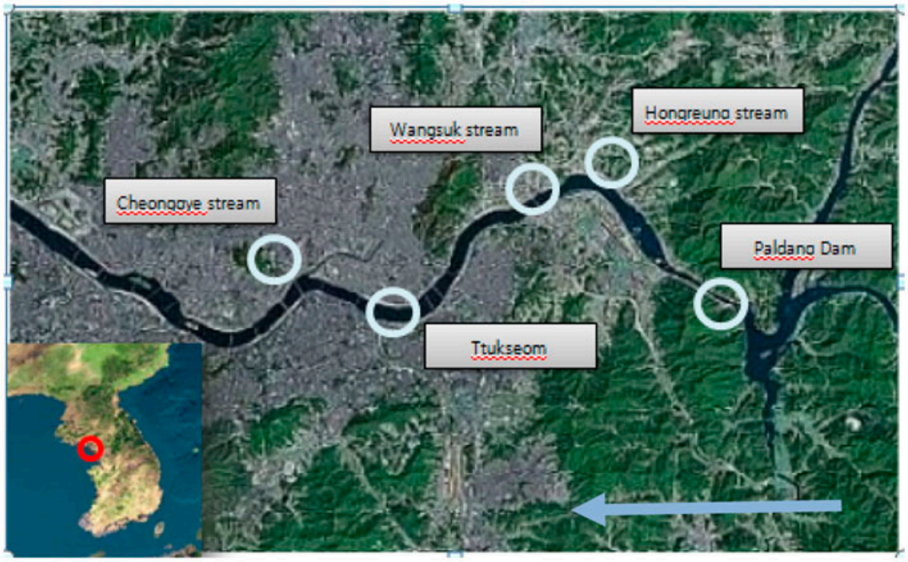

Fig. 1. Sampling points in Han River and River Basin.

2.2. Reagents and chemicals

Melamine is manufactured and sold as fine, white, and powdered crystals. The most important physical data relating to melamine are summarized in Table 2.

The s-triazine ring in melamine is very stable and cleaves only under drastic conditions (for example, heating above 600˚C or fusion with alkali compounds). Melamine is hydrolyzed both by mineral acids and inorganic alkalis, which proceeds stepwise, with the loss of one, two, or all three amino groups (Fig. 2) [1].

The spectra of products produced by melamine vary with temperature, pH, and concentration; the end product is Cyanuric acid. Even small amounts of the oxotriazines (especially Cyanuric acid and Ammelide) markedly effect the condensation of melamine with formaldehyde by increasing the rate of condensation. The standards and reagents used in this study are listed in Table 3.

Stock solutions of melamine, Cyanuric acid, Ammeline, and Ammelide, each at a concentration of 1,000 μg/mL, were separately prepared in a mixture of Diethylamine/H_2O (20/80) and stored at 4˚C.

Table 2
Physical & chemical properties of melamine

Classification	Melamine
Form	Powder
Color	White
Odor	Inodorous
Molecular weight	126.12
Molecular formula	C_3–H_6–N_6
Melting point	345˚C
Vapor density	4.34
Solubility in water	3,240 mg/L at 20˚C
Octanol/water partition coefficient	−1.37
Density	1.573 at 16˚C

2.3. SPE-clean-up and TMS-derivatives

For the analyses of the samples, melamine, Ammeline, Ammelide, and Cyanuric acid were processed through SPE-clean-up. For melamine, Oasis MCX 6 mL, 150 mg cartridges were used for the analyses of alkaline substances, and for Ammeline, Ammelide, and Cyanuric acid Oasis MAX 6 mL, 150 mg cartridges were used for the analyses of acidic substances. A refined method using cartridges is shown in Fig. 3.

2.4. Derivatives

About 160 μL of the filtrate from the cartridges was transferred to a glass GC vial and evaporated to dryness under a stream of nitrogen, at approximately 70˚C, with 200 μL of internal standard (2, 6-diamino-4-chloropyrimidine) and 200 μL of BSTFA, containing 1% TMCS, was then added. The sample was vortex

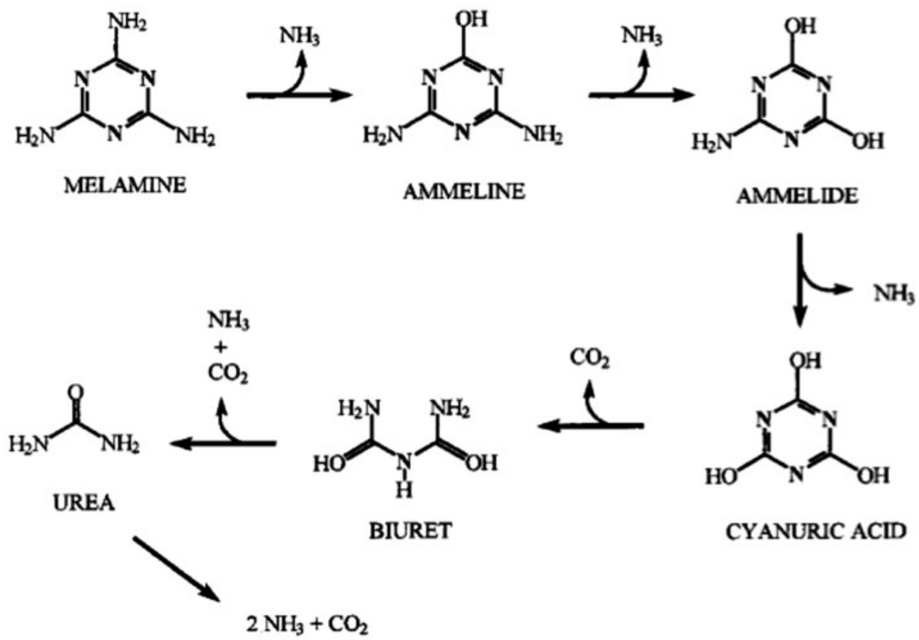

Fig. 2. Hydrolysis of melamine by mineral acids and inorganic alkalis.

Table 3
Standards and reagents

Standard	Melamine	Sigma-Adrich	>99% purity
	Cyanuric acid	TCI-GP	>98.0%
	Ammeline	TCI-ER	>98.0%
	Ammelide	TCI-ER	>98.0%
	Internal standard	Sigma-Adrich	98%
Solvent	Diethylamine	Sigma-Adrich	SigmaUltra Grade
	Pyridine	SamChun	HPLC grade
	Acetonitrile	SamChun	HPLC grade
Silyating reagent	BSTFA with 1% TMCS	TCI	Derivatization grade

mixed and incubated at 70˚C for 45 min prior to its injection into the GC column [5].

2.5. GC-TOF

All the analyses were performed on an Agilent 6890 N gas chromatograph, equipped with a PegasusHT (Time of Flight) selective detector, 7683B autosampler, and Agilent DB-5MS column (30 m × 0.25 mm × 0.25 μm), supplied by Agilent Technologies. The injection port temperature was set at 280˚C. The injection volume was 1 μL. The transfer line and MS temperatures were set to 290 and 230˚C, respectively. The instrument conditions are listed in Table 4 [5].

Instrument detection limit of melamine is 200 ng/L and method detection limit is 100 ng/L.

2.6. AOP process

Advanced oxidation process (AOP) and GAC process have been commonly used for the removal of trace substances. The AOP device used in the experiments, as shown in Fig. 4, consisted of a semi-batch device, with 1L capacity, and had the provision for stirring using a dosing pump.

To prevent the target materials from being absorbed in the pipelines, tubes coated internally with Teflon were used, with corrosion prevented using SUS-316 and Teflon as materials for the ozone dissolving device and pipelines, respectively. Fixed quantities of ozone and peroxide were injected into an effector via the automatic syringe device. The reaction time was 20 min and the experiments were carried out under the same conditions [9,10].

2.7. GAC

Prior to the activated carbon experiment, the parameters required were calculated through a Freundlich isothermal absorption experiment with an activated carbon absorption experiment conducted on the basis of the parameters obtained. In the experi-

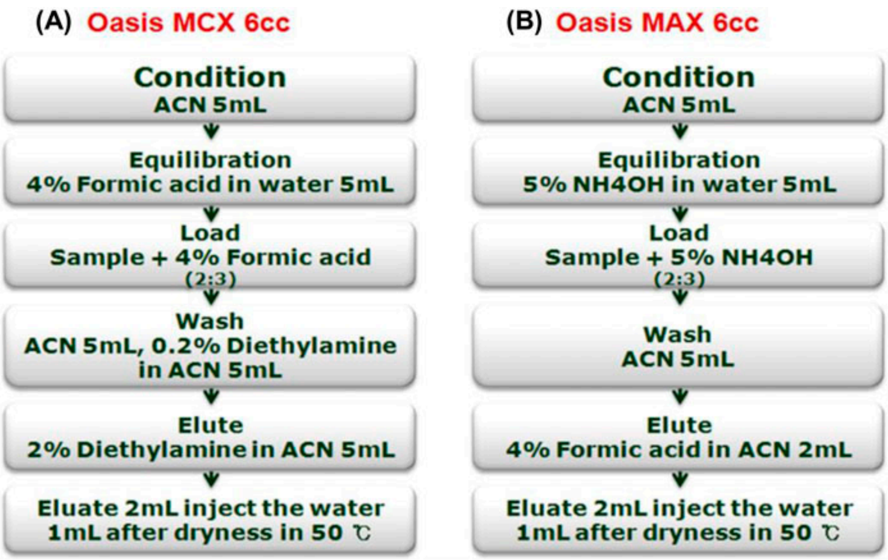

Fig. 3. Clean-up process. (A) MCX 6 mL, 150 mg cartridges, (B) MAX 6 mL, 150 mg cartridges.

Table 4
Gas chromatograph and mass spectrometer conditions

	Conditions
Column	30 m × 0.25 mm × 0.25 um DB-5 ms column
Inlet temp.	280℃
Inlet pressure	12.9 psi
Carrier gas	Helium, constant flow mode, 1.2 mL/min
Pulsed splitless	25 psi at 0.5 min
Oven program	100℃(1 min hold), 10℃/min to 210℃
Injection volume	1 μL
Transfer line	290℃
Tune	Autotune
MS temp.	Source 230℃

ment, 1 mg/L of melamine was passed through a column containing 0.3 g of activated carbon at a velocity of 3.5 mL/min. The activated carbon used in the experiments was Norit GAC, from the Norit Company. The absorption experiment was conducted after sifting the activated carbon via 20 and 80 mesh sieves, followed by pulverizing, sifting, cleaning, and drying immediately prior to use [11].

3. Results and discussion

3.1. Melamine distribution of Han River and River Basin

Melamine analysis result of Han River and River Basin is shown in Table 5. This River is an important drinking water source for populations in the Seoul metropolitan area.

The lowest melamine was detected at the suburbs of Paldang Dam and it was detected at Ttukseom amusement park, the downstream of it, in the concentration of 0.406 μg/L. Although the concentration was low in general, melamine detection could be checked at every point.

3.2. Removal evaluation experiment results by ozone

Melamine, Cyanuric acid, Ammeline, and Ammelide for use in the experiments were prepared as 1 mg/L solutions in distilled water. The concentration of ozone ranged from 0.5 to 10 mg/L, with the degree of removals of the above substance checked by their reactions with 11 different concentrations of ozone for 20 min. The concentration of the substance and the removal efficiencies are shown in Fig. 5.

Ammelide showed about 47.1 and 52.8% removals at ozone concentrations of 0.5 and 10 mg/L, respectively, indicating only a slight change with respect to the ozone concentration. Ammeline showed about 24.6 and 47.5% removals at ozone concentrations of 0.5 and 10 mg/L, respectively, which was the lowest removal among the four substances. Cyanuric acid showed about 79.4% removal at an ozone concentration of 10 mg/L, and showed the highest removal. Finally, melamine showed the lowest removal at an ozone concentration of 0.5 mg/L, but about 68.7% at an ozone concentration of 10 mg/L, which was the second highest removal among the four substances. From these results, the removal efficiencies were in the order: Ammelide, Cyanuric acid, Ammeline, and melamine at an ozone concentration of 0.5 mg/L, but

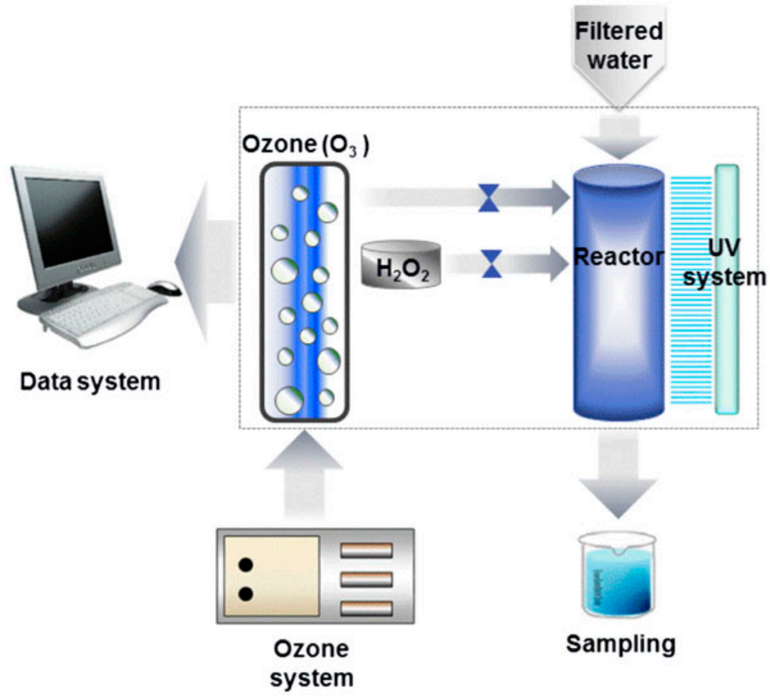

Fig. 4. Schematic diagram of the AOP.

Table 5
Analysis of melamine in Han River and River Basin

	Concentration (μg/L)			
	Min.	Max.	Average	±SD (%)
Ttukseom	0.321	0.539	0.406	12
Cheonggye stream	0.215	0.387	0.295	7
Wangsuk stream	0.327	0.673	0.589	17
Hongreung stream	0.085	0.179	0.121	4
Paldang Dam	0.016	0.056	0.025	2

with an ozone concentration of 10 mg/L, the removal efficiencies were in the order: Cyanuric acid, melamine, Ammelide, and Ammeline.

3.3. Removal evaluation experiment results with ozone/hydrogen peroxide

3.3.1. Change in the removal efficiency according to the concentration of hydrogen peroxide

The concentration of ozone was fixed at 0.5, 2 or 5 mg/L in the AOP device, with various concentrations of peroxide injected, the results of which are shown in Fig. 6.

The highest removal was observed when ozone concentration was 5 mg/L with a peroxide concentration of 0.5 mg/L. With an ozone concentration of 2 mg/L, the best removal efficiency was observed with a peroxide concentration of 1 mg/L, and at an ozone concentration of 5 mg/L, the best removal efficiency was with a peroxide concentration of 2 mg/L. You look at the graph, efficiency was the best at 1:0.5 ratio of peroxide and ozone. When the peroxide concentration reached more than a certain amount, the removal efficiency was reduced because low concentration cannot cause sufficient oxidation due to OH radicals, but higher concentrations can suppress this reaction [12]. However, the certain amount of the removal of by-products by the ozone/hydrogen peroxide process is possible, but this is limited in the case of melamine; therefore, subsequent processes, such as GAC, need to be considered.

3.3.2. Removal change according to the concentration of ozone

Fixing the concentration of peroxide and varying the concentration of ozone at 0.5, 1, 2, and 5 mg/L, the removal efficiencies of the four substances were observed, the results of which are shown in Fig. 7.

From the results, it is seen that the higher the ozone concentration, the higher the overall removal efficiency. This shows that the ozone concentration

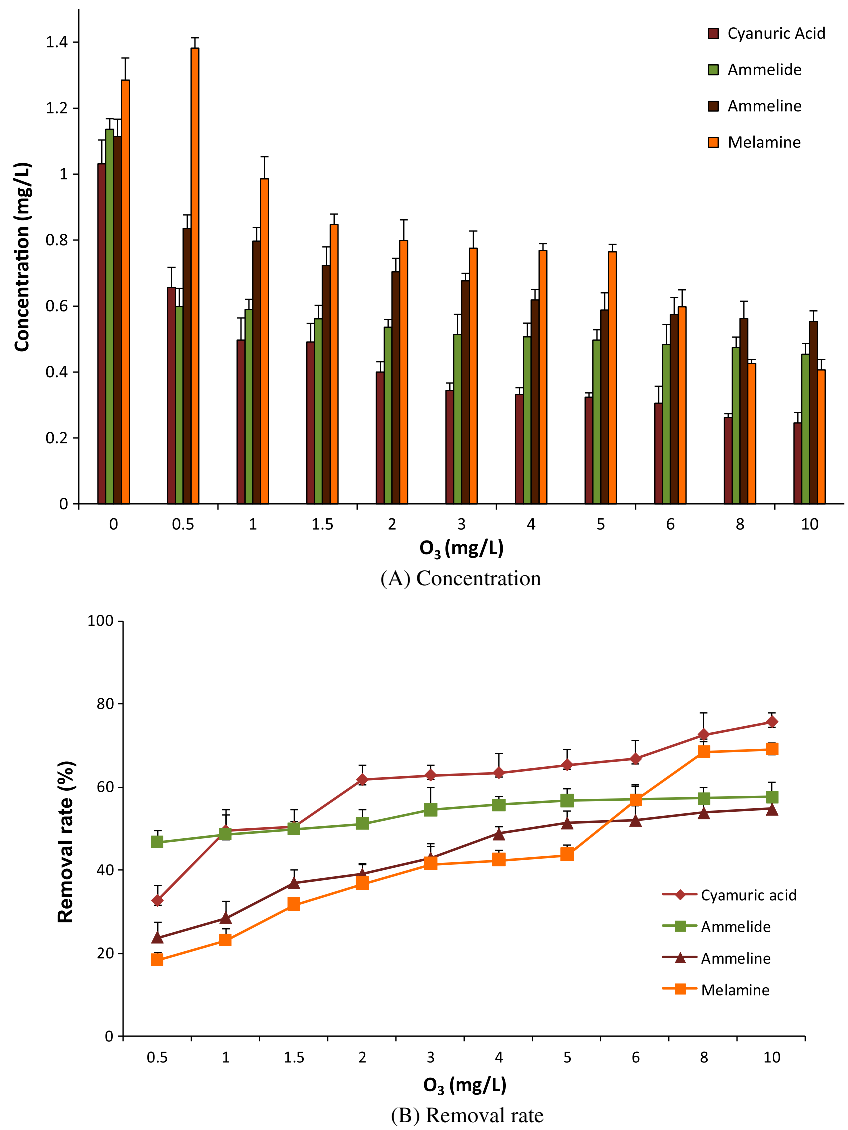

Fig. 5. Ozonation of melamine & by-products (A) concentration, (B) removal rate.

has a greater impact on the removal of melamine and its by-products than that of hydrogen peroxide.

3.4. GAC

3.4.1. Melamine removal using activated carbon

The Freundlich parameter was calculated from the absorption characteristics of melamine into GAC via a constant temperature absorption experiment [13]. The Freundlich parameter was calculated experimental, as shown in Fig. 8.

From the results, K_f and $1/n$ were found to be 11.298 and 0.534, respectively. A plug flow reactor allows the same flow of a substance in the reactor as in a tube. That is, the flow of a substance induced in a reactor reacts via mixing in the radial direction only, without any axial direction mixing, and the state (temperature, formation, and flux) will be constant in one cross section and change continuously depending on the distance from the entrance. When designing a plug flow reactor for 1 g of GAC, with a flux of 1 mg/L at a flow rate of 3.5 mL/min, based on 90% removal, the amount of melamine absorbed by 1 g of GAC can be calculated via the Freundlich constant temperature absorption equation, as follows:

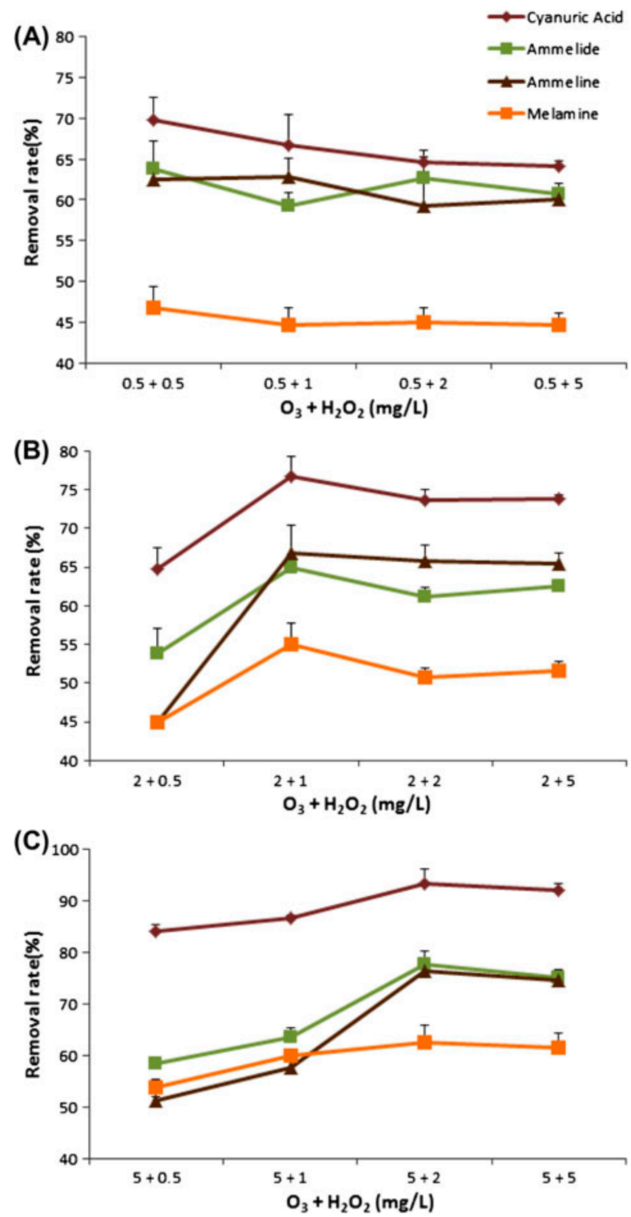

Fig. 6. Removal efficiencies of melamine & its by-products by ozone/hydrogen peroxide, the concentration of ozone was fixed at 0.5, 2 or 5 mg/L in the AOP device, with the concentration of peroxide varied. (A) 0.5 mg/L, (B) 2 mg/L, (C) 5 mg/L.

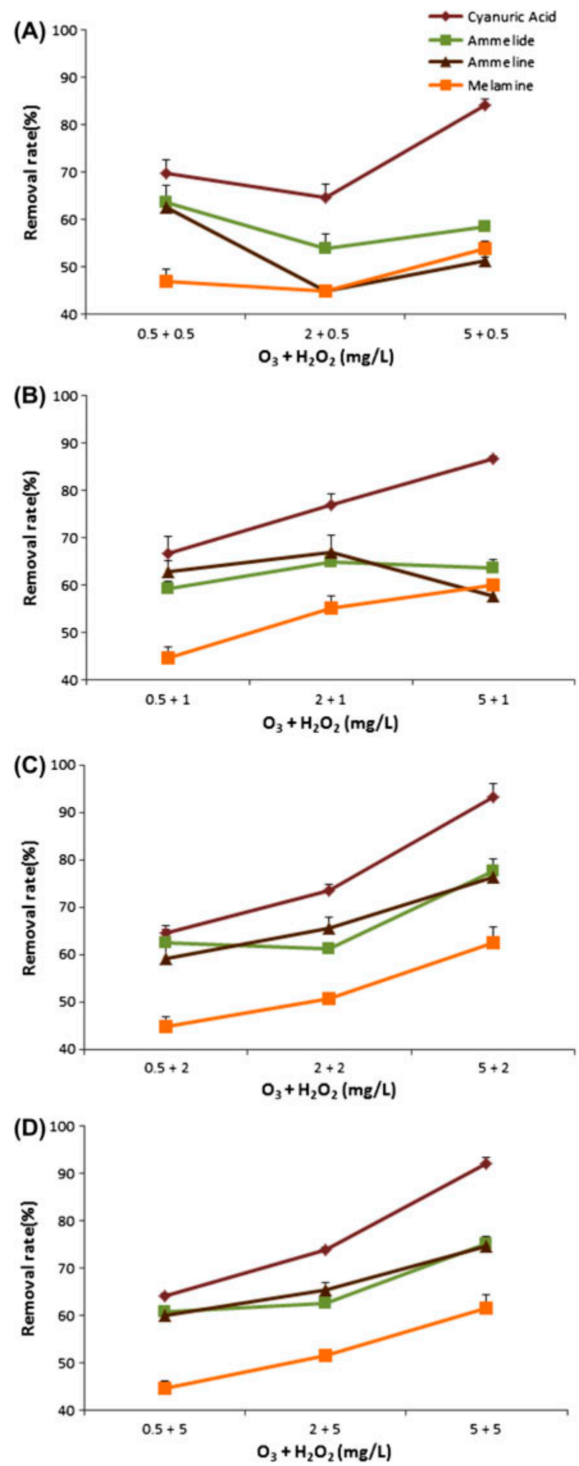

Fig. 7. Removal efficiency of melamine and the by-products by ozone/hydrogen peroxide The concentration of peroxide constant and the concentration of ozone different as 0.5, 1, 2, and 5 mg/L of O_3.

$$11.298 \times [1\ \text{mg/L} \times (100 - 90)\%]^{0.516} = 3.304\ \text{mg/L} \tag{1}$$

Therefore, based on 90% absorption, the amount absorbed was 3.304 mg/L, and by dividing this by the amount of substance used, the absorptivity exhaustion corresponding to 90% removal can be calculated, as follows:

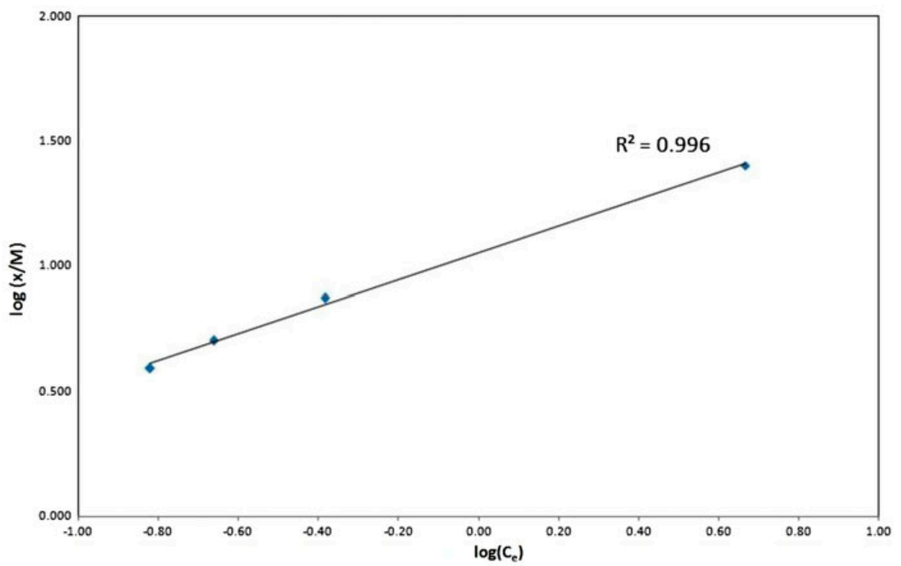

Fig. 8. Freundlich isotherm for the removal of melamine.

$$3.304\ \text{mg/L} \div (1\ \text{mg/L} \times 3.5\ \text{ml/min} \times 1\text{L}/1,000\ \text{mL}) = 943.9\ \text{min} \quad (2)$$

Therefore, the expected breakthrough time through adsorptivity exhaustion is about 15.7 h.

3.4.2. Activated carbon treatment by column reactor

The basic design equation of a column charging reactor, including the inactive factor, α, in the rate expression is as follows:

$$\frac{W}{F_{A0}} = \int_o^X \frac{dX}{-kC_A\alpha} \quad (3)$$

W: mass of adsorbate; F_{A0}: material influx quantity; X: removal ratio; k: reaction rate constant; C_A: concentration of water; α: non-active factor.

If the linear equation over time controls the inactive factor, α, then α can be rewritten as e^{-kd}, where k_d is called the inactive constant. Therefore, the reaction equation can be deployed, as shown below [11,14]. The result obtained by calculating k_d and ln ($k\tau$) until that time by linear trend line is shown in Table 6.

$$k\tau e^{-k_d} = [-\ln(1 - X_a)] \quad (4)$$

k: reaction rate constant; τ: $\frac{WC_{A0}}{F_{A0}}$; k_d: inactive factor; X_a: control ratio,

The square of the Pearson product moment correlation coefficient (RSQ), which shows whether the trend lines of the inactive factor slope expression corresponding to 510 min are in agreement, was 0.921, indicating a value relatively close to 1 when passing through the activated column of 80 mesh. Therefore, the absorption of melamine by the GAC can be judged as being the first breakthrough. The expected breakthrough time for attaining 0% removal from the value of the inactive factor, 0.001, as calculated from the above, is shown in Fig. 9. Circles mean a 50% removal rate in the graph.

3.4.3. Removal by activated carbon mesh

Melamine, with a concentration of 1 mg/L, was passed through a column filled with 0.3 g of activated carbon, at a flow rate of 3.5 mL/min, and also through 20, 80 mesh activated carbon, with the experimental results shown in Fig. 10.

In the experiment, the size of the activated carbon has shown to affect the removal. As the size of the activated carbon got smaller, the removal during the early stage was somewhat high, but regardless of the size of activated carbon the breakthrough point tended to appear about 900 min. After about 1,200 min, about 10% removal was achieved but it was found that melamine passes through without being absorbed.

Table 6
The deactivation factor and coefficient constant in GAC treatment of melamine, (A) 80 mesh, (B) 20 mesh

Values time (min.)	ln [-ln(1–XA)]	$-k_d$	ln(k)	RSQ	Values time (min.)	ln [-ln(1–XA)]	$-k_d$	ln (k)	RSQ
(A) 80 mesh									
10	1.195	–	–	–	780	−0.147	−0.002	1.329	0.830
20	1.161	−0.003	1.228	1.000	810	−0.199	−0.002	1.347	0.843
30	1.130	−0.003	1.227	1.000	840	−0.261	−0.002	1.362	0.856
60	1.101	−0.002	1.200	0.897	870	−0.317	−0.002	1.376	0.868
90	1.089	−0.001	1.187	0.852	900	−0.380	−0.002	1.389	0.879
120	1.054	−0.001	1.183	0.908	930	−0.463	−0.002	1.401	0.888
150	1.032	−0.001	1.180	0.932	960	−0.569	−0.002	1.414	0.896
180	1.020	−0.001	1.176	0.934	990	−0.667	−0.002	1.428	0.903
210	0.989	−0.001	1.174	0.950	1,020	−0.780	−0.002	1.442	0.909
240	0.989	−0.001	1.169	0.943	1,050	−0.949	−0.002	1.460	0.912
270	0.985	−0.001	1.164	0.929	1,080	−1.121	−0.002	1.481	0.914
300	0.981	−0.001	1.158	0.912	1,110	−1.275	−0.002	1.503	0.914
330	0.978	−0.001	1.153	0.893	1,140	−1.466	−0.002	1.528	0.914
360	0.971	−0.001	1.148	0.879	1,170	−1.653	−0.002	1.556	0.912
390	0.933	−0.001	1.146	0.895	1,200	−1.921	−0.002	1.589	0.907
420	0.925	−0.001	1.144	0.905	1,230	−2.183	−0.002	1.626	0.902
450	0.916	−0.001	1.142	0.912	1,260	−2.441	−0.003	1.666	0.896
480	0.843	−0.001	1.146	0.923	1,290	−2.754	−0.003	1.712	0.888
510	0.782	−0.001	1.152	0.921	1,320	−2.821	−0.003	1.752	0.887
540	0.734	−0.001	1.159	0.917	1,350	−2.903	−0.003	1.788	0.888
570	0.589	−0.001	1.174	0.871	1,380	−2.972	−0.003	1.820	0.891
600	0.458	−0.001	1.193	0.829	1,410	−3.040	−0.003	1.848	0.895
630	0.287	−0.001	1.219	0.790	1,440	−3.214	−0.003	1.877	0.899
660	0.194	−0.001	1.244	0.784	1,470	−3.471	−0.003	1.908	0.901
690	0.140	−0.001	1.266	0.795	1,500	−3.508	−0.003	1.935	0.905
720	0.038	−0.001	1.287	0.806	1,530	−3.512	−0.003	1.956	0.910
750	−0.041	−0.001	1.308	0.818	1,560	−3.519	−0.003	1.973	0.914
(B) 20 mesh									
10	1.182	–	–	–	780	−0.317	−0.002	1.288	0.926
20	1.130	−0.005	1.235	1.000	810	−0.439	−0.002	1.300	0.930
30	1.082	−0.005	1.232	0.999	840	−0.473	−0.002	1.310	0.936
60	1.039	−0.003	1.189	0.891	870	−0.523	−0.002	1.317	0.941
90	1.003	−0.002	1.174	0.897	900	−0.628	−0.002	1.327	0.945
120	0.986	−0.002	1.161	0.879	930	−0.744	−0.002	1.337	0.948
150	0.952	−0.001	1.154	0.897	960	−0.854	−0.002	1.349	0.950
180	0.931	−0.001	1.147	0.905	990	−1.002	−0.002	1.364	0.951
210	0.921	−0.001	1.140	0.899	1,020	−1.269	−0.002	1.386	0.947
240	0.906	−0.001	1.133	0.896	1,050	−1.515	−0.002	1.413	0.939
270	0.899	−0.001	1.126	0.885	1,080	−1.718	−0.002	1.444	0.931
300	0.881	−0.001	1.120	0.885	1,110	−2.015	−0.002	1.481	0.921
330	0.877	−0.001	1.114	0.877	1,140	−2.414	−0.003	1.527	0.905
360	0.832	−0.001	1.111	0.894	1,170	−2.523	−0.003	1.570	0.898
390	0.805	−0.001	1.110	0.910	1,200	−2.802	−0.003	1.616	0.891
420	0.744	−0.001	1.113	0.926	1,230	−2.884	−0.003	1.657	0.889
450	0.691	−0.001	1.117	0.936	1,260	−2.928	−0.003	1.692	0.891
480	0.596	−0.001	1.126	0.930	1,290	−2.928	−0.003	1.720	0.896
510	0.498	−0.001	1.139	0.916	1,320	−3.029	−0.003	1.745	0.901
540	0.347	−0.001	1.158	0.886	1,350	−3.171	−0.003	1.770	0.905
570	0.273	−0.001	1.176	0.879	1,380	−3.303	−0.003	1.794	0.909
600	0.189	−0.001	1.193	0.879	1,410	−3.478	−0.003	1.818	0.913
630	0.109	−0.001	1.210	0.883	1,440	−3.684	−0.003	1.844	0.916

(*Continued*)

Table 6
(*Continued*).

Values time (min.)	ln [-ln(1–XA)]	$-k_d$	ln(k)	RSQ	Values time (min.)	ln [-ln(1–XA)]	$-k_d$	ln (k)	RSQ
660	0.028	−0.002	1.226	0.889	1,470	−3.756	−0.003	1.866	0.920
690	−0.050	−0.002	1.241	0.896	1,500	−3.848	−0.003	1.886	0.924
720	−0.122	−0.002	1.255	0.903	1,530	−3.938	−0.003	1.904	0.927
750	−0.175	−0.002	1.267	0.911	1,560	−3.964	−0.003	1.918	0.931

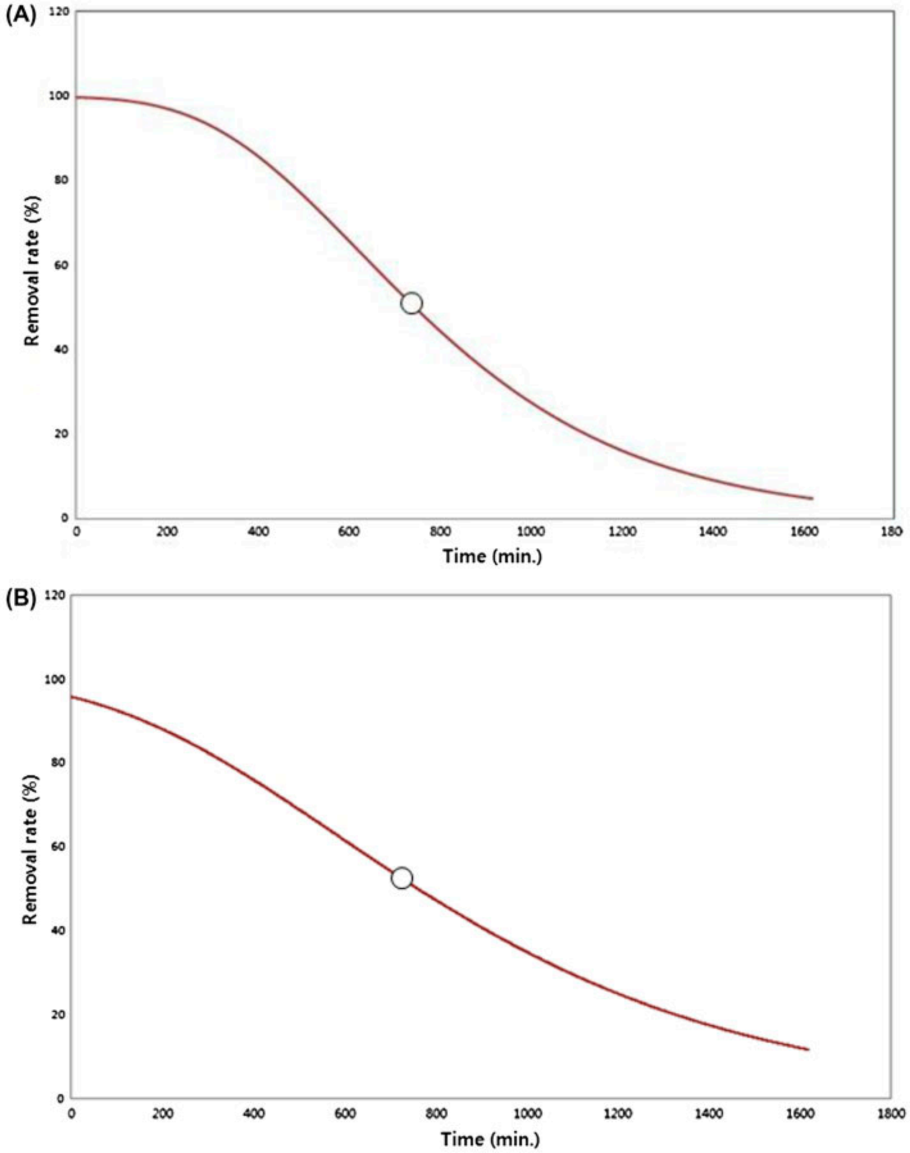

Fig. 9. Expected removal rate of melamine via the GAC treatment. And the circles mean a 50% removal rate. (A) 80 mesh, (B) 20 mesh.

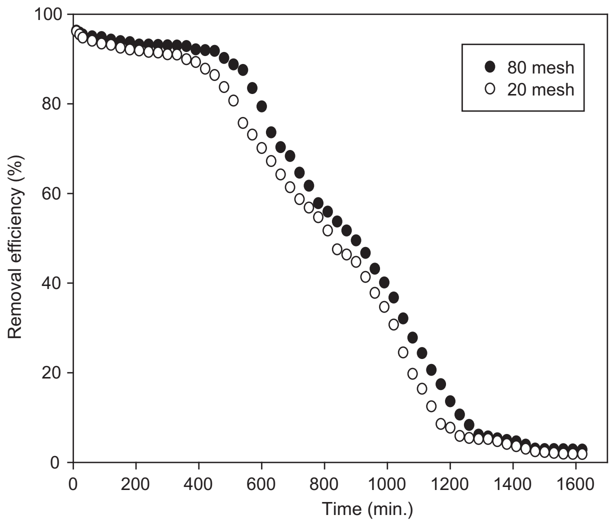

Fig. 10. Removal efficiency and concentration according to size of GAC.

4. Conclusions

Currently, the melamine concentration in the Han River and its tributaries is low, but this is expected to increase in the future due to its increased use. Therefore, melamine and three other substances, Cyanuric acid, Ammelide, and Ammeline which are melamine by-products, were analyzed using GC/TOF with removal characteristics and efficiencies examined using ozone, ozone/hydrogen peroxide, and GAC processes.

(1) The removals of melamine, Cyanuric acid, Ammelide, and Ammeline, at a concentration of 1 mg/L in distilled water, were examined using ozone. The removals of the substances with an ozone concentration of 10 mg/L were approximately 79, 69, 53, and 48% for Cyanuric acid, melamine, Ammelide, and Ammeline, respectively. However, the removal of Ammelide was approximately 47% at an ozone concentration of 0.5 mg/L, with no significant change on increasing the ozone concentration.

(2) The removal efficiencies were also examined on fixing the ozone concentration and varying the peroxide concentration. The highest efficiency was shown with 0.5 mg/L peroxide with an ozone concentration of 0.5 mg/L. Good efficiency was shown with 1 mg/L of peroxide with an ozone concentration of 2 mg/L. The best efficiency was shown with a peroxide concentration of 2 mg/L and ozone concentration of 5 mg/L.

(3) On fixing the peroxide concentration and varying the ozone concentration, in general, the higher the ozone concentration, the greater the removal. The removal efficiencies were in the order: Cyanuric acid, Ammelide, Ammeline, and then melamine.

(4) In the process using ozone and peroxide, the greatest efficiency was observed when the ratio of ozone to peroxide was 1:0.5. Excess peroxide did interfere with the removal. Also, the treatment using ozone/peroxide, rather than ozone alone, was more effective in the treatment of melamine and its by-products.

(5) In the absorption experiment using the GAC process, the removal by 20, 80 mesh showed some differences, but these were only slightly. Most of the breakthroughs occurred in about 900 min, and after 1,200 min, approximately 10% of the melamine had been absorbed, with that remaining leaking from the column.

(6) Using the trend line, predicted values can be obtained, given that the linear equation over time dominates the inactive factor, α, in the rate expression, which was consistent with the 80 mesh. Therefore with the 20 mesh inactivated carbon which has a large particle size, it would appear that other mechanisms, such as internal spread along with absorption, affect the absorption of melamine.

According to the experimental results, the treatment of melamine, Cyanuric acid, Ammelide, and Ammeline via the AOP process using ozone and peroxide (1:0.5) is more efficient than the process with ozone alone. If the GAC process is also added at the latter stage of the AOP process, melamine and its by-products, when present in water, can be removed more effectively.

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