Malaysian Journal of Chemistry, 2003, Vol. 5, No. 1, 067 - 072

Minimizing the Use of Mercuric Salts for Chloride and Bromide Corrections in Chemical Oxygen Demand Test

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Abstract: Chemical Oxygen Demand (COD) is one of the most important parameters for assessing the pollution strength of wastewaters in terms of the concentrations of chemically oxidizable substances in water. In the standard COD test, mercuric sulphate ($HgSO_4$) is added as a complexing agent for minimizing the chloride interference. Other than having an undesirable effect on the environment, $HgSO_4$ does not exhibit a satisfactory result in minimizing the bromide interference. This study was conducted to find other complexing agents which are effective for suppressing both chloride and bromide interferences so as to minimize the use of $HgSO_4$ in the COD test. Chromium(III) and aluminum(III), respectively, were found to be effective in suppressing the interferences of chloride and bromide. For chloride concentration of 3000 mg/L in a standard reference potassium hydrogen phthalate solution of 200 mg/L COD, a 9.5:1 weight ratio of Cr:Cl or 6.9:1 weight ratio of Al:Cl was found to be adequate in suppressing the chloride interference completely. For bromide concentration of 3000 mg/L in the same standard reference solution, a 11.3:1 weight ratio of Cr:Br was able to reduce the bromide interference by 88%. A 8:1 weight ratio of Al:Br was adequate to suppress the bromide interference completely. The effectiveness of Cr(III) and Al(III) in neutralizing the halide interferences in the COD tests of environmental water samples was also discussed.

Abstrak: Tuntutan oksigen kimia (COD) merupakan salah satu parameter yang sangat penting untuk menilai kekuatan pencemaran air buangan dari segi kepekatan zat teroksida secara kimia dalam air. Dalam ujian COD piawai, merkurik sulfat ($HgSO_4$) ditambahkan sebagai agen pengkompleksan untuk meminimumkan gangguan klorida. Selain daripada menimbulkan kesan buruk terhadap persekitaran, $HgSO_4$ juga tidak menunjukkan keputusan yang memuaskan dalam meminimumkan gangguan bromida. Kajian ini dijalankan untuk mencari agen pengkompleksan lain yang berkesan untuk meredakan gangguan klorida dan bromida supaya penggunaan $HgSO_4$ dalam ujian COD dapat diminimumkan. Kromium (III) dan aluminum (III) masing-masing didapati berkesan untuk meredakan gangguan klorida dan bromida. Bagi kepekatan klorida 3000 mg/L dalam larutan kalium hidrogen ftalat rujukan piawai yang berCOD 200 mg/L, nisbah berat Cr:Cl sebanyak 9.5:1 atau nisbah berat Al:Cl sebanyak 6.9:1 didapati mencukupi untuk meredakan gangguan klorida sepenuhnya. Bagi kepekatan bromida 3000 mg/L dalam larutan rujukan piawai yang sama, nisbah berat Cr:Br sebanyak 11.3:1 dapat meredakan gangguan bromida sebanyak 88% manakala nisbah berat Al:Br sebanyak 8:1 adalah mencukupi untuk meredakan gangguan bromida sepenuhnya. Keberkesanan Cr(III) dan Al(III) dalam meredakan gangguan halida dalam ujian COD terhadap sampel air persekitaran juga dibincangkan.

Received : 10.04.03; accepted : 24.06.03

Introduction

The Chemical Oxygen Demand (COD) is recognized as one of the most important parameters for assessing the pollution strength of wastewaters and natural waters in the fields of wastewater treatment and water quality management, respectively. In fact, the parameter of COD is indispensable in characterizing the pollution strength of toxic waste discharge. However, the use of a strong oxidizing agent such as acidified dichromate in the test also oxidizes certain inorganic compounds which may be present in the water sample resulting in erroneous COD values [1,2]. Halides are among those which can cause such a problem in the COD test.

Over the years, much research work had been conducted in an attempt to correct for the chloride interference in the COD test [1,3-7]. The recommended procedure in the Standard Methods [8] using a 10:1 weight ratio of $HgSO_4$:Cl for neutralizing the interference of chloride at the chloride concentrations up to 2000 mg/L was based on the work carried out by Cripps and Jenkins [5]. The mercuric ion works by combining with the chloride ions to form a poorly ionized mercuric chloride complex. Thus, the remaining chloride ion concentration is so small that it is not oxidized to any significant extent by dichromate. However, minimization of bromide interference in the COD test using mercuric sulphate was found to be not effective [9]. Concern over the potentially hazardous nature of mercuric salts has prompted researchers to look for alternative complexing agents for chloride. Thompson *et al*. [7] found that the presence of chromium(III) was capable of minimizing the chloride interference in the COD test for samples at low chloride concentrations (<10000 mg/L). However, there were no reports of suitable complexing agents for bromide.

The objective of this study is to assess the effectiveness of chromium(III) and aluminum(III) as alternative complexing agents for neutralizing both chloride and bromide interferences so that the use of $HgSO_4$ in the COD test can be minimized. The complex formed between Cr(III) and halides (X^-) is thought to be CrX_6^{3-} and that between Al(III) and X^- is AlX_4^-.

Materials and Methods

<u>*COD determinations*</u>

The COD determinations followed the closed reflux titrimetric method [8]. Samples with digestion solution and sulphuric acid reagent in borosilicate culture tubes (16 x 100 mm) with Teflon-lined screw caps were placed in an aluminum block which was heated on a laboratory hot plate for 2 h at 150 °C. The digestion solution was prepared by adding 4.9035 g of $K_2Cr_2O_7$ and 83.5 mL of concentrated H_2SO_4 (sp. gr.1.84) to 200 mL of distilled water and diluting it to 500 mL. The acid reagent was prepared by dissolving 5.5 g of Ag_2SO_4 in 1 kg of concentrated $HgSO_4$. Sample volume was always maintained at 2.5 mL with 1.5 mL of digestion solution and 3.5 mL of sulphuric acid reagent to give a total volume of 7.5 mL of digest. Complexing agent of $HgSO_4$ was added to the digest in the solid form whereas those of Cr(III) and Al(III) were added as $Cr(NO_3)_3$ and $Al_2(SO_4)_3$ solutions with the increase in volume always maintained at <2%. After the digestion, the remaining $K_2Cr_2O_7$ was titrated with 0.0125 M $Fe(NH_4)_2(SO_4)_2$ solution using ferroin as indicator.

<u>*Solutions and samples*</u>

- *Sodium chloride stock solution*: a 30.0 g/L Cl^- solution was repared by dissolving 24.7 g of NaCl in distilled water and the solution diluted to 500 mL.
- *Potassium bromide stock solution*: a 30.0 g/L Br^- solution was prepared by dissolving 22.3 g of KBr in distilled water and the solution diluted to 500 mL.
- *Potassium hydrogen phthalate (KHP) stock solution*: 8.500 g of KHP was dissolved in distilled water and the solution diluted to 1 L. This solution has a theoretical COD of 10000 mg/L.
- *Chromium (III) solution*: 50.0 g of $Cr(NO_3)_3.9H_2O$ was dissolved in distilled water and the solution diluted to 100 mL yielding 65.0 g/l Cr^{3+}.
- *Aluminum (III) solution*: 50.0 g of $Al_2(SO_4)_3.18H_2O$ was dissolved in distilled water and the solution diluted to 100 mL yielding 40. g/l Al^{3+}.
- *Domestic wastewater*: raw domestic wastewater samples were collected from the sewage treatment plant in the Universiti Sains Malaysia campus.
- *River water*: river water samples were collected from the non-tidal segment of Sg. Pinang.

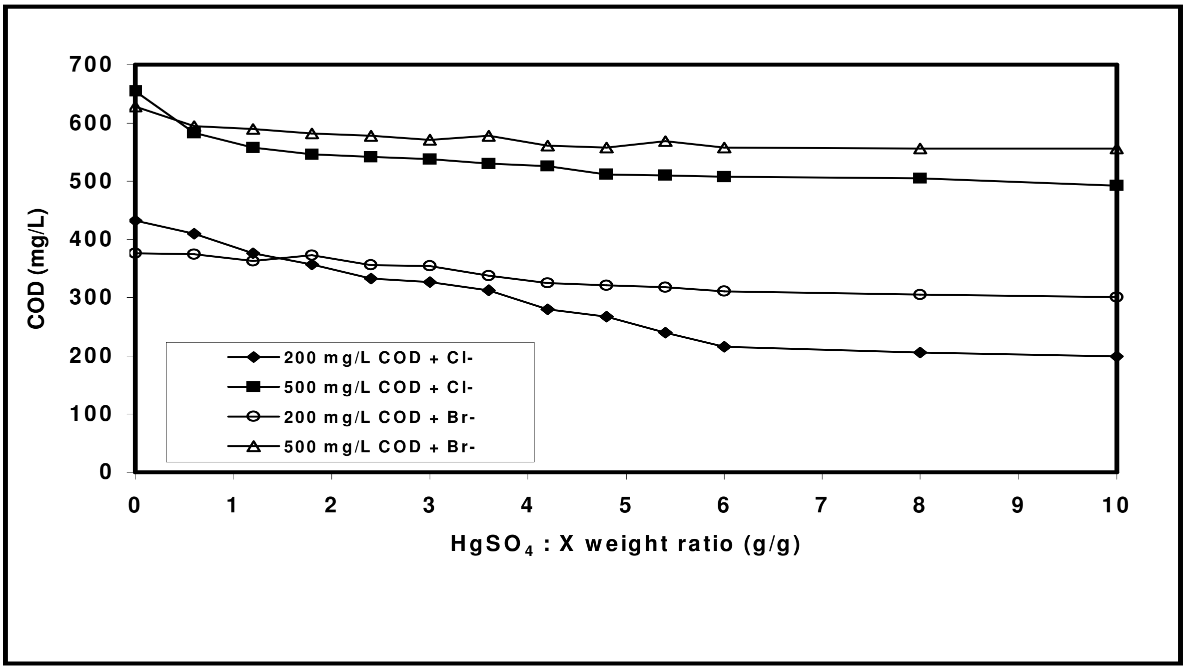

Figure. 1. Effect of $HgSO_4$:X weight ratio (X = Cl or Br) on the COD of KHP solutions (200 and 500 mg/L COD) spiked with 3 g/L halides.

Results and Discussion

The COD values were plotted as a function of the $HgSO_4$:halogen weight ratio for chloride and bromide concentrations of 3 g/L, respectively, in standard reference KHP solutions of 200 and 500 mg/L as shown in Fig. 1. It is evident that interference caused by chloride level at 3 g/L was effectively neutralized by HgSO at a $HgSO_4$:Cl weight ratio of 10:1. In contrast, the addition of $HgSO_4$ was ineffective against bromide interference. This result is in agreement with Belkin *et al.* (1992) who reported that bromide-derived COD values were almost independent of the $HgSO_4$:Br ratio.

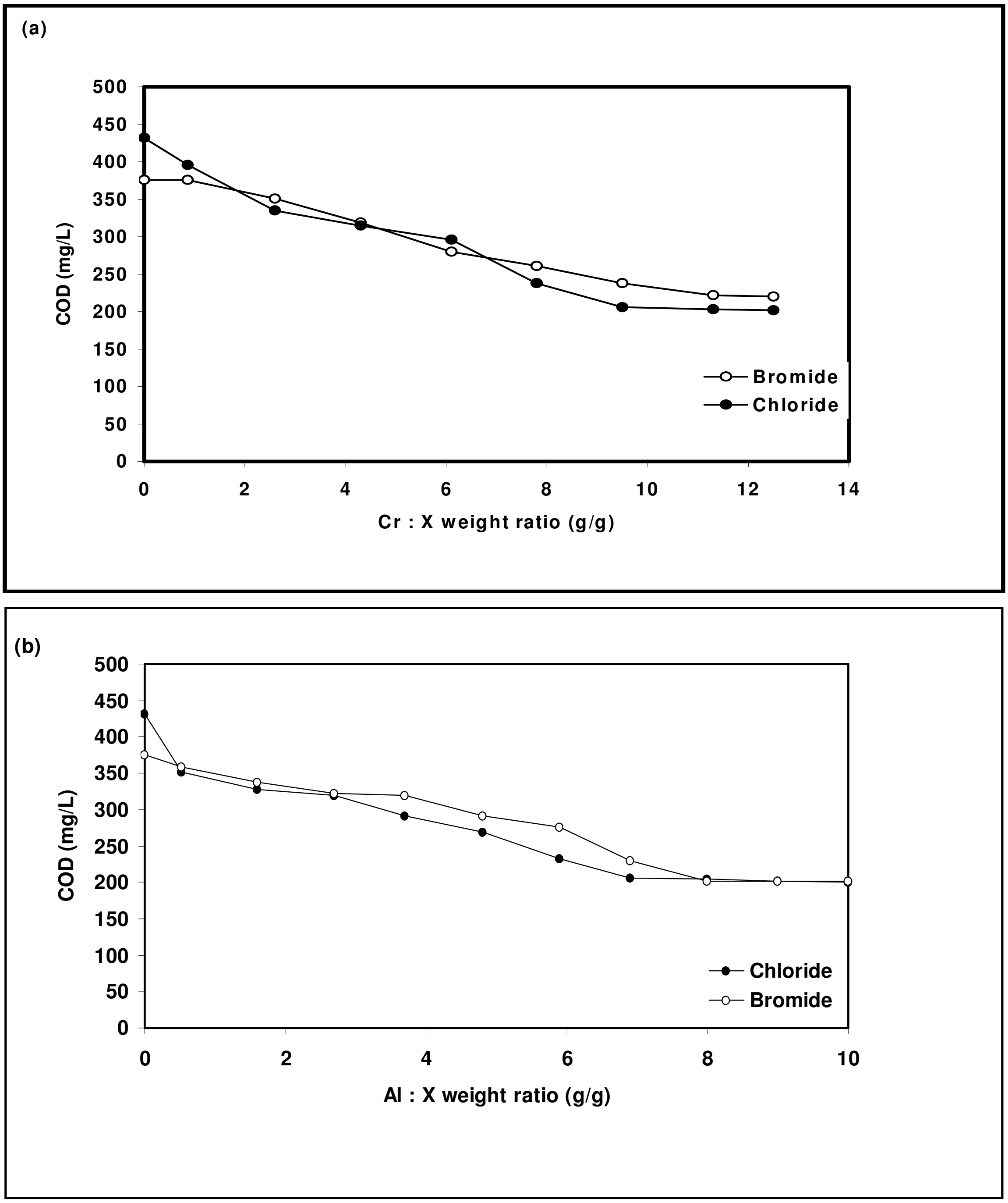

Figure 2. Effect of (a) Cr:X and (b) Al:X weight ratio (X = Cl or Br) on KHP solutions (200 mg/L COD) spiked with 3 g/L halides.

Figure 2(a) depicts the COD values of 200 mg/L KHP solution containing 3 g/L Cl^- and Br^-, respectively, as a function of Cr(III):halogen weight ratio. It is observed that chloride interference was effectively suppressed at 9.5 weight ratio of Cr:Cl. On the other hand, a weight ratio of Cr:Br as high as 11.3 was only able to reduce the bromide interference by 88%. Aluminum(III) seems to be more effective than chromium(III) in neutralizing the halide interferences. This is demonstrated in Fig. 2(b) which depicts the effect of increasing Al(III) concentrations added to 200 mg/L KHP solution containing 3 g/L Cl^- and Br^-, respectively, on the COD values. A 6.9:1 weight ratio of Al:Cl and 8:1 ratio of Al:Br, respectively, were found to be adequate in neutralizing the chloride and bromide interferences.

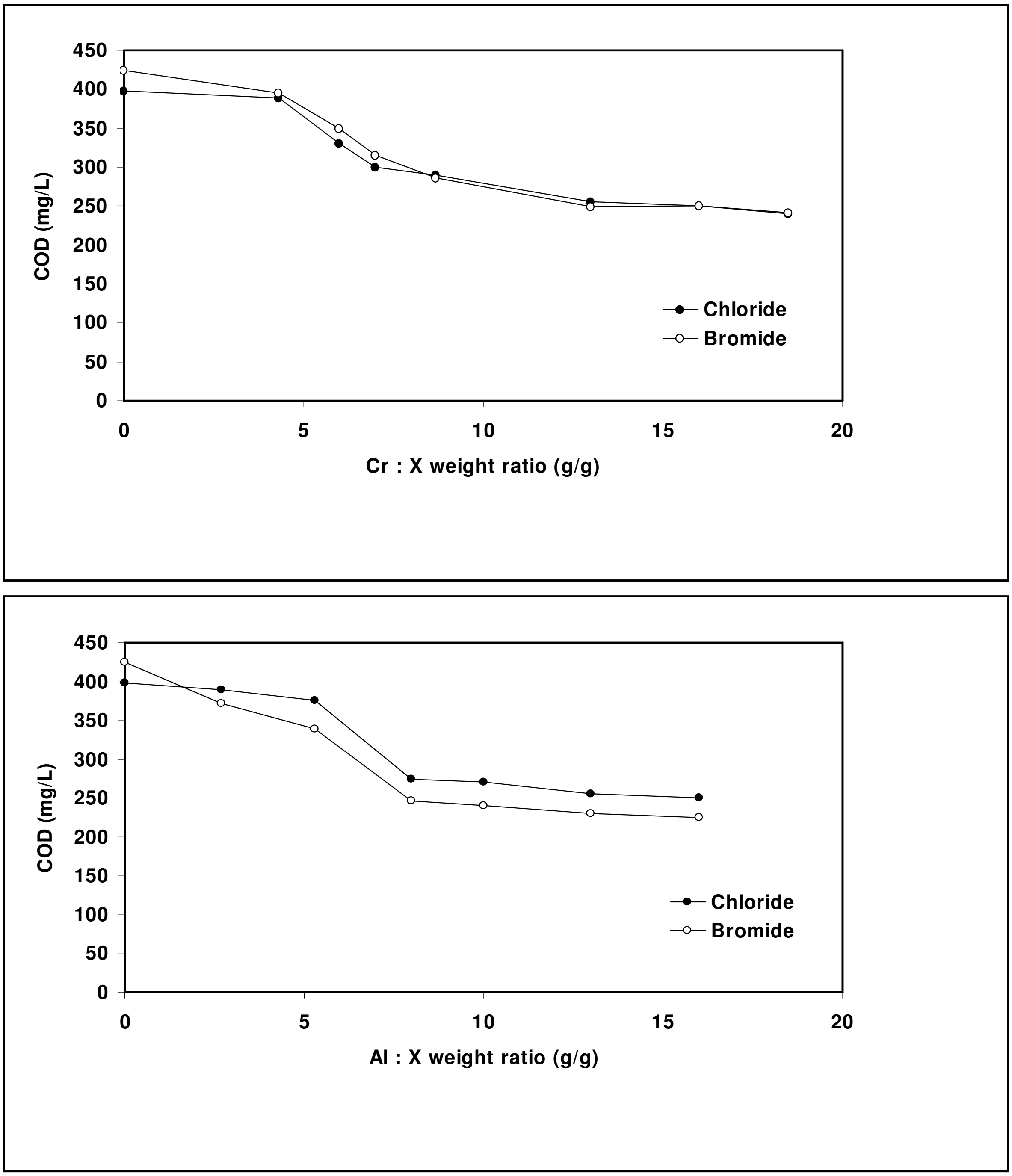

Figure 3. Effect of (a) Cr:X and (b) Al:X weight ratio (X = Cl or Br) on domestic wastewater samples (218 mg/L COD) spiked with 3 g/L halides.

The performance of Cr(III) and Al(III), respectively, in neutralizing the halide interferences was tested for domestic wastewater. Figure 3(a) depicts the COD values of unfiltered domestic wastewater (original COD of 218 mg/L) spiked with 3 g/L Cl^- and Br^-, respectively, as a function of Cr:halogen weight ratio. It shows that the chloride and bromide-derived COD values were almost independent of the Cr:halogen weight ratio above 13:1. At this weight ratio, the chloride interference was reduced by 78% and the bromide interference by 85%. Using Al(III) instead for the same wastewater spiked with the halides, a weight ratio of 8:1 and above for Al:halogen proved to be ineffective in neutralizing the chloride and bromide interferences further [Fig. 3(b)]. At the weight ratio of 8:1, the reduction in chloride and bromide interferences were found to be 69 and 86%, respectively.

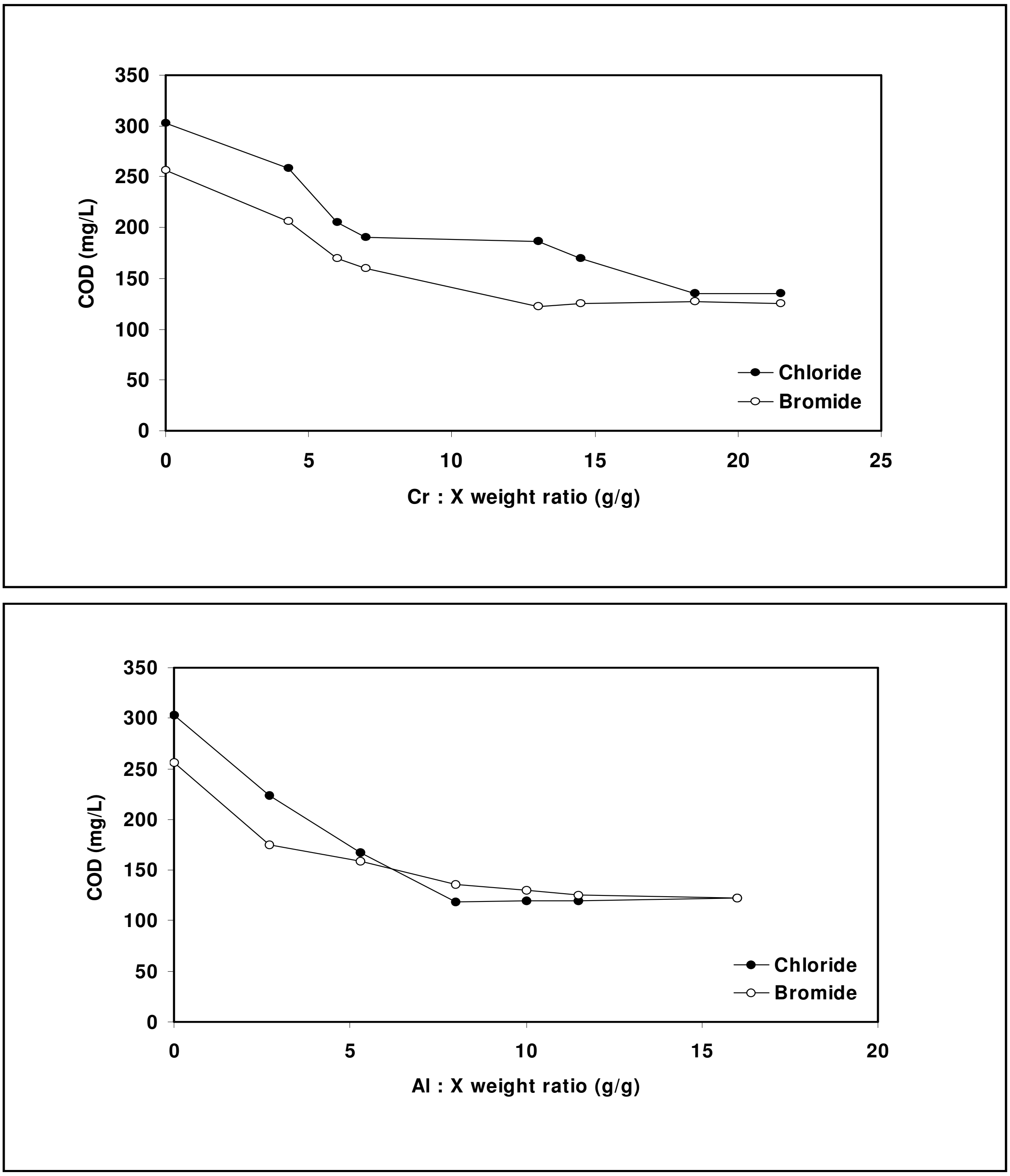

Figure 4. Effect of (a) Cr:X and (b) Al:X weight ratio (X = Cl or Br) on river water samples (95 mg/L COD) spiked with 3 g/L halides.

The effectiveness of Cr(III) and Al(III), respectively, in neutralizing the halide interferences was tested for natural water samples, in this case unfiltered river water samples from Sungai Pinang. Figure 4(a) shows the COD values of river water (original COD of 95 mg/L) spiked with 3 g/L Cl^- and Br^-, respectively, as a function of Cr:halogen weight ratio. It demonstrated that Cr(III) was no longer effective in neutralizing the halide interferences for Cr:Cl greater than 18.5:1 and for Cr:Br greater than 13:1. At the respective weight ratios, the chloride interference was reduced by 82% and the bromide interference by 83%. In the case of Al(III), Fig. 4(b) shows that an increase of Al:halogen weight ratio above 8:1 was no longer effective in neutralizing the halide interferences. At this weight ratio, the reduction in chloride and bromide interferences were found to be 88 and 75%, respectively.

The results show that, generally, higher weight ratio of Cr:halogen is required as compared to Al:halogen in attaining comparable suppression of halide interferences in the COD test. It is evident that complete suppression of the halide interferences in the COD tests of environmental water samples containing low halide concentrations (<3000 mg/L) was not achievable using Cr(III) or Al(III) as the complexing agent. Nonetheless, both exhibit the capability of neutralizing a significant portion (>65%) of both chloride and bromide interferences in the domestic wastewater and river water samples. In this respect, they are superior to $HgSO_4$ which has difficulty in neutralizing bromide interference. If complete replacement of $HgSO_4$ in the COD test is not feasible at this stage, perhaps a methodology involving the use of a combination of $HgSO_4$ and Cr(III) or $HgSO_4$ and Al(III) should be developed to suppress the halide interferences. This will at least minimize the use of mercuric salts in the COD test.

Conclusions

Chromium(III) and aluminum(III), respectively, were found to be effective in neutralizing the interferences of chloride and bromide in the COD tests of synthetic samples at halide concentrations up to 3 g/L. Partial suppression of halide interferences by either species in the COD tests of environmental water samples was found to be achievable. Higher Cr:halogen weight ratio is required as compared to Al:halogen in achieving comparable suppression of halide interferences. A methodology involving the use of a combination of $HgSO_4$ and Cr(III) or $HgSO_4$ and Al(III) should be developed to minimize the use of mercuric salts in the COD tests.

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