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Research Article

## Electrochemical Reduction of Hexavalent Chromium from Chemical Oxygen Demand Hazardous Waste Chemicals using Graphite Electrode

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**Abstract:** The removal of hexavalent chromium, Cr (VI), from highly acidic, essentially nonaqueous laboratory waste by electrochemical reduction was studied using graphite electrode. This study evaluated the effectiveness of graphite electrode to electrochemically reduce the unreduced Cr (VI) in the hazardous spent chemical oxygen demand (COD) reagent to trivalent chromium. The effect of four factors were investigated in the experiment which are the initial Cr (VI) concentration ( $[\text{Cr}^{6+}]_0$ ,  $1/2[\text{Cr}^{6+}]_0$ , and  $1/4[\text{Cr}^{6+}]_0$ ), the initial acidity of the COD spent chemicals ( $[\text{Acidity}]_0$ ,  $1/2[\text{Acidity}]_0$  and  $1/4[\text{Acidity}]_0$ ), applied electric current (0A, 1A, and 6A), and reaction time. The voltage, type and size of graphite electrodes were held constant. The result shows that the varied factors significantly affect the effectiveness of graphite electrode in reducing Cr (VI) to Cr (III). Optimum reduction of 100% is attained at the following conditions: maximum Cr (VI) concentration in spent reagent (i.e. at  $[\text{Cr}^{6+}]_0$ ),  $1/4[\text{Acidity}]_0$ , and with 6 ampere of electric current for reaction time of 2.5 hours. However, total removal of Cr (VI) can still be achieved even if the acidity is not lowered that is maintaining it at  $[\text{Acidity}]_0$ .

**Key words:** Hazardous waste, chemical oxygen demand (COD), hexavalent chromium, electrochemical reduction, graphite.

## INTRODUCTION

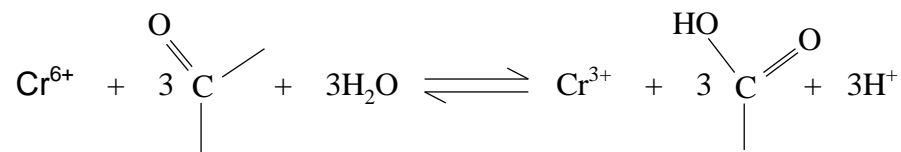
The chemical oxygen demand (COD) is an important parameter in evaluating the extent of organic pollutants in water and the efficiency of the wastewater treatment processes where it measures the amount of oxygen required to oxidize the organic matter present in water. In the determination of oxygen demand, the course of the reaction involves a redox reaction between the dichromate ion and the organic matter where the hexavalent chromium, Cr (VI), in the dichromate ion is being reduced into a trivalent chromium, Cr (III), upon the oxidation of the organic matter. The COD determination of a sample is dependent upon the excess dichromate ion whether through titration method or spectroscopic method.

The COD analysis generates heavy metals which cause serious environmental problem if not properly disposed because these are not biodegradable and can affect a living organism through accumulation in the living tissue, resulting to a variety of diseases and disorders. The spent COD reagent contains heavy metals such as unreduced Cr (VI), Hg, and Ag. The Cr (VI) is a toxic metal ion that has carcinogenic effect which affects the normal body functions when accumulated by a human being. The disposal of Cr (VI) into the environment is therefore not ideal since it can cause harm. However, there are processes that can help eliminate hexavalent chromium in the environment and industrial waste such as membrane filtration, phytoremediation, ion-exchange, adsorption, solvent extraction, chemical reduction with coprecipitation, and electrochemical reduction. The attenuation of Cr (VI) into Cr (III), before being discharged into the environment, is one credible process to eliminate hexavalent chromium. Thus, this study explored the electrochemical process of eliminating Cr (VI) in the spent COD reagent by investigating the optimum conditions that efficiently reduce Cr (VI) to Cr (III) using graphite electrode.

Due to the low toxicity and mobility of Cr (III), the reductive transformation of Cr (VI) into Cr (III) is a very important natural reduction<sup>1</sup>. There are several reductants of Cr(VI) into Cr(III) which include sulfur dioxide (SO<sub>2</sub>), sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>), sodium bisulfite (NaHSO<sub>3</sub>), and ferrous sulfate (FeSO<sub>4</sub>), iron filings, sodium metabisulfite (Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>), S(IV), and zero-valent iron<sup>2-5</sup>. According to Barrera-Díaz, Lugo-Lugo, & Bilyeu<sup>6</sup>, due to the vast reactive surface of graphite, it is an interesting alternative for Cr(VI) treatment especially in electrochemical techniques. Aside from this, it has a minimal reactivity over a wide range of process conditions, is of low cost, and is easy to handle.

The graphite electrode consists of a layer of carbon atom. When the graphite is immersed in the waste COD reagent which is highly acidic and has a strong oxidant (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), its surface is being altered forming some functional groups such as carbonyl, epoxide, and hydroxyl<sup>7</sup>. Although there is no available full reaction mechanism since the exact chemical structure of the product is still ambiguous, typically when the reaction between the carbon surfaces and oxygen begin, it activates the carbon by increasing the surface area then as the reaction proceeds, organic functional groups are introduced on the carbon surfaces<sup>8</sup>.

There are two phase mechanisms for the interaction of Cr (VI); the carbon has the sorption of Cr(VI) and the reduction of Cr(VI) into Cr(III) through the oxidation of functional groups. Thus, it is reasonable to theorize that the absorbed Cr(VI) is reduced to Cr(III) with the oxidation of the functional groups C-H, C-OH and C=O<sup>9</sup>. Figure 1 shows plausible mechanism for the reduction of Cr (VI) into Cr(III).

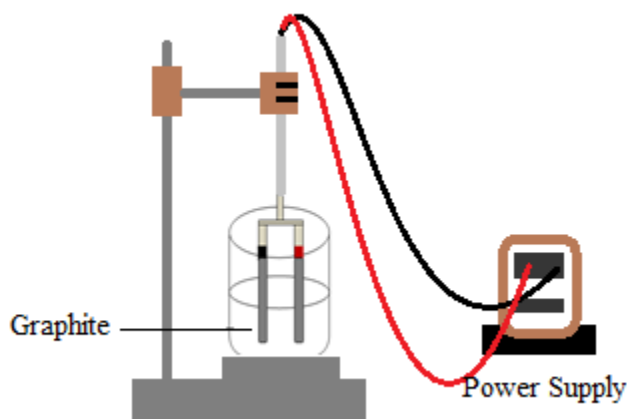


**Figure 1.** Plausible reaction mechanism for the reduction of Cr (VI) into Cr(III)<sup>9</sup>.

## EXPERIMENTAL

A series of experiments were carried out to collect the needed information. Five batches of samples (spent COD reagents from two industrial plants) were prepared for the electrochemical reduction experiment. The spent COD reagents contain precipitates which were separated through decantation. The supernatant liquids were used for the reduction experiment while the precipitates were stored for containment.

Dilution was employed to vary either the initial Cr (VI) concentration or the acidity of the spent COD reagents. Dilution, however, would change both Cr (VI) concentration and acidity of the reaction mixture, hence, calculated amounts of either K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> or H<sub>2</sub>SO<sub>4</sub> were added to held constant the Cr (VI) concentration or acidity, respectively. The sample was subjected to electrolysis for the electrochemical Cr (VI) reduction using the graphite electrode at the specified conditions and reaction time. Figure 2 shows the schematic diagram of the electrochemical reduction set-up.



**Figure 2:** Set-up for the electrochemical reduction of Cr (VI) with graphite electrode.

The determination of Cr (VI) concentration was made by titration with standard ferrous ammonium sulfate solution while the acidity was determined by titration with standard sulfuric acid solution.

## RESULTS AND DISCUSSION

**The spent COD reagents.** The characteristics of the spent COD reagent in terms of Cr (VI) concentration and acidity are shown in table 1. It is evident that the spent COD reagent is highly acidic thus, the acidity of the sample was expressed as molarity of sulfuric acid. Considering that initial concentration of Cr (VI) was variable, raw data were converted to percent reduction.

**Table 1:** Hexavalent chromium concentrations and acidities of spent COD reagents

Spent COD Reagent (Batch)	Cr(VI) Concentration (ppm)	Acidity (M H <sub>2</sub> SO <sub>4</sub> )
1	1,132.46	9.13
2	976.49	9.47
3	942.59	9.27
4	881.55	9.00
5	935.81	9.13

**Percentage reduction of hexavalent chromium.** The percent reduction of Cr (VI) to Cr (III) at different conditions are presented in table 2. Practically 100% removal of Cr (VI) were attained after 2.5 hour of electrochemical reduction at current of 6 ampere regardless of the initial concentration of Cr (VI) and level of acidity.

**Effects of Cr (VI) concentration.** The effects of Cr(VI) concentration in the electrochemical reduction of Cr(VI) into Cr(III) using a graphite electrodes indicates that lowering the Cr(VI) concentration lowers the rate of electrochemical reduction. It is apparent that complete reduction of Cr (VI) was achieved at the maximum Cr (VI) concentration of the spent reagents (i.e. at  $[\text{Cr}^{6+}]_0$ ).

**Effects of acidity of the reaction mixture.** The effects of varying the acidity demonstrates that by lowering the acidity of the reaction mixture the rate of reduction of Cr (VI) significantly increased. The total reduction of Cr (VI) was achieved at  $\frac{1}{4}$  of the original acidity of the sample.

These results are in agreement with the findings of Besagas and Del Rosario<sup>2</sup> that the efficiency in reducing Cr (VI) in spent COD reagents by zero-valent iron increased as the acidity of the reaction mixture decreased. These findings, however, seems to contradict with other findings in literature that the rate of Cr(VI) reduction increases with decreasing pH<sup>1</sup>. However, it should be noted that unlike the study of Niu *et al.*<sup>3</sup> and Alowitz *et al.*<sup>10</sup> that the samples they used were highly aqueous solution, the waste chemicals generated in the determination of COD are essentially non-aqueous highly-acidic solutions and lowering the acidity by  $\frac{1}{4}$  through dilution would basically not affect the pH of the solution. Theoretically, pH will change by 1 unit if there is a ten times increase or decrease in  $\text{H}^+$  concentration. Adding water to satisfy the condition considered in this study only decreased the  $\text{H}^+$  concentration by four and would only dilute the sample while the highly acidic environment was maintained. It could be inferred, therefore, that removal of Cr (VI) in spent COD reagent is faster in an aqueous but highly acidic environment.

**Effects of applied electric current.** The effect of the applied electric current in the electrochemical reduction of Cr (VI) into Cr (III) reveals that by increasing the applied electric current the rate of Cr (VI) reduction likewise increase and that complete reduction of Cr (VI) was achieved when the current applied was 6A. Correspondingly, at 0A or when there was no electric current being applied to the system, minimal reduction of Cr (VI) was observed.

Table 2: Percent reduction of Cr (VI)

Percent Reduction (%)															
	([Acidity]) <sub>0</sub>														
	0 Ampere					1 Ampere					6 Ampere				
	0.5 h	1 h	1.5 h	2 h	2.5 h	0.5 h	1 h	1.5 h	2 h	2.5 h	0.5 h	1 h	1.5 h	2 h	2.5 h
[Cr(VI)] <sub>0</sub>	0.63	1.42	2.06	2.69	3.33	7.10	11.97	15.40	18.83	23.16	56.53	66.09	77.99	89.36	100
1/2 [Cr(VI)] <sub>0</sub>	0	0.71	1.42	2.49	3.20	6.74	11.35	14.90	18.44	22.70	53.20	65.96	75.18	87.94	95.04
1/4 [Cr(VI)] <sub>0</sub>	0.00	0.77	1.55	2.32	3.10	7.75	11.63	15.50	18.60	23.26	51.94	59.69	67.44	83.72	92.25
	1/2 [Acidity] <sub>0</sub>														
	0 Ampere					1 Ampere					6 Ampere				
	0.5 h	1 h	1.5 h	2 h	2.5 h	0.5 h	1 h	1.5 h	2 h	2.5 h	0.5 h	1 h	1.5 h	2 h	2.5 h
[Cr(VI)] <sub>0</sub>	0.74	1.48	2.41	2.96	3.89	8.52	12.96	16.67	19.82	24.26	57.96	71.48	84.26	89.07	100
1/2 [Cr(VI)] <sub>0</sub>	0.31	1.23	2.16	2.78	3.71	8.33	12.34	16.05	19.14	23.77	56.17	70.99	80.86	88.58	100
1/4 [Cr(VI)] <sub>0</sub>	0.00	0.69	2.08	2.78	3.47	8.33	12.50	15.97	19.44	23.61	55.55	61.11	71.53	84.72	92.36
	1/4 ([Acidity]) <sub>0</sub>														
	0 Ampere					1 Ampere					6 Ampere				
	0.5 h	1 h	1.5 h	2 h	2.5 h	0.5 h	1 h	1.5 h	2 h	2.5 h	0.5 h	1 h	1.5 h	2 h	2.5 h
[Cr(VI)] <sub>0</sub>	0.82	1.64	2.46	3.28	4.37	8.74	13.11	16.94	20.22	24.32	61.20	78.96	87.43	100	100
1/2 [Cr(VI)] <sub>0</sub>	0.41	1.63	2.44	3.25	4.47	8.54	13.01	16.67	19.92	23.98	58.94	72.36	83.33	93.50	100
1/4 [Cr(VI)] <sub>0</sub>	0.00	1.39	2.08	2.78	3.47	5.55	15.97	24.30	29.86	36.11	54.86	67.36	81.94	90.28	100

These observations are in line with the fundamental principle that electrolysis is an electrochemical route in which the electrical energy is the driving force of the chemical reaction. Since the electric current is the driving force of the electrochemical reduction of Cr (VI) to Cr (III), the application of electric current will force the reaction to proceed to the right producing more Cr (III) ions thus increasing the effectiveness of the graphite electrode as reducing agent.

**Interaction of factors.** Among the factors being investigated, four interactions between them were observed to be statistically significant. These are the Cr (VI) concentration—acidity interaction, Cr(VI) concentration—applied electric current interaction, acidity—applied electric current interaction, and applied electric current—reaction time interaction. These interactions have joint effects on the electrochemical reduction of Cr (VI).

## CONCLUSIONS

The study offers another practical and effective solution in dealing with the hazardous and toxic laboratory waste which is the spent reagents used in the analysis of chemical oxygen demand. Electrochemical reduction of Cr (VI) to Cr (III) in the spent reagent shows that graphite is a suitable electrode. The optimum condition of the electrochemical reduction of hexavalent chromium by graphite electrode is at the  $[\text{Cr (VI)}]_0$  of the spent COD reagent,  $1/4[\text{Acidity}]_0$ , 6 amperes of applied electric current and 2.5 hours of electrolysis. The graphite can be used a number of times, hence, this method is more economical. Lowering the acidity to  $1/4[\text{Acidity}]_0$  requires dilution, however for practical application, electrochemical reduction can be applied directly to spent reagent. Total removal of Cr (VI) can still be achieved even if the acidity is not lowered by dilution.

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