DIGESTION OF WASTEWATER USING OZONATION FOR THE DETEMINATION OF TOTAL MERCURY BY COLD VAPOUR ATOMIC ABSORPTION SPECTROMETRY

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TÓM TẮT

PHƯƠNG PHÁP OZONE HÓA XỬ LÝ NƯỚC THẢI NHẰM PHÂN TÍCH TỔNG THỦY NGÂN BẰNG QUANG PHỒ HẤP THU NGUYÊN TỬ

Khí ozone có tính oxy hóa mạnh được dùng để phân hủy nền mẫu hữu cơ trong nước thải trước khi phân tích tổng thủy phân bằng phương pháp quang phổ hấp thu nguyên tử kỹ thuật hóa hơi lạnh. Khí ozone được tạo ra từ oxygen bằng thiết bị tạo ozone thương mại. Sự phối hợp giữa ozone, hydrogen peroxide, tác nhân tạo phức như ion chloride và ion bromide được nghiên cứu ở các tỷ lệ khác nhau. Sự nhiễm bẩn của thủy ngân từ hóa chất, sự mất mát thủy ngân trong suốt quá trình xử lý và bảo quản mẫu được giảm thiểu. Hiệu quả xử lý mẫu bằng ozone hóa trên một số mẫu nước thải đô thị tiêu biểu chứa hàm lượng cao các chất hữu cơ được đánh giá thông qua hiệu suất thu hồi của thủy ngân vô cơ và methyl thủy ngân và phương pháp tiêu chuẩn EPA-1631. Đối với các mẫu nước thải chứa hàm lượng COD < 250 mg/L, điều kiện ozone hóa tốt nhất là dùng 0.50 mL H₂O₂ 30%, 3 Ml HCl 37%, 3mL KBr 0.19M cho 300mL nước thải và sục với dòng ozone chứa 3.8 mg O₃/min ở lưu lượng 0.5 L/phút trong 60 phút. Đối với các mẫu nước thải chứa hàm lượng COD trong khoảng 250 – 1000 mg/L, điều kiện ozone hóa tốt nhất tương tự nhưng dùng 15 mL HCl 37% thời gian sục ozone là 120 phút.

Từ khóa: ozone hóa, nước thải, thủy ngân tổng, methyl thủy ngân, COD, hóa hơi lạnh.

1. INTRODUCTION

Mercurious compounds are toxic to living organism since mercuric species are strongly bound to nucleotides hence deforms the cell structure and inhibits the biological activities. The main exposure path of mercury to human beings are due to the ingestion of mercury-rich food, especially carnivorous fish. Aquatic organisms can bioaccumulate and biomagnify mercury by a factor of 10^6 - 10^7 from the water through the foodchain. Due to this fact, it is critical to monitor the concentration of mercury in any types of samples, particularly water and wastewater, in the mercury cycle [1]. The most commonly used analytical methods can provide the analysis of mercury down to ultra-trace levels (ng/L-pg/L). Among them, techniques the analytical based on

almagamation cold vapour atomic absorption and fluorescence spectrometry are prevalent nowadays owing to their good accuracy, high sensitivity and low cost [2]. For the techniques, elemental mercurv is generated from mercurious compounds with SnCl₂ or NaBH₄ then evaporated and preconcentrated prior to be detected. SnCl₂ can readily be used for unstable Hg(II) complexes while NaBH₄ effectively reacts stable mercury compounds although some recent studies revealed that even NaBH₄ is not able to reduced many organically bound mercury compounds to elemental mercury [1]. It is therefore mandatory to convert all mercury species to mercuric ion (Hg²⁺) for chemical atomisation in cold vapour technique [2].

Natural water and wastewater usually contain

soluble or suspended organic compounds such as humic acid, mercaptans etc... bearing functional groups of thiol (-SH), amine (-NH₂), sulfides, disulfides which can form very stable complexes or sparingly precipitates with mercury [3]. During analysis, the physical and chemical conversion processes of mercury from the inactive forms into chemically reducible species may therefore be relatively slow, irregular and incomplete resulting in inaccurate analytical results.

The digestion of water sample for total mercury analysis has been carried out using strong acids and/or strong oxidation reagents such as HNO₃, HNO₃/HCl, HNO₃/HCl/H₂O₂, H₂SO₄/KMnO₄/K₂S₂O₈, BrCl/HCl... [4-6]. The use of BrCl as an oxidation reagent has been standardised in EPA-1631 and Vienam Standards TCVN-5993:1995 for pretreatment of water sample containing total organic carbon less than 35 mg/L. For wastewater containing high total organic carbon, the use of a mixture of H₂SO₄/KMnO₄/K₂S₂O₈ was standardised by TCVN 5989:1995 or ISO 5666-1. Losses and/or contamination of mercury are very critical especially for water samples containing mercury at very low levels Hg-contaminated (ng/L)using reagents indicated by very high signal fluctuation as well as high blank levels [7-9]. Furthermore, the removal of excess amounts of reagents used for digestion may pose the risk of contamination [10-15].

We recognised that the use of ozone as an oxidizing reagent $(E_{o_3/o_2,H^+}^0 = +2.07 \text{ V})^{\text{was}}$

relevant to sample treatment owing to the following reasons [16-18]: i. Ozone is a strong oxidizing chemical that generates highly active radicals such as OH^* similar to commonly used chemicals such as $K_2S_2O_8$, $KMnO_4$, and H_2O_2 for sample pretreatment prior to mercury analysis, ii. Ozone can be generated directly, easily, and safely from air, or pure oxygen; iii. The Hg contamination of the generated ozone can be controlled by using mercury-free air or oxygen and good generator; iv. Excessive

ozone decomposes easily; and v. the mechanism of the ozonisation of organic compounds has been thoroughly studied [18,19].

In this study, we investigated the use of ozone to digest wastewater for the analysis of mercury. Ozone produced from an ozonizer was purged into organic polluted wastewater samples containing various H_2O_2 concentrations, acidified with HCl and stabilized with bromide as a complexing reagent for Hg(II). Mild and harsh reducing reagents (SnCl₂ and NaBH₄) were used to release elemental mercury from the digested samples. The efficiency of the digestion approaches on various wastewates samples polluted with organic matters at various levels was discussed.

2. EXPERIMENTAL

Chemicals and reagents: HNO₃ (65-67%), HCl (37%), H₂O₂ (30%) MeHgCl, Hg(NO₃)₂, KBr, KBrO₄, SnCl₂ and CH₃HgCl (>98%) were purchased from Merck (Germany). NaBH₄ was from Sigma-Aldrich (USA). KI, Ag₂SO₄, HgSO₄, K₂Cr₂O₇ were purchased from Xilong (China). All the chemicals were prepared with deionised water (>18.2 M Ω .cm). Instrumentation: an atomic absorption spectrometer ALPHA4 equipped with a batch type impinger and a gold trap for Hg° was used for low level mercury analysis. Ozone was generated using high purity oxygen from a Resun - RO 25. This generator provided 270 mg O_3 .h⁻¹ at a flow rate of 0.5 L.min⁻¹.

Sampling: two wastewater samples were collected from Tân Hóa canal, Hòa Bình street, District 11 and one from Bình Điền market Binh Chanh district, Hochiminh City. The chemical oxygen demand values were 193 mg/L and 258 mg/L for samples from Tân Hóa canal and 1211 mg/L for the sample Bình Điền market

Chemical Oxygen Demand (COD) for the samples was determined using dichromate method from "Standard Methods for the Exammination of Water and wastewater".

Sample pretreament using BrCl (according

to EPA 1631)

30 mL of unspiked wastewater or wastewater spiked with certain amounts of Hg^{2+} or/and CH_3HgCl was placed into a 40-mL threaded glass vial provided with silicone/PTFE septum. The desired pH of the sample was adjusted using HNO₃ 1N followed by the addition of 0.50 mL BrCl solution. The solution was mixed and let stand for 30 minutes. The excess BrCl was eliminated with NH₂OH.HCl 10% until pale yellowish of BrCl was disappeared. The blank soluton was made in the same manner as the sample.

Ozonisation of wastewater for mercury analysis.

The ozonisation scheme for wastewater was described as Fig. 1. Briefly, 300 mL of unspiked wastewater or wastewater spiked with certain amounts of Hg^{2+} or/and CH_3HgCl was placed into an impinger. The spiked samples were equilibrated for 2 hours. The desired pH of the sample was adjusted using HNO₃ 1N followed by the addition of proper chemicals. The sample solution was purged with very fine bubbles of ozone through a Teflon scrubber. The ozonisation of water samples was performed based on one of

the following approaches: a. O only; b.





During the ozonisation, an aliquot of 15 mL of

sample was taken every 30 minutes for total mercury analysis to monitor the efficiency of the treatment.

Analysis of total mercury in ozonated wastewater.

An appropriate volume of the ozonated wastewater containing approximately 1 ng Hg was taken for the determination of total mercury. SnCl₂, weak reducing reagent, or NaBH₄, strong reducing reagent, were used. All Hg vapour emerged from the sample was trapped on a gold-coated sand then released at 600 °C, swept to a quartz cell mounted in the sample compartment of the AAS and measured at 253.7 nm. The concentration of mercury was calculated via a 7-point linear calibration curve. The detection and quantitation limits for the analytical method were 0.0057 and 0.019 μ g/L, respectively.

3. RESULT AND DISCUSSION

Concentrations of mercury in wastewater samples determined using EPA-1631

EPA-1631 has been recommended for water samples containing low COD contents (< 50 mg/L). In the method, the amount of oxidizing reagent, BrCl, of 0.5 mL BrCl 1% was sufficient to decompose organic compounds. Table 1 showed that for samples containing high COD contents used in this study, the digestion approach was modified by increasing the concentration of BrCl. Concentrations of Hg in TanHoa 1 obtained by SnCl₂ and NaBH₄ were in good agreement demonstrating that strongly bound mercury in organic matters was completely released as easily reduced forms. The standardised EPA-1631 was therefore shown to be effective for Tan Hoa 1 wastewater although its COD content (193 mg/L) was much higher than the applicable limits (50 mg/L). However, further the increase in COD contents made the standardised amount of BrCl impossible to decompose efficiently the organic compounds in sample. For TanHoa2 wastewater sample, the strong reducing agent, NaBH₄, still gave reasonable result but significant lower Hg concentration was obtained when weak reducing agent, SnCl₂, was used. This indicated that significant amount of Hg still existed at non-reducible forms since the amount of BrCl was not sufficient. The further increase of BrCl amounts was not effective to decompose organic contents in sample. Recoveries of Hg concentration was only 80-85% for TanHoa 2 sample using $SnCl_2$ even increased amounts of BrCl were used (Fig. 2).

Table 1. Mercury concentration (in μ g/L with standard deviation in parenthesis) following the sample digestion EPA 1631 on wastewater samples heavily polluted with organic matter

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Wastewater	COD (mg/L)	BrCl	C _{Hg} / SnCl ₂	C _{Hg} /NaBH ₄
TanHoa 1	193	BrCl	68.9	70.8 (1.7)
TanHoa 2	258	BrCl	(1.1) 59.9 (2.2)	78.8 (1.9)
BinhDion	1211	170 BrCl	(3.2)	*
DimDich	1411	5%		

For BinhDien sample (COD 1211 mg/L), after treatment with 5% BrCl, the digested sample solution was still turbid with slighly dark color and rotten smell indicating that some organic compounds with thiol and amine ligands which bind strongly to mercury were still existing. Consequently, the analytical measurement was wathing to mercury was shown and the strongly to mercury was shown and the strongly to mercury was shown and the strongly to mercury were still existing.



Fig. 2. Hg recovery of TanHoa 2 wastewater samples digested by EPA-1631 at various amount of BrCl. V_{sample}: 50 mL; digestion time: 2 hrs. Replicate: 2; [Hg]_{incipient}: 0.0813 ppb. [MeHgCl]_{snike}: 0.5143 ppb. COD = 258 mg/L

The break-down of organomercury compounds by O₃ and the role of hydrogen peroxide

The analysis of metals by atomic absorption spectrometry is usually performed in acidic medium to prevent the hydrolysis of metals as non-dissolved compounds causing loss of the mercury. It was demonstrated that SnCl₂ hardly reduced CH₃HgCl, however NaBH₄ indicated to be stronger reagent that approximately 60% of CH₃HgCl was decomposed to Hg. It is therefore mandatory to chemically decompose stable mercurial compounds to mercuric ion prior to further reducing to elemental mercury by either SnCl₂ or NaBH₄ for measurement. The reduction of methylmercury is considered to be completed if 100% recovery of mercury is achieved with SnCl₂. It can therefore be concluded that recovery of mercury using SnCl₂ is relevant indication for the efficiency of the break-down of stable mercurial compounds. The decomposition of methylmercury in the presence of ozone was time-dependent and this process was completed after 60 minutes (see Fig 3). Hydrogen peroxide was showed to accelerate the decomposition owing to the formation of hydroxyl radicals that induced the cleavage of the Hg-C bond.



The formation of radical as the following

OH*

reaction: $2O_3 + H_2O_2 \rightarrow 2OH^* + 3O_2$ whose reaction rate, K, is $1.1 \times 10^5 L.mol^{-1}s^{-1}$ which is much higher than the reaction of O_3 with $OH^{-, (}K = 70 L.mol^{-1}s^{-1})$ (Gottschalk, 2010) [19]. It can be concluded that pH was not a crucial factor for the ozonisation of methymercury in the presence of H O. $2^2 2$ According to Masschelein et. al. [20] and Lukes et.al. [21], the appropriate O_3/H_2O_2 molar ratios for the reaction were in a range of $2 \div 3.4$ corresponding to 0.50 mL H₂O₂ 30% and 457.32 mg O₃ for the reaction time of 120 minutes in this experiment. In the presence of H₂O₂, the decomposition of methylmercury was completed after 30 minutes. The results indicated that the mixture of O₃ and H₂O₂ was promising in the pretreatment of water samples for total mercury analysis.

Ozonisation of wastewater

The ozonisation of water for mercury analysis was performed in wastewater samples containing real matrix and low mercury concentration. wastewater collected from Tân Hóa canal was domestic wastewater directly discharged from houses along the canal. Two samples were taken, one labelled as TanHoa 1(192.7 mg/L COD) and the another as TanHoa 2 (258.4 mg/L COD).

For reference, this wastewater sample was digested with BrCl using EPA 1631, followed by the analysis of Hg by cold vapour AAS using NaBH₄ and SnCl₂ as reducing reagents. The concentrations of mercury corresponding to NaBH₄ and SnCl₂ were 70.8 \pm 2.7 ng/L (n=4) and 68.9 \pm 1.8 ng/L (n=4), respectively.

For the Hg^{2+} recovery test, different ozonisation approaches were used: i. Appr A: O_3/H_2O_2 ; ii. Appr B: $O_3/H_2O_2 + HCl$; and iii. Appr C: $O_3/H_2O_2 + HCl + KBr$. The reference was BrCl as EPA-1631.

Hg recoveries for wastewater spiked with Hg^{2+} , using different approaches of sample pretreatment.

As can be seen in Fig 4, Hg²⁺ bounds strongly to organic matrices in wastewater to form nonreactive compounds. The Hg complexes are too stable to be reduced even by the very reactive agent, NaBH₄ illustrated by only less than 5% recovery. The decomposition of stable Hg-complexes by ozonisation seemed to be completed after 30 min represented by the identical recoveries obtained by SnCl₂ as well as NaBH₄. Lower recoveries, c.a. 75% of mercury were observed in Appr. A indicating that loses of mercury during digestion was likely. This was probably due to the volatilisation of elemental mercury forming by the reaction of unstable hydrated Hg²⁺ with organic matrices. The use of appropriate concentrations of non-reducible complexing agents such as chloride and bromide ions was

shown to be effective to preserve Hg(II) in less reactive forms such as stable mercuric chloride or/and mercuric bromide complexes. However, chloride ion did not efficiently preserve Hg²⁺ at relatively low concentrations due to its less stable complexes ($\beta_{1-4}^{HgCl_4^2-} = 10^{15.07}$). The combination of chloride and bromide ions showed more effective since mercuric bromide complexes are more stable ($\beta_{1-4}^{HgBr_4^2-} = 10^{21}$).

For all experimental conditions regarding digestion periods of various time, а combination of 0.50 mL H₂O₂ 30%, 3.00 mL conc. HCl, 3.00 mL KBr 0.19 M (Appr. C2) for a volume of 300 mL of the wastewater sample achieved almost 100% Hg recoveries for conventional reducing reagents, e.g., SnCl₂ and NaBH₄. The efficiency of the studying digestion approach was compared with the standardised method (EPA-1631). The results obtained from the testing method (Fig 4) were in good agreement with those from the EPA-1631.



Fig. 4. Recovery of Hg in wastewater TanHoa 1 spiked with 0.427 μg/L Hg²⁺ using various digestion approaches: A: 0.5 mL H₂O₂, 30%; B1: 0.5 mL H₂O₂ 30%, 2 mL conc. HCl; B2: 0.5 mL H₂O₂ 30%, 3 mL conc. HCl; C1: 0.5 mL H₂O₂ 30%, 2 mL conc. HCl, 2 mL KBr 0.19 M; C2: 0.5mL H₂O₂ 30%, 3 mL conc. HCl, 3 mL KBr 0.19 M; V_{sample} = 300 mL; purge flow: 0.5 L/min;

COD = 192.7 mg/L

Hg recoveries for wastewater spiked with MeHg+

Based on the recovery tests performed on the TanHoa 1 spiked with Hg^{2+} using various digestion approaches, the best approach, C2 (0.17% $H_2O_2 + 1\%$ HCl (v/v) + 1% KBr 0.19 M (v/v)), was used for recovery test with MeHg on TanHoa 2 wastewater sample containing relatively higher COD content (258 mg/L).

As can be seen from the Fig 5, the digestion

approach C2 was also effective to decompose MeHg in organic matrices after 60 min of digestion.



Fig. 5. Recovery of T-Hg from a MeHg-spiked wastewater sample digested by currently optimised C2 V_{sample}: 300 mL; T_{purge}: 2 hrs;
F_{purge}: 0.5 L/min. n=2. [Hg]_{incipient}: 0.0813 ppb.
[MeHgCl]_{spiked}: 0.5143 ppb; [COD]_o = 258 mg/L
Ozonisation of wastewater containing high COD content.

This test was performed on BinhDien wastewater sample containing high COD content (1211 mg/L) which far above the limit of the EPA-1631 applicable (50 mg/L). The standardised digestion approach for this type of sample used a combination of H SO, KMnO 4 and K S O followed by NH OH that may pose 2 2 8 serious contamination. To decompose such a high COD content, the ozonisation approach was once modified to increase the HCl concentration. The modified approach (C3) was 0.5 mL H O (30%), 5 mL concentrated 2 2 HCl and 3 mL KBr 0.19 M (v/v) for a batch of 300 mL wastewater. It can be seen (Fig 6) that the concentration of Hg obtained from both SnCl₂ and NaBH₄ reached plateau and were in agreement after 90 min digestion indicating that the decomposition of stable organic bound Hg complexes was completed.



Fig. 6. Hg concentrations in BinhDien

wastewater sample, V_{sample} = 300 mL; purge flow: 0.5 L/min. COD = 1211 mg/L; C3: 0.50 mL H₂O₂ 30%, 15 mL conc. HCl, 3.00 mL KBr 0.19 M; n_{ks}: 2.

Recovery of Hg in BinhDien wastewater sample

The recovery tests were carried out using the best studied digestion approaches, C2 and C3.

For wastewater spiked with MeHgCl, the analytical results (Fig 7) showed that the digestion completed after 60 min of digestion demonstrated by recoveries values for both digestion approaches reached plateau as well as there was no significant difference between SnCl₂ and NaBH₄. However, losses of mercury (only 85% recovery) was observed from sample digested by C2 approach which used low HCl concentration. Complete recovery was achieved for C3 approach which used high HCl concentration.

For wastewater spiked with Hg²⁺, similar trend to sample spiked with MeHgCl was observed with 97% Hg recovered after 60 min of



Fig. 7. Recoveries of Hg of BinhDien
wastewater sample (COD = 1211 mg/L) spiked with; MeHgCl: 0.5028 ppb. Digestion
approaches: C2 (0.50 mL H₂O₂ 30%, 3 mL conc. HCl, 3 mL KBr 0.19 M) and C3 (0.5 mL H₂O₂ 30%, 15 mL conc. HCl, 3 mL KBr 0.19
M). V_{sample}: 300 mL; F_{khipurge}: 0.5 L/min. n_{ks}: 2.





Fig. 8. Recoveres of Hg of BinhDien wastewater sample (COD = 1211 mg/L) spiked with; Hg²⁺: 0.518 ppb. Digestion approaches: C3 (0.5 mL H₂O₂ 30%, 15 mL conc. HCl, 3 mL KBr 0.19 M). V_{sample} : 300 mL; $F_{khipurge}$: 0.5 L/min

The stability of digested sample solution

The digested sample solution should be stable during a certain period of time until analysis. For mercury analysis, loss of Hg from digested solution may occur due to incomplete decomposition of organic matters or/and the existing of easily reduced forms of Hg(II) such as hydrated Hg(II) complexes resulting the formation of volatile elemental mercury. In this study, digested samples obtained from the digestion approaches A and C2 were investigated for loss of mercury during storage time. It can be seen that (Fig 9) in the absence of chloride/bromide ions, losses of Hg were occurred during studied storage of 4 hrs. While the sample solution digested with HCl/KBr, the Hg concentration was remained constant during the studied storage period since Hg(II) was in form of stable chloride or bromide complexes.



Fig 9. Stability test for TanHoa 2 digested wastewater sample (COD = 258.4 mg/L) using digestion approaches A and C2. Digestion time: 120 min; V_{sample} : 300 mL; F_{purge} : 0.5 L min⁻¹. n_{ks} : 2; reducing reagent: SnCl₂.

Recommended digestion methods and its application for analysis of total mercury in wastewater.

Two disgetion methods were suggested in this study for wastewater sample containing different levels of COD contents: i. for wastewater samples containing COD contents up to 250 mg/L: a portion of 300 mL wastewater is added with 0.5 mL H₂O₂ 30%, 3 mL concentrated HCl and 3 mL KBr 0.19M. The sample solution is purged with a stream of ozonated oxygen containing O_3 (270 mg.h⁻¹) for at least 60 minutes. The sample should be stored for analysis during 4 hrs. ii. for wastewater samples having COD contents from 250 mg/L up to 1000 mg/L: a portion of 300 mL wastewater is added with 0.5 mL H₂O₂ 30%, 15 mL concentrated HCl and 3 mL KBr 0.19M. The sample solution is purged with a stream of ozonated oxygen containing O₃ (270 mg.h⁻¹) for at least 90 minutes. The sample should be stored for analysis during 4 hrs.

Mercury in wastewater samples, which were heavily polluted with organic carbon, were treated with our suggested approaches then determined by CV Amalgam AAS using mild and harsh reducing reagents (SnCl₂ and NaBH₄). The two reducing reagents used in the digestion approaches C2 and C3 gave comparative results (Table 2) for all samples analysed indicating that the oxidation by the recommended approaches has released all mercury species bound to organic matrices. The precision of the mercury analysis using mild and harsh reducing reagents was also relevant revealing that loss and contamination of mercury during sample pretreatment and analysis were excellently controlled.

Table 2. Mercury concentration (in μ g/L with standard deviation in parenthesis) following the recommended sample digestion on wastewater samples heavily polluted with

rganic	matter
0	

0

Westerreter	COD	Digestion	C _{Hg} /	
wastewater	(mg/L)	approach	SnCl ₂	∪ _{Hg} /1NaDΠ4
TanHoa 1	193	C2	62.5 (0.2)63.0 (0.6)
TanHoa 2	258	C2	79.8 (2.1)81.3 (1.4)
BinhĐien	1211	C3	36.0 (1.2	36.1 (1.6)

It can be concluded that the oxidation of organic matters by ozone, accelerated by hydrogen peroxide in acidic medium in association with the use of bromide as a stabilising reagent was effective for the complete digestion in the determination of total mercury in wastewater by cold vapour atomic spectrometry.

CONCLUSION

In this study, we have successfully established several digestion methods for total mercury

analysis wastewater containing organic carbon ranging from 200 ppm to 1000 ppm (as COD concentration) which could be among the most probably existing samples to analyse. The recommended sample pretreatment approaches are superior in term of contamination, simplicity and digestive efficiency to the currently used standard methods such as TCVN 5989:1995 and ISO 5666-1. These methods are therefore highly applicable for total mercury analysis in wastewater.

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