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## Research Article

# Determination of Hexavalent Chromium (Cr(VI)) Concentrations via Ion Chromatography and UV-Vis Spectrophotometry in Samples Collected from Nacogdoches Wastewater Treatment Plant, East Texas (USA)

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The concentration of hexavalent chromium (Cr(VI)), a toxic environmental pollutant and carcinogen, was determined in samples collected from Nacogdoches Wastewater Treatment Plant (NWWTP) using ion chromatography and UV-visible spectrophotometry (IC, UV-Vis). On reaction with 1,5-diphenylcarbazide (DPC)  $\text{Cr}^{+6}$  forms a 1,5-diphenylcarbazide-Cr(VI) complex, which is then analyzed at 530 nm and 540 nm, respectively. Via ion chromatography Cr(VI) concentrations were in the range of  $0.00190 \pm 0.0020$  and  $0.0010 \pm 0.0006$  ppm at the influent and effluent, respectively. With the use of standard addition wastewater samples were spiked with a 0.5 ppm Cr(VI) standard of various amounts and subsequently analyzed with UV-Vis spectrophotometry. The spiked concentrations gave Cr(VI) concentrations in the range of  $0.0090 \pm 0.0060$  ppm and  $0.0040 \pm 0.0061$  ppm at the influent and influent wastewater, respectively. The determined Cr(VI) concentrations through the ion chromatography and UV-Vis spectrophotometry are below the maximum USEPA contaminant concentration of 0.1 ppm. From the analysis, the NWWTP efficiently removes Cr(VI) before discharge into the environment through La Nana Creek. The removal efficiency for Cr(VI) was determined to be  $\geq 92.8\%$  along the wastewater treatment stages from the influent (aeration stage) to the effluent stages prior to discharge into the La Nana Creek.

## 1. Introduction

Chromium metal (Cr) occurs naturally in the environment and has both beneficial and potential human risks. Cr exists in many oxidation states with Cr(III) and Cr(VI) being the primary existing oxidation states in the environment. Cr(III) is an essential nutrient for maintaining lipid, insulin, and glucose metabolism and its deficiency may lead to diabetes [1]. Of the many Cr species, hexavalent chromium (Cr(VI)) is one of the most toxic, especially when compared to trivalent chromium [2]. Carcinogenic Cr(VI) and other Cr(VI) forms are used in various industries including leather tanning, electroplating, painting, and metallurgy industries. Although

determination of total chromium is important, the speciation of metals is much more important for environmental impact studies [3].

Speciation of chromium usually includes preconcentration or the use of complexing reagent. Various studies have used both spectroscopic and chromatographic techniques for Cr speciation in environmental samples including wastewater, drinking water, and soils. Some of these studies are cited here below.

Tetraphenylphosphonium bromide impregnated polyurethane foam (PUF) packed column was used to determine nanomolar concentrations of Cr(III), Cr(VI), and total inorganic chromium in industrial wastewater samples [4]. A

flame atomic absorption spectrometric determination method was established for Cr(III) and Cr(VI) based on coprecipitation of Cr(III) by using praseodymium(III) hydroxide. Application of the method to wastewater analysis gave Cr(III) and Cr(VI) concentrations of 2.9–26.4 and 2.5–4.5  $\mu\text{g/L}$ , respectively [5]. A micro-column packed with nanometer zirconium phosphate coupled with electrothermal atomic absorption spectrometer (ETAAS) was used to determine Cr(VI) in different water samples. Analysis of tap water showed Cr(III) and Cr(VI) concentrations of 1.01–3.04 ng/mL and 0.31–3.26 ng/mL [5], respectively. In the same study Cr(VI) and Cr(III) concentrations from lake water samples were found in the range of 8.06–18.16 and 3.66–7.41 ng/mL, respectively [5]. In other study Cr(III), Cr(VI), and total chromium concentrations were determined using spectroscopic methods (AAS, UV-Vis) and found in the range of 5.43–10.57 ppb, 7.33–13.05 ppb, and 12.9–18.1 ppb, respectively [6]. An HPLC-ICP-MS method was used for speciation of Cr in sediments and pore water collected from the Baltimore Harbor with tetrabutylammonium hydroxide (TBAH) as the ion-pair reagent and EDTA as the Cr(III) complexing agent. Total Cr and Cr(VI) concentrations were found in sediments in the range of 2.5–1,050 mg/kg and 0.10–0.38 mg/kg, respectively. In the same study the total Cr and Cr(VI) amounts in pore water were determined in the range of 0.20–2.16  $\mu\text{g/L}$  and 0.73–1.17  $\mu\text{g/L}$ , respectively [7]. A method based on the use of ICP-MS and instrumental neutron activation analysis (INAA) together with a Chelex 100 resin column studied Cr(III) and Cr(VI) in surface waters. Concentrations of Cr(III) and Cr(VI) were found in the range of 0.24–52.28  $\mu\text{g/L}$  and 2.24–11.13  $\mu\text{g/L}$ , respectively [4].

In addition to the above analytical methods developed for Cr speciation other analytical techniques have used UV-Vis spectrophotometry, voltammetry, cloud-point extraction with AAS and HPLC, electrophoresis, and chromatographic methods [8]. These methods normally use two or more hyphenated techniques prior to separation, preconcentration, including coprecipitation, cloud-point extraction, ion-exchange separation, and liquid-liquid and solid-phase extraction [9].

In order to determine Cr(VI) in the environment, we examined Cr(VI) concentrations from the Nacogdoches Wastewater Treatment Plant (NWWTP), which serves ~33,000 residents of Nacogdoches City in East Texas. Although a recent study [9] determined total Cr metal concentrations during the wastewater treatment process, there is no reported chromium speciation from NWWTP. The need to determine Cr(VI) concentrations is pertinent to human and environmental safety. We thus were motivated to determine Cr(VI) concentrations in wastewater samples collected from the Nacogdoches Wastewater Treatment Plant (NWWTP) with a Dionex ion chromatographic method [10] with UV detection. In addition, a UV-visible standard addition method was used [11]. The determination of Cr(VI) by ion chromatography is based on postcolumn reagent reaction with 1,5-diphenylcarbazide to complex Cr(VI) and measured at a wavelength of 530 nm [10]. This method is fast, sensitive, and selective and does not require preconcentration. For the UV-Vis the Cr(VI)-DPC complex solution is detected at  $\lambda = 540 \text{ nm}$ .

This study is important for regular monitoring of toxic Cr(VI) concentrations in environmental samples.

## 2. Materials and Methods

### 2.1. Instrumentation

**2.1.1. Ion Chromatography.** Hexavalent chromium was analyzed with an ion chromatograph, Dionex ICS-2100 (Thermo Scientific, Sunnyvale, CA, USA) equipped with a DS6 heated conductivity detector (Thermo Scientific), pump, connected to a postcolumn reagent system, and pneumatic controller (PC 10). A guard column (Dionex IonPac CG5A,  $4 \times 50 \text{ mm}$ ) connected to the analytical separator column, Dionex IonPac CS5A,  $4 \times 250 \text{ mm}$ , was used. The measurements were performed at the following conditions: eluent: 250 mM ammonium sulfate and 100 mM ammonium hydroxide; eluent flow rate: 0.36 mL/min; injection volume: 1000  $\mu\text{L}$ /5000  $\mu\text{L}$ ; temperature: 30°C; back pressure: 0–5000 psi. Postcolumn reagent system was used with the following conditions: flow rate: 0.12 mL/min; wavelength for analysis: 530 nm; noise: 6–8  $\mu\text{AU}$ ; runtime: 10 min; PCR pressure: 20 psi.

**2.1.2. UV-Vis Spectrophotometry.** A Shimadzu UV-2550 double beam UV-visible spectrophotometer with a 1 cm quartz cell was used for Cr<sup>+6</sup> measurements at  $\lambda = 540 \text{ nm}$ . The pH meter (HANNA Instruments) was calibrated at pH of 4, 7, and 10 with appropriate buffer solutions (Merck, USA).

### 2.2. Reagents

**2.2.1. Reagents and Standard Preparations for Ion Chromatographic Analysis.** All reagents were of analytical-reagent grade and were used as supplied. Reagents and solutions were prepared with 18.2 M $\Omega$ -cm deionized water. The pH of samples and standards was adjusted with a sample adjustment buffer (ammonium hydroxide from Sigma Aldrich) and ammonium sulfate (Sigma Aldrich,  $\geq 98\%$  purity, ACS reagent grade). A postcolumn reagent was prepared by dissolving 0.25 g of 1,5-diphenylcarbazide in 50 mL of methanol (Sigma Aldrich,  $\geq 99.9\%$  purity, Chromasolv) and added to 0.2 N sulfuric acid. A standard stock solution of 1000 ppm was made by dissolving 0.106 g of dried potassium chromate ( $\text{K}_2\text{CrO}_4$ , Sigma Aldrich, St. Louis, MO, USA,  $\geq 99\%$  purity) in deionized water. The stock solution was stored at 4°C to minimize degradation. Working standards of concentrations 0.125, 0.25, and 0.5 ppm were prepared daily from the stock solution. Sample calibration curves were used for the determination of Cr(VI) in wastewater samples.

**2.2.2. Reagents and Standard Preparations for UV-Visible Spectrophotometric Analysis.** A standard stock solution of 500 ppm was prepared by dissolving 0.05 g dried  $\text{K}_2\text{CrO}_4$  (Sigma Aldrich,  $\geq 99\%$  purity) in 18.2 M $\Omega$ -cm deionized water and diluted to 100 mL. A 0.2 N sulfuric acid (Sigma Aldrich) was prepared by adding 1 mL of concentrated sulfuric acid to deionized water and diluted to 100 mL. A 1,5-diphenylcarbazide (DPC) solution was prepared by

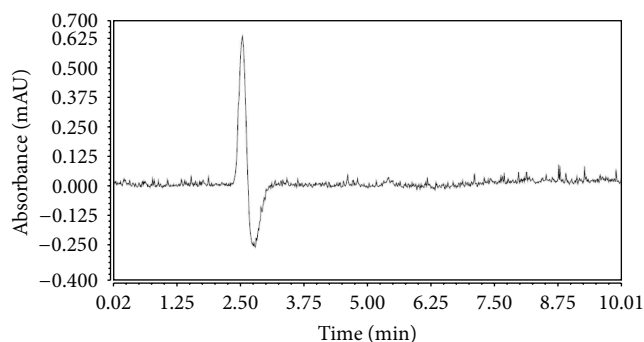


FIGURE 1: Chromatogram of blank sample measured using a Dionex ICS-2100 ion chromatograph. The following conditions were used: Dionex IonPac CS5A,  $4 \times 250$  mm column; a Dionex IonPac CG5A,  $4 \times 50$  mm guard column; eluent flow rate: 0.36 mL/min, injection volume: 5000  $\mu$ L; temperature: 30°C; back pressure: 200–3000 psi; postcolumn reagent system conditions: flow rate: 0.12 mL/min; detection: visible absorbance, 530 nm; noise: 6–8  $\mu$ AU; runtime: 10 minutes.

dissolving 250 mg of DPC (Fluka, Sigma Aldrich,  $\geq 99\%$  purity) in 50 mL methanol. Working standard Cr(VI) concentrations of 0.2, 0.4, 0.5, 0.8, and 1 ppm were prepared from the stock solution. The pH of solutions was adjusted to  $\sim 2$  with phosphoric acid (ACS certified reagent, 85%) and dilute sulfuric acid before complexation. The absorbance-concentrations calibration curves were plotted with a correlation coefficient,  $r^2$ , of 0.999 (see Section 3.1.2).

**2.3. Sampling Site.** Samples were collected from Nacogdoches Wastewater Treatment Plant (NWWTP) in Nacogdoches City (East Texas), from four treatment stages, namely, aeration chamber, clarifier, chlorination chamber, and the sulfur dioxide chamber. The NWWTP site was recently described in [9]. The NWWTP has a capacity of 12.8 million gallons per day (MGD) and an average pumping capacity of 3–4 MGD [9].

**2.4. Collection of Wastewater Samples for Cr(VI) Analysis.** Wastewater samples collected in acid-washed polythene bottles were filtered through a 0.45  $\mu$ m membrane filter (GE Whatman Membrane Filters, GF/F) and stored at 4°C until analyzed. The solution was adjusted to pH 9–9.5 with an adjustment buffer as recommended following a modified USEPA Method 218.6 [11].

**2.5. Detection Limit for Ion Chromatographic (IC) Analysis.** The detection limit of the instrument was determined by analyzing ten reagent blanks. The pH of ten deionized water samples was adjusted to 9–9.5 with an adjustment buffer consisting of 250 mM ammonium hydroxide and 1000 mM ammonium sulfate [18]. The detection limit determined by  $3\sigma$  of the ten blanks was found to be 0.006 ppm. A representative chromatogram of a blank solution is shown in Figure 1.

### 3. Results

#### 3.1. Calibration Curves Used for Analysis

**3.1.1. Ion Chromatographic (IC) Analysis of Wastewater Samples.** The calibration curve for  $\text{Cr}^{+6}$  analyses was prepared

from 0.125, 0.25, and 0.50 ppm  $\text{Cr}_2\text{O}_4^{2-}$  standards. The linear calibration curve with the equation  $\text{absorbance} = 29.13\text{Conc} - 0.0035$ , where absorbance units are in milliabsorbance- $\text{min}^{-1}$  and concentration is measured in ppm, gave a correlation coefficient  $r^2 > 0.999$ .

**3.1.2. UV-Vis Spectrometric Analysis of Samples.** A calibration equation ( $y = 0.2299x + 0.0004$ ,  $R^2 = 0.999$ , where  $y$  is absorbance and  $x$  is concentration in ppm) derived from a calibration curve was plotted from standards (0.2 ppm, 0.4 ppm, 0.5 ppm, 0.8 ppm, and 1.0 ppm) for the quantitation of Cr(VI) in wastewater samples. However, due to the low sensitivity to low Cr(VI) concentrations and low detection limits of Cr(VI) in wastewater samples, no pink color developed on complexation with 1,5-diphenylcarbazide. A standard addition method [19] was therefore employed for Cr(VI) determination. Wastewater samples were spiked with 5 mL, 10 mL, and 15 mL of a 0.5 ppm Cr(VI) standard. Figures 2(a), 2(b), 2(c), and 2(d) show the spiked curves that were used for the quantitation of Cr(VI) at the aeration, clarifier, chlorine chamber, and sulfur dioxide chamber, respectively. Table 1 shows general concomitant decrease in  $\text{Cr}^{+6}$  concentrations along the treatment stages.

**3.2. Analysis of Cr(VI) Concentrations via Ion Chromatography.** Figures 3(a), 3(b), 3(c), and 3(d) depict representative ion chromatographic profiles of Cr(VI) concentrations, with corresponding retention times at the four treatment stages. In agreement with reported literature [11] the Cr(VI)-diphenyl carbohydrazide complex formed in standards and wastewater samples was detected after 6–7 minutes. Table 2 shows mean Cr(VI) concentrations of  $0.0019 \pm 0.0020$ ,  $0.0006 \pm 0.0002$ ,  $0.0011 \pm 0.0006$ , and  $0.0010 \pm 0.0006$  ppm from the aeration chamber, clarifier, chlorine contact chamber, and sulfur dioxide chamber, respectively. It is worth noting that the high % RSDs from the analysis, particularly at the aeration chamber, may be due to the seasonal variations and different sources of wastewater samples entering the treatment plant at the aeration stage. While the aeration chamber showed the highest Cr(VI) concentration (Figures 3(a) and 4), low [Cr(VI)] amounts were detected in the chlorination and

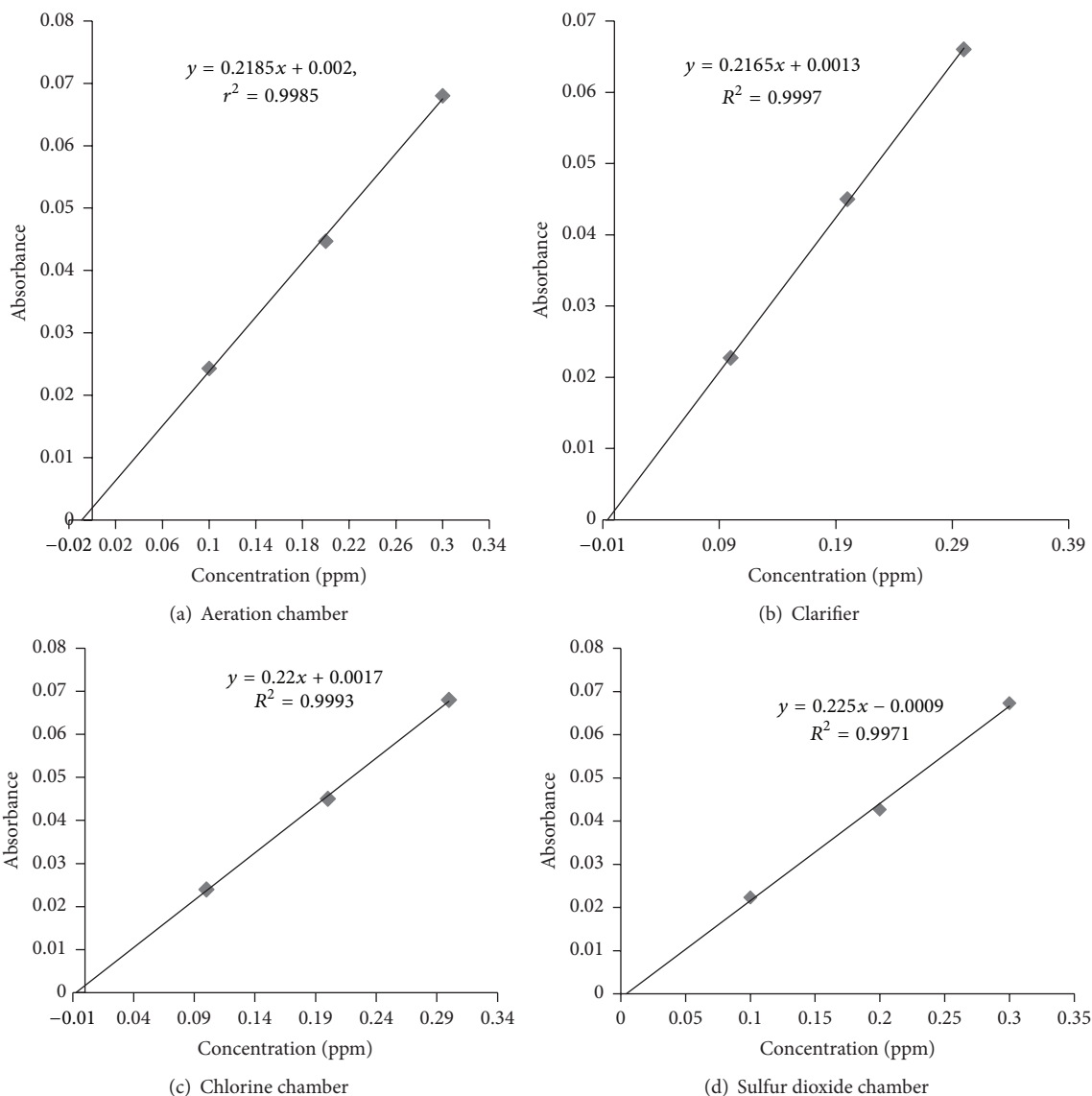


FIGURE 2: Absorbance/concentrations of the samples from aeration chamber, clarifier, chlorine chamber, and sulfur dioxide chamber spiked with 5, 10, and 15 mL of 0.5 ppm Cr(VI) standards. A 2550 UV-Vis spectrophotometer was used for measurements at  $\lambda = 540$  nm.

sulfur dioxide chambers (Figure 4), attributable to efficient removal of the WWTP along the treatment stages. The Cr(VI) concentrations (Table 2) fall below USEPA and WHO standard contaminant limits of 100 ppb and 50  $\mu\text{g/L}$  [20, 21], respectively. Thus, Cr(VI) concentrations in water discharged from NWWTP to La Nana Creek may not have adverse effects on humans and the environment.

**3.3. Analysis of Cr(VI) in Spiked Wastewater Samples Using UV-Visible Spectrophotometry.** Samples filtered through a 0.45  $\mu\text{m}$  pore filter were treated in the same manner as standards, prior to reaction with DPC. The pH of standard solutions and samples was then adjusted to  $\sim 2$  [22]. A  $\text{Cr}^{+6}$ -DPC complex developed no purple color for the standard samples, indicating low Cr(VI) amounts in wastewater samples. This necessitated employing the standard addition method. The

samples were spiked with different volumes (5 mL, 10 mL, and 15 mL) of 0.5 ppm Cr(VI) standard solution. Figures 5(a)–5(d) show absorbance-concentration plots of Cr(VI) in spiked samples, after reaction with 1,5-diphenylcarbazine. Subsequently, samples and solutions were analyzed in the 300–700 nm range. The good linearity, with  $r^2$  of  $> 0.997$ , enabled Cr(VI) concentration in the wastewater samples in the range 0.004–0.0077 ppm (Table 1). The determined concentrations are within USEPA Cr(VI) MDL of 100 ppb [20]. Thus, NWWTP is efficient in the removal of chromium (VI) at the effluent stages.

## 4. Discussion

There are many sources of Cr(VI) in Nacogdoches City including paints, pigments, soils, tobacco smoke, and effluents



TABLE 1: UV-Vis absorbance and concentrations of wastewater samples spiked with different volumes of a 0.5 ppm Cr<sup>+6</sup> standard at 540 nm using standard addition method;  $n = 12$ .

NWWTP treatment stages	Concentration (ppm) of Cr(VI) spiked	Absorbance (mean $\pm$ SD)	Determined Cr(VI) concentration (ppm)	% RSD
Aeration chamber	0.1	0.024 $\pm$ 0.002	0.009 $\pm$ 0.006	67
	0.2	0.045 $\pm$ 0.001		
	0.3	0.068 $\pm$ 0.001		
Clarifier	0.1	0.023 $\pm$ 0.001	0.007 $\pm$ 0.005	71
	0.2	0.045 $\pm$ 0.001		
	0.3	0.066 $\pm$ 0.001		
Chlorination chamber	0.1	0.024 $\pm$ 0.001	0.008 $\pm$ 0.006	75
	0.2	0.045 $\pm$ 0.001		
	0.3	0.068 $\pm$ 0.002		
Sulfur dioxide chamber	0.1	0.022 $\pm$ 0.001	0.004 $\pm$ 0.006	150
	0.2	0.043 $\pm$ 0.001		
	0.3	0.067 $\pm$ 0.001		

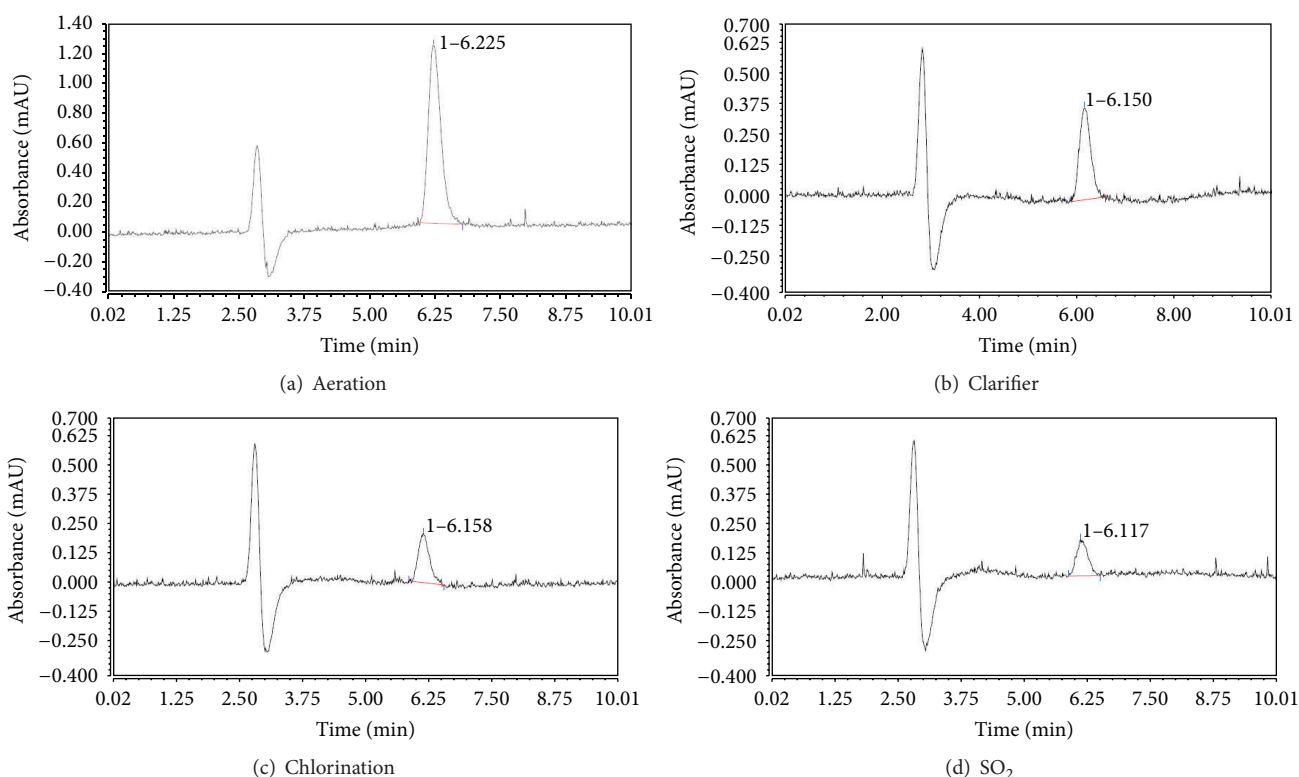


FIGURE 3: ((a) and (b)) Chromatogram of Cr<sup>+6</sup> in aeration chamber (a) and clarifier (b). A Dionex ICS-2100 ion chromatograph was used with the following conditions: Dionex IonPac CS5A, 4  $\times$  250 mm column; Dionex IonPac CG5A, 4  $\times$  50 mm guard column; eluent flow rate: 0.36 mL/min; injection volume: 5000  $\mu$ L; temperature: 30°C; back pressure: 200–3000 psi; postcolumn reagent system conditions: flow rate: 0.12 mL/min; detection: visible absorbance, 530 nm; noise: 6–8  $\mu$ AU; runtime: 10 minutes. ((c) and (d)) Chromatogram of Cr<sup>+6</sup> in chlorine contact chamber (c) and sulfur dioxide chamber (d). A Dionex ICS-2100 ion chromatograph was used with the following conditions: Dionex IonPac CS5A, 4  $\times$  250 mm column; Dionex IonPac CG5A, 4  $\times$  50 mm guard column; eluent flow rate: 0.36 mL/min; injection volume: 5000  $\mu$ L; temperature: 30°C; back pressure: 200–3000 psi; postcolumn reagent system conditions: flow rate: 0.12 mL/min; detection: visible absorbance, 530 nm; noise: 6–8  $\mu$ AU; runtime: 10 minutes.

TABLE 2: Concentration of Cr(VI) in the four treatment stages measured by ion chromatography (Dionex ICS 2100 with column: Dionex IonPac CS5A, 4 × 250 mm; guard column: Dionex IonPac CG5A, 4 × 50 mm; eluent flow rate: 0.36 mL/min; injection volume: 1000 μL; temperature: 30°C; back pressure: 1700–2000 psi; postcolumn reagent system conditions: flow rate: 0.12 mL/min; detection: visible absorbance, 530 nm; noise: 6–8 μAU; runtime: 10 min).

Treatment stages	Cr(VI) concentration, ppm (mean ± standard deviation, $n = 12$ )	% RSD
Aeration chamber	0.0019 ± 0.0020	105
Clarifier	0.0006 ± 0.0002	33.3
Chlorination chamber	0.0011 ± 0.0006	54.5
Sulfur dioxide chamber	0.0010 ± 0.0006	60.0

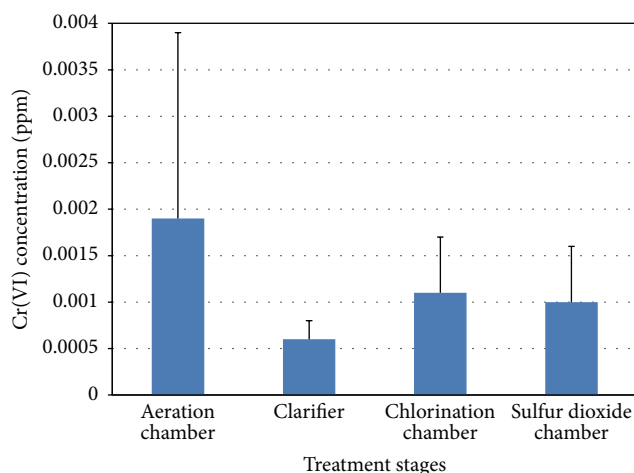


FIGURE 4: Cr(VI) concentrations along the treatment stages. Data are means of at least three determinations.

from chemical plants. The carcinogenic and mutagenic properties of Cr(VI) motivated us to examine the Cr(VI) concentration in NWWTP. In a recent study, the total Cr concentration of 0.085 ppm [9] was determined in the aeration chamber via inductively coupled plasma-optical emission spectroscopy (ICP-OES). Although valuable, the total concentration by itself may not give useful accurate information on the toxicity and mobility of Cr(III) and Cr(VI). Therefore Cr(VI) concentrations from the NWWTP wastewater samples were analyzed using ion chromatography (IC) and UV-Vis spectrophotometry. It is worth noting that during the treatment process Cr(VI) may be adsorbed to biosolids which is removed and later dried and sent to the landfill.

During analyses, the pH of samples for IC analysis was adjusted to 9–9.5. At this pH Cr exists as  $\text{CrO}_4^{2-}$  species [9]. The low Cr(VI) concentrations in samples necessitated spiking WWT samples with 0.5 ppm amounts of potassium chromate standard solution. The adjustment of pH of samples to 2 ensured that Cr exists as  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  [22]. From the present analysis, we presume two chromium species, namely, Cr(III) and Cr(IV), predominate in wastewater samples [23].

TABLE 3: Comparison of Cr(VI) concentrations to other literature studies in river, wastewater, and drinking waters.

Samples	[Cr(VI)] amounts	Reference
River samples	3.7–3.31 ppb	[7]
	4.2 ppb	[8]
	Below detection limits	[9]
	0.03–2 ppb	[10]
	0.097–9.84	[11]
	31–498 ppm (in lakes)	[12]
	21–984 ppm (in tap water)	[12]
Wastewater samples	25.1–45.5 ppb	[13]
	1.2–6.7 ppm	[14]
	567.2 ppb	[15]
	4–9 ppb	This study
Drinking water samples	0.12–20 nM	[16]
	14 nM	[16]
	0.3–1.0 ppb	[17]

From the total chromium concentration (0.085 ppm), Cr(III) and Cr(VI) were calculated. Using the equations

$$[\text{Cr}_{(\text{Total})}] - [\text{Cr}(\text{VI})] = [\text{Cr}(\text{III})], \quad (1)$$

$$\frac{[\text{Cr}]_{\text{Total}} - [\text{Cr}(\text{VI})]}{[\text{Cr}]_{\text{Total}}} \times 100\%$$

2.24% and 97.8% were apportioned in aeration samples to Cr(VI) and Cr(III) concentration (0.083 ppm), respectively.

Thus, the Cr(III) is prevalent in the wastewater vis-à-vis  $[\text{Cr}^{+6}]$ . Cr(III) is essential for human health and is less toxic and desirable in waters vis-à-vis hexavalent  $\text{Cr}^{+6}$ . A comparison to USEPA maximum contaminant level of 0.1 ppm [20] shows low Cr comparative amounts. In discussions below, we compare the Cr(VI) concentrations in NWWTP with various investigations from river samples, wastewater effluents, and surface water drinking samples. Table 3 summarizes the comparisons discussed with similar works in Section 4.1

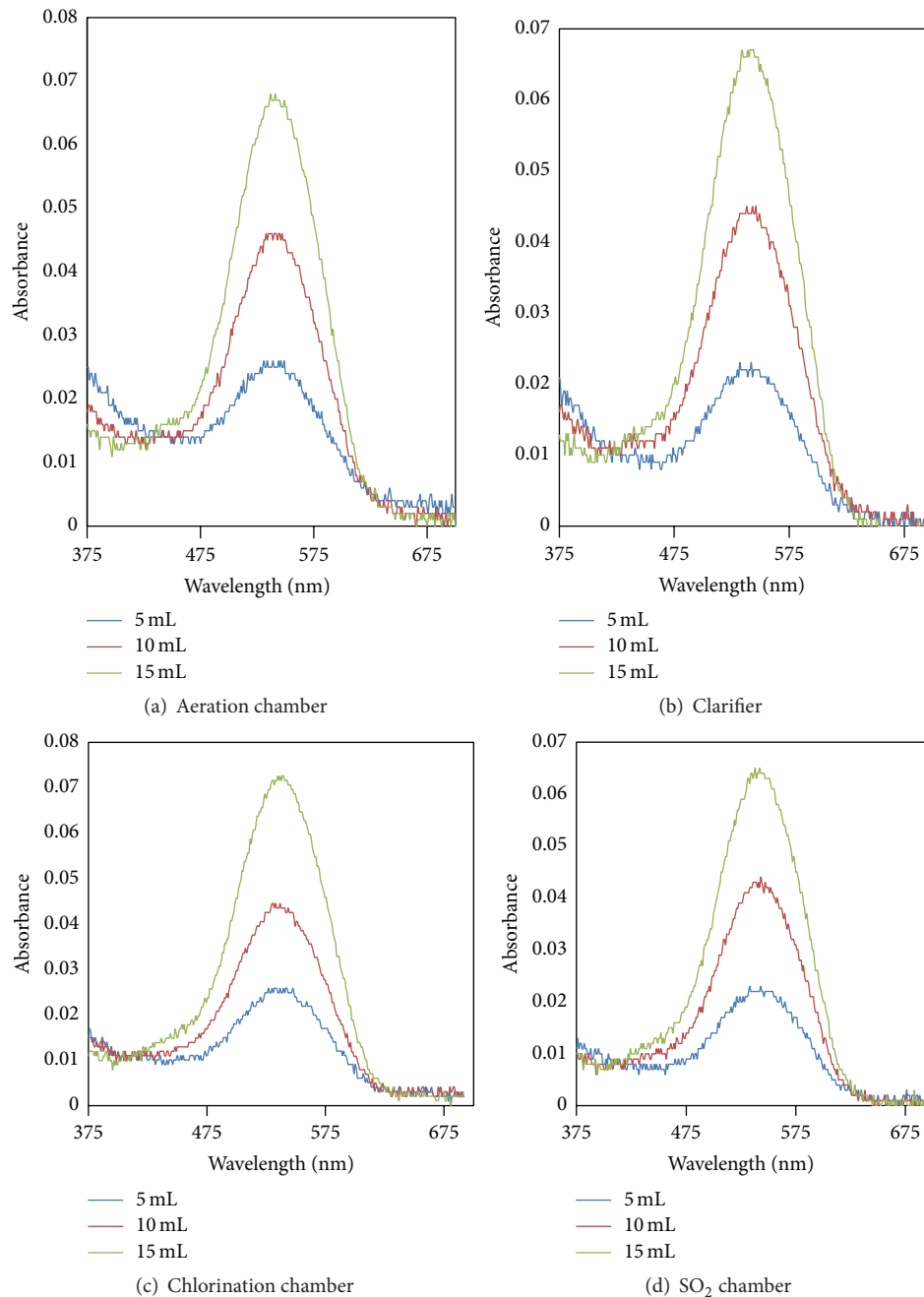


FIGURE 5: ((a)–(d)) UV-Vis spectra of samples spiked with 5, 10, and 15 mL of 0.5 ppm Cr(VI) standard solution from the four treatment stages: aeration, clarifier, chlorination chamber, and sulfur dioxide chamber.

#### 4.1. Comparisons of Cr(VI) Concentrations in NWWTP to Other Studies

**4.1.1. Comparisons of Cr<sup>+6</sup> Concentrations in River Samples.** The Cr(VI) concentration obtained from the current study was higher as compared to a study in which river and sea water contained 3.7 and 2.31 ppb [7], respectively (Table 3). Liquid-liquid extraction and flame atomic absorption spectrometry techniques [24] were used for speciation of

chromium in tap water and rivers. Rivers contained 4.2 ppb Cr(VI) amounts. The levels of Cr(VI) in tap water were found to be 10.30 ppb after spiking with 10 ppb of Cr(VI) solution. The concentrations of Cr(VI) in rivers were found lower than concentrations obtained in wastewater. This is feasible given the high wastewater metal loads (see Table 3).

Driscoll et al. [25] evaluated the concentration of hexavalent chromium in sediment pore water in Hackensack River, New Jersey. The total Cr concentrations in pore water were



in the range <2.0 to 5.3 mg/L, while Cr(VI) was not detected though Hackensack River was adjacent to a chromite ore processing residue site (see Table 3). The results showed limited bioavailability and toxicity in sediment at this site. In another study [10] Cr<sup>+6</sup> was determined in saline and fresh waters by a solvent extraction-atomic spectrometric technique. Concentration of hexavalent chromium was in the range 0.03–2 µg/L with a detection limit of 0.024 µg/L and is low compared to concentration in NWWTP wastewater samples.

Using activated carbon modified with tris(hydroxymethyl)aminomethane as an adsorbent, the selective adsorption of Cr<sup>+6</sup> was quantified in surface water samples [26]. With the use of a standard addition, recoveries of Cr<sup>+6</sup> were found in the range 92.10%–97.40%. In another study, Cr was used for speciation of in effluent streams by extraction and spectrophotometric method [27]. Water samples spiked with chromium and Cr(VI) concentration were found in the range 0.097–0.984 µg/L with a detection limit of 2.22 ng/L (Table 3). These concentrations were slightly different vis-à-vis results from NWWTP. In another study, Wandoyo et al. [12] determined Cr(VI) concentrations in river samples in the range 0.03–0.04 ppm (Table 3). Wandoyo et al.'s [12] results were attributed to the introduction of Cr into the river located near a leather processing plant. In contrast, Cr(VI) concentrations in lakes and tap water samples [28] were found in the range of 31–498 and 21–984 ppm (Table 3), respectively. The average recovery was ~100%. In other studies [23] high Cr(VI) concentrations were obtained in rivers in the range 0.48–1.06 ppm vis-à-vis the present studies.

**4.1.2. Cr<sup>+6</sup> Concentrations vis-à-vis Studies from Wastewater and Drinking Waters.** Melaku et al. [13] found Cr(VI) concentration in the range 25.1–45.5 ppb in wastewater samples, attributed to effluent discharges from tanneries (Table 3). In another study [14] Cr(VI) concentrations in industrial effluent were found in the range 1.2–6.7 ppm (Table 3). The reported higher concentrations vis-à-vis current studies were attributed to the use of Cr in the tanning industries.

A sensitive spectrophotometric method, involving dapsone diazotization in hydroxylamine hydrochloride medium and coupling with N-(1-naphthyl)ethylenediamine dihydrochloride by electrophilic substitution, was used for the determination of chromium in waters [15]. The application of the method [15] to industrial effluents found Cr concentrations of 567.2 µg/L, which is 300 to 567 times greater than in the current wastewater studies. This shows the high efficiency of NWWTP, in removal of influent Cr amounts.

An analytical flow injection method was used for trace analysis of Cr(VI) in drinking waters with a liquid core waveguide capillary cell [16]. The obtained Cr(VI) concentrations were found in the range 0.12–20 nM and about 14 nM in bottled waters and tap waters [16] (Table 3), respectively. Other speciation methods for chromium determinations in drinking water samples have used coupled methods such as the ion-pair reversed-phase HPLC-ICP-MS [17]. Subsequent analysis of drinking water samples with and without spiking found Cr(VI) concentration in the range 0.3–1.0 µg/L [17] (Table 3). As would be expected the ion-pair reversed-phase

HPLC-ICP-MS [17] method shows lower detection for Cr vis-à-vis the UV-Vis or IC-DPC method used Cr<sup>+6</sup> analysis in NWWTP.

**4.2. Cr<sup>+6</sup> Removal from NWWTP and Environmental Implications.** This study has demonstrated for the first time the removal efficiency of NWWTP for Cr(VI). As shown in Figure 5 there is a 3-fold decrease in Cr<sup>+6</sup> concentrations in influent vis-à-vis effluent wastewater in NWWTP before discharge into La Nana Creek. This is important to the designs and future management of the municipal treatment plants. Future investigations can be extended to other WWTPs in East Texas. Such studies will be important in determining efficiency levels vis-à-vis USEPA regulated standards. However it is worth noting that the Cr(VI) concentrations found do not meet the proposed lower limits (20 ng L<sup>-1</sup>) in tap water set by the California Office of Environmental Health Hazard Assessment (OEHHA) [29] as a public health goal for chromate. This is a goal worth targeting in WWTPs in the future.

## 5. Conclusion

In the present study ion chromatography and UV-Vis spectrophotometry were used to assess the Cr<sup>+6</sup> concentrations from the Nacogdoches Wastewater Treatment Plant, in East Texas, USA, along the treatment stages. The concentrations of Cr<sup>+6</sup> from samples were found below the maximum contaminant level vis-à-vis USEPA guidelines. The photometric method used is easy to apply for determination of Cr(VI) in wastewater samples. The method provides LOD lower than the maximum allowable level (50.0 µg L<sup>-1</sup>) of chromium recommended by WHO [21]. Thus, the treatment plant is efficient in the removal of chromium during the treatment process. These studies are useful for future studies of WWTPs in East Texas and USA.

## Disclaimer

Any opinions expressed in this paper are those of the authors, and therefore, no official endorsement should be inferred.

## Conflict of Interests

The authors declare no competing financial interests.

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