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Hazardous Waste Chemicals from Dichromate Chemical Oxygen Demand Analysis: Toxicity Reduction, Recovery, Recycling, and Testing

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Abstract

This study aims to find a solution to a pressing hazardous waste problem involved in the determination of Chemical Oxygen Demand (COD) testing by the dichromate method. Specifically, it investigated the effects of chromium(VI) concentration and acidity on the reduction-based detoxification of this dangerous ion, the recovery of the mercuric sulfate, and the reuse of the recovered substance. The study adopted the experimental research design. For the reduction experiments, the supernatant liquid of the spent reagents containing the Cr(VI) was used as sample. Iron filings are used as the reductant. It was added at an amount equal to 1:1 Fe to Cr(VI) stoichiometric mass ratio. For the recovery experiments, the precipitate consisting mainly of mercury-chloride complex was used as sample. Synthetic water solutions were used in all COD determinations employed for evaluating the masking effectiveness of the recovered mercuric sulfate. Results revealed that at decreasing initial Cr(VI) concentration, the efficiency of chromium reduction by iron filings decreases; while at decreasing initial acidity, the efficiency of the reduction increases. Furthermore, mercury in spent reagents can be eliminated and mercuric sulfate can be recovered but its masking ability is not known because, under the conditions used for COD analysis (spectrophotometric with closed-tube digestion), there is indication that chloride is not at all oxidized.

Keywords: COD, hexavalent chromium, reduction, recovery, hazardous waste

1. Introduction

1.1 The Nature of the COD Determination

The chemical oxygen demand (COD) is a measure of the amount of oxygen needed to oxidize organic matter present in water. It is an important parameter in determining the extent of organic pollution in water and in

evaluating the efficiency of waste treatment processes. The dichromate titration and spectrophotometric method are commonly used methods for its determination. In either method, a dichromate ion, a strong oxidizing agent which is quite toxic, is used in excess amount. In the course of the reaction, the hexavalent chromium (Cr^{+6} or Cr(VI)) in dichromate ion is reduced to the trivalent chromium (Cr^{+3} or Cr(III)) as it oxidizes organic matter. The excess dichromate ion in the titration method is back titrated with ferrous ammonium sulfate (FAS) solution, while in the spectrophotometric method the absorbance due to excess dichromate ion is measured. Titration with FAS solution leads to further reduction of excess chromium(VI) to chromium(III). The COD of the sample is determined based on the result of the titration or the absorbance reading.

1.2 The Dangers of the Spent COD Reagents

Spent reagents in the determination of COD by the spectrophotometric method contain unreduced hexavalent chromium ion that represents major health and environmental risk due to its genetic effects. Chromium(VI) is known to cause cancer and various health effects in human. The carcinogenic effect of chromium(VI) has been substantiated both in animal experiments and by epidemiological studies on group of the population subject to workplace exposure (GTZ/BMZ, 1995). Some health problems that are caused by chromium(VI) are: skin rashes, upsets stomachs and ulcers, respiratory problems, weakened immune systems, kidney and liver damage, alteration of genetic material, lung cancer, and death (Lenntech Water Treatment and Air Purification Holding, 2006). In plants chromium(VI) causes root and leaf damage (GTZ/BMZ, 1995).

Aside from the dichromate, other dangerous reagents are also used in this analysis, namely, silver sulfate (Ag_2SO_4)-sulfuric acid (H_2SO_4) solution and mercuric sulfate (HgSO_4) which is used as oxidation catalyst and masking reagent for chloride, respectively. Mercury is very toxic and disposal is usually not a legal option. The only legal method for waste mercury handling is recycling.

1.3 The Problem Situation and Research Objectives

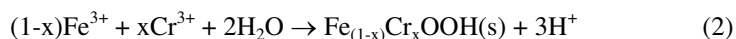
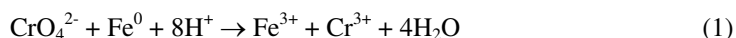
The situation presents some kind of a dilemma. On the one hand, protection of the environment and the control of wastewater treatment need constant and rapid testing of oxygen demand. On the other hand, the most convenient, fast, and economical method of determining oxygen demand introduces a

serious problem—hazardous wastes. A logical and practical resolution of this problematic situation was the general objective of this study, namely, to eliminate or transform chromium(VI) to a safer form and to recover or recycle mercuric sulfate in the spent COD reagents prior to disposal. Specifically, this study investigated the following: (1) the effect of the initial chromium(VI) concentration in the reduction-based detoxification of the ion found in the spent COD reagents; (2) the effect of the initial acidity in the same reduction process above; (3) the possibility of eliminating toxic mercury in the waste by recovering and regenerating it; and (4) the effectivity of the recovered mercury (as mercuric sulfate) as a masking agent for chloride interference in COD testing.

1.4 Related Technical Information

In contrast to chromium(VI) compounds, there is no evidence of the carcinogenic effect of chromium(III) compounds. Trivalent chromium is an important trace element for humans and animals in the insulin metabolism. This would be a channel for detoxifying the dichromate—reduction of chromium(VI) to chromium(III) utilizing a suitable reducing agent.

Hexavalent chromium is reduced by iron filings to trivalent chromium, Cr(III) (Swadle, 1997). Zero-valent iron, an important natural reductant of Cr(VI), is an option in the remediation of contaminated sites, transforming Cr(VI) to essentially non-toxic Cr(III) according to the following reactions (equation 1,2) involving coprecipitation (Shao-feng, Yong, Xin-hua and Zhang-hua, 2005):



Ponder, Darab, and Mallouk (2000), on the other hand, presented a quite different reaction (equation 3) for Cr(VI) reduction by zero-valent iron:



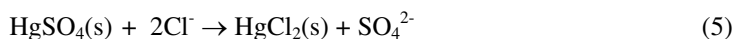
Both reactions made use of chromate ion, CrO_4^{2-} , as a source of Cr(VI).

In spent COD reagent, the reduction of Cr(VI) from dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$ by zero-valent iron, could be described as (equation 4):



H^+ and Cr^{6+} are reactants in the reduction process, thus, the extent of their effects on the reduction efficiency using iron filings (a zero-valent iron) is investigated. The use of iron filings is of considerable practical importance due to its availability and lower cost.

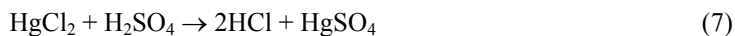
Mercuric sulfate ($HgSO_4$) is used to mask the interfering effect of chloride in the COD analysis. Mercuric sulfate eliminates chloride in the sample by forming the stable mercury-chloride complex (equation 5). The fundamental reaction involves the formation of mercuric chloride as follows:



Mercuric sulfate could theoretically be recovered from the COD spent reagents. Digesting the precipitate (Hg-Cl complex) with concentrated sulfuric acid (H_2SO_4) will produce hydrogen chloride (HCl) gas and regenerate $HgSO_4$. Sulfuric acid has been used to produce hydrochloric acid (HCl). Hydrochloric acid is prepared by reacting sodium chloride (NaCl) with sulfuric acid (H_2SO_4) (equation 6). The reaction is described by the following equation:



Thus, the reaction between $HgCl_2$ and H_2SO_4 could theoretically be described by the following equation (equation 7):



2. Methodology

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 recovery and reduction experiment. The liquid in the spent reagent was then separated from the precipitate through decantation. The supernatant liquid and precipitate were used for reduction and recovery experiments, respectively.

In the reduction experiment, two reaction conditions were investigated. One was in which the $Cr(VI)$ concentrations were varied while the acidity was held constant and the other was in which the acidities were varied while the $Cr(VI)$ concentration was held constant. These were done in order to evaluate the effect of $Cr(VI)$ concentration and acidity on the ability of iron

filings to reduce hexavalent chromium to trivalent chromium. Dilution was employed in order to vary both the Cr(VI) concentration and the acidity to 1/2, 1/3, and 1/4 of that of the undiluted sample. Dilution, however, would change both the Cr(VI) concentration and acidity of the solution, thus, calculated amounts of potassium dichromate or sulfuric acid were added prior the dilution to hold the Cr(VI) concentration or the acidity constant, respectively. Iron filings were then added to the sample at an amount equal to 1:1 Fe to Cr(VI) stoichiometric mass ratio. The concentration of the hexavalent chromium was then determined at 0hr, 2hr, 12hr, 24hr, and 36hr reaction time by titrating an aliquot of the sample with standard ferrous ammonium sulfate solution. The initial Cr(VI) concentrations of the collected spent reagents were also determined using the same method while the initial acidities were analyzed by titrating with standard sodium hydroxide solution.

The recovery of mercuric sulfate was done by digesting the sample (precipitate in the spent COD reagents) in concentrated sulfuric acid for four hours. The resulting white precipitate that was actually the solid HgSO_4 was collected through vacuum filtration using a fiberglass filter. It was then washed with ice-cooled distilled water and dried in an oven for 4 to 5 hours. The recovered mercuric sulfate was tested for its effectiveness to mask chloride in the COD analysis using the spectrophotometric method with closed-tube digestion. To test the masking ability of the recovered mercuric sulfate, three batches of COD analysis were conducted. In each batch, synthetic water solutions—with 20 ppm COD due to the organic matter, potassium hydrogen phthalate (KHP), and 1,000 ppm chloride—were analyzed with fresh mercuric sulfate, with recovered mercuric sulfate, and without mercuric sulfate added.

3. Results and Discussion

3.1 Reduction of Hexavalent Chromium

Table 1 shows the effect of initial Cr(VI) concentration in the reduction of Cr(VI) to Cr(III) by iron filings. The results indicate that the removal efficiency of iron filings in eliminating Cr(VI) decreased with decreasing initial concentration of Cr(VI). Total reduction could be attained at about 24 hours at higher hexavalent chromium concentration of approximately 1000 ppm.

Table 1. Percent reduction of Cr(VI) at different initial Cr(VI) concentrations

Initial Cr(VI) concentration	Percent reduction			
	2 hr reaction time	12 hr reaction time	24 hr reaction time	36 hr reaction time
$[\text{Cr}^{6+}]_0$	59.3(± 7.4)	81.7(± 2.9)	100(± 0.0)	100(± 0.0)
$1/2[\text{Cr}^{6+}]_0$	46.1(± 2.2)	72.0(± 2.0)	81.6(± 1.1)	100(± 0.0)
$1/3[\text{Cr}^{6+}]_0$	32.8(± 4.5)	66.9(± 1.7)	76.6(± 1.6)	83.9(± 1.9)
$1/4[\text{Cr}^{6+}]_0$	31.7(± 4.2)	65.6(± 1.1)	73.7(± 1.7)	81.1(± 2.4)

The two-way analysis of variance (Table 2) confirms the statistically significant effect of Cr(VI) concentration on the removal efficiency. In addition, the table shows the significant effect of reaction time and the initial Cr(VI) concentration-reaction time interaction on the removal efficiency.

Table 2. Analysis of variance for percent reduction of Cr(VI) at different initial Cr(VI) concentrations and reaction times

Source of variation	Sum of squares	Degrees of freedom	Mean of squares	F computed	P value
Initial Cr(VI)	6,268.44	3	2,089.48	255.18	0.0001
Concentration	27,286.46	3	9,095.49	1,110.80	0.0001
Reaction time	709.69	9	78.85	9.63	0.0001
Interaction	524.05	64	8.19		
Error within total	34,788.63	79			

$\alpha = 0.05$

Figure 1 shows the reduction that took place at different initial Cr(VI) concentration. It is apparent that a higher reduction rate occurred at the start but could not be maintained and tapers down later. Among others, this could be due to an initial sorption rate that caused the higher reduction rate and followed by the agglomeration of iron filings that decreased reactivity due to a decrease in the surface area of the iron filings.

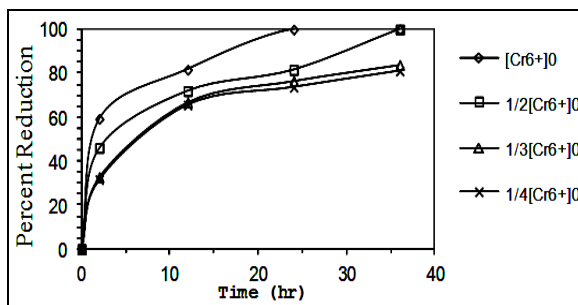


Figure 1. Effect of initial Cr(VI) concentration

The above findings were obtained when the initial acidity of the sample of spent COD reagents is maintained at 4.46 M H_2SO_4 , the acidity when the original sample was diluted with water at 1:1 ratio. At this condition, it was clear that removal efficiency of Cr(VI) in spent COD reagents decreased significantly when its concentration was lowered to 1/2, 1/3, and 1/4 by dilution. However, there seems to be no significant difference in the rate at which Cr(VI) was reduced to Cr(III) at an initial concentration between 1/3 and 1/4 of the Cr(VI) concentration of the undiluted sample.

Table 3 and Figure 2 show the effect of the initial acidity on the reduction efficiency of iron filings in eliminating Cr(VI) in spent COD reagents. The results indicate that lowering the acidity of the sample by dilution significantly increased the reduction rate. Complete reduction of Cr(VI) was achieved at about 12 hours reaction time when the acidity of the spent COD reagents was lowered to about 2.25 M H_2SO_4 which was 1/4 of the acidity of the undiluted sample.

Table 3. Percent reduction of Cr(VI) at different initial acidities

Initial acidity	Percent reduction			
	2 hr reaction time	12 hr reaction time	24 hr reaction time	36 hr reaction time
$[\text{Acidity}]_0$	3.8(± 1.4)	18.6(± 2.8)	30.9(± 4.9)	52.1(± 10.8)
$1/2[\text{Acidity}]_0$	59.3(± 7.4)	81.7(± 2.8)	100(± 0.0)	100(± 0.0)
$1/3[\text{Acidity}]_0$	63.9(± 3.9)	84.7(± 8.9)	100(± 0.0)	100(± 0.0)
$1/4[\text{Acidity}]_0$	64.7(± 3.9)	96.3(± 8.4)	100(± 0.0)	100(± 0.0)

The two-way analysis of variance (Table 4) confirms the statistically significant effect of acidity on the removal efficiency. In addition, the table

shows the significant effect of reaction time and the acidity-reaction time interaction on the removal efficiency.

Table 4. Analysis of variance for the percent reduction of Cr(VI) at different initial acidity and reaction time

Source of variation	Sum of squares	Degrees of freedom	Mean of squares	F computed	P value
Initial acidity	56,284.73	3	18,761.58	760.88	0.0001
Reaction time	19,340.03	3	6,446.68	261.38	0.0001
Interaction	1,563.91	9	173.77	7.05	0.0001
Error within total	1,578.51	64	24.66		
	78,767.17	79			

For samples with lowered acidities, Figure 2 shows that there seemed to be an initial sorption phase that was responsible for a higher rate of Cr(VI) removal initially.

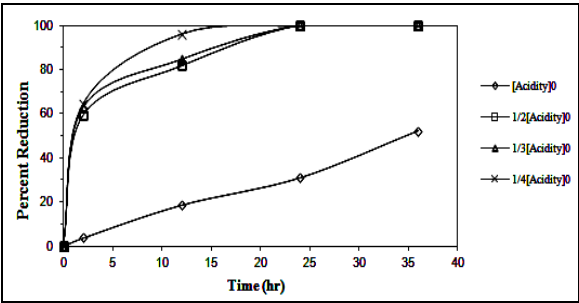


Figure 2. Effect of initial acidity

These results seem to contradict the findings of Shao-feng *et al.* (2005) that Cr(VI) removal efficiency increased significantly with decreasing pH, hence increasing the acidity. However, unlike the sample used by them in their study which was a highly aqueous solution, the waste chemicals generated in the determination of COD are essentially non-aqueous highly-acidic solutions and lowering the acidity by 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 H^+ concentration. Adding water to satisfy the condition, as considered in this study, only decreased the H^+ concentration by four and would only dilute the sample, while the highly acidic environment is maintained. It could be inferred, therefore, that removal of Cr(VI) by iron filings is faster in an aqueous but highly acidic environment.

In summary, the two experiments revealed that: (1) iron filings are effective for reducing Cr(VI) to Cr(III) as found in spent COD reagents that utilize $K_2Cr_2O_7$ as oxidant. As an effective reductant, it can, therefore, serve as a good detoxifying agent for this hazardous laboratory waste as far as the toxic Cr(VI) is concerned; (2) the speed of the Cr(VI) reduction is proportional to the concentration of the ion. It is faster at higher concentration. Therefore, the reduction process is best when the Cr(VI) in the waste reagent is maintained. This is about 1000 ppm.; and (3) the level of acidity is an important factor in the speed of the reduction since the speed increases as the acidity level decreases. For the waste COD reagents, reduction is best achieved at an acidity level which is 25% of the initial.

For practical application, a 1:1 dilution ratio of the waste was enough for a total removal of Cr(VI) in the sample. Although at this water-to-sample ratio acidity was lowered by half which enhanced reduction efficiency, Cr(VI) concentration was also decreased by half which slowed down the reduction. In spite of this, total removal of Cr(VI) is still achieved. Non-dilution was not an option for the treatment. As can be seen clearly in Figure 2, the reduction for undiluted sample occurred at a very slow rate even at the start.

3.2 Recovery of Mercuric Sulfate

Figure 3 shows the mercuric sulfate recovered in this study in the form of basic mercuric sulfate, $HgSO_4 \cdot 2HgO$. Mercuric sulfate, $HgSO_4$, is a white powder while $HgSO_4 \cdot 2HgO$ is a yellow powder—an insoluble product formed between $HgSO_4$ and water. As mentioned in the methodology, ice-cooled water was used in washing the recovered $HgSO_4$ after H_2SO_4 digestion, thus, formation of $HgSO_4 \cdot 2HgO$ was inevitable in this investigation.

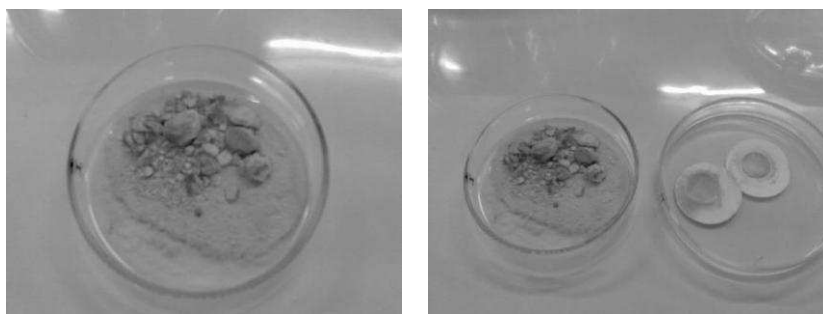


Figure 3. Basic mercuric sulfate as recovered mercuric sulfate. (Left) close-up photo of $HgSO_4 \cdot 2HgO$ (Right) $HgSO_4 \cdot 2HgO$ with fiber glass filter.

Table 5 shows the results in the COD determination of synthetic water solutions with 20 ppm COD and 1,000 ppm Cl^- analyzed with recovered HgSO_4 , with fresh HgSO_4 , and without any masking agent added. The column “COD expected” in the table is the COD of the sample if Cl^- was oxidized to the extent of 50%.

Table 5. COD of Chloride-containing synthetic water solutions analyzed with recovered and fresh HgSO_4 as masking agent and without masking agent

Types of masking agent	COD (mg/L O_2)		
	As prepared	Expected	Actual [mean(sd,n)]
Recovered HgSO_4	20	133	20.4 ($\pm 5.6, 29$)
Fresh HgSO_4	20	133	20.6 ($\pm 2.6, 24$)
No HgSO_4 added	20	133	24.2 ($\pm 1.6, 27$)

Statistical test by ANOVA in Table 6 reveals that a significant difference exists among the COD results. Further test by Scheffe shown in Table 6 reveals that the actual COD of the sample analyzed without adding HgSO_4 is significantly different from the COD of the sample analyzed with recovered HgSO_4 and with fresh HgSO_4 while there is no significant difference in the COD between sample analyzed with recovered HgSO_4 and with fresh HgSO_4 .

Table 6. Analysis of variance for the COD of chloride-containing synthetic sample analyzed with recovered and fresh HgSO_4 as masking agent and without masking agent

Source of variation	Sum of squares	Degrees of freedom	Mean of squares	F computed	P value
Treatment					
Between	183.41	2	91.79	5.30	0.007
Error within	1333.38	77	17.32		
total	1516.79	79			

$$\alpha = 0.05$$

Although statistical tests reveal that a significant difference exists between samples analyzed with masking agents (fresh or recovered) and samples analyzed without masking agent; from the practical point of view in the field, the observed results are small and not conclusive to establish a difference in COD between ‘with masking agent’ and ‘without masking agent’. Recovered HgSO_4 was just as good as fresh HgSO_4 .

Table 7. Scheffé method for the recovered HgSO_4 , fresh HgSO_4 , and no HgSO_4 added

	No HgSO_4 added	Fresh HgSO_4	Recovered HgSO_4
Recovered HgSO_4	2.69*	0.35	
Fresh HgSO_4	2.92*		
No HgSO_4 added			
Critical value = 2.49			*Statistically significant

Table 5 show statistically significant difference between the samples analyzed, it also seem to reveal negligible effect of HgSO_4 as masking agent for chloride. In this method of COD determination, chloride in the sample appeared to remain practically unoxidized. The 133-ppm expected COD of the sample when Cl^- would be oxidized by 50% was not attained, instead, COD results were closer to 20-ppm COD of the organic matter, KHP, present in the sample. To further verify this finding, another test was conducted comparing the COD of chloride-containing and non-chloride-containing synthetic samples both analyzed spectrophotometrically without adding HgSO_4 . The test also evaluated the oxidizability of chloride in the sample under the spectrophotometric method of COD determination with closed-tube digestion.

Table 8 shows the COD of a chloride-containing and non-chloride containing synthetic water solutions analyzed without the chloride masking agent, HgSO_4 . The results show that the actual COD of the chloride-containing and non-chloride-containing samples is comparable.

Table 8. COD of chloride- and non-chloride containing samples

Samples	Chloride content (ppm)	COD (ppm)	
		Theoretical (as prepared)	Actual (as analyzed) [mean(sd,n)]
Chloride-containing	1,000	20	24.2 ($\pm 1.6, 27$) (no HgSO_4 added)
Non-Chloride containing	0	20	22.4 ($\pm 2.5, 10$) (no HgSO_4 added)

To scrutinize the data more closely, a t-test for two independent samples was employed. Results, as shown in Table 9, reveal that the 24.2 ppm COD for the chloride-containing solution does not differ significantly from the 22.4 ppm COD for the non-chloride-containing solution both with 20 ppm COD

and analyzed without adding mercuric sulfate. This clearly indicates that in this method of COD determination chloride was not oxidized by COD reagent to any significant extent. One possible reason could be that the closed-vessel digestion prevented the escape of oxidized chloride as chlorine gas. This in turn prevented the oxidation from proceeding following the Le Chatelier's Principle. This is an interesting result because it could mean eliminating the use of a highly toxic HgSO_4 in the analysis. But still, further investigation must be conducted to explore and understand this phenomenon.

Table 9. t-test of independent samples: COD of chloride containing sample vs. COD of non-chloride containing sample

Difference between means	1.8
Standard deviation	2.9198
t-value	2.122
Degrees of freedom	11
Probability	0.972992
Significance level	0.05
Conclusion	Not statistically significant

4. Conclusions and Recommendations

This research has succeeded to establish a relatively simple process for treating the hazardous spent COD chemicals through the reduction of toxic chromium (VI) with ordinary iron and the recovery of mercuric sulfate by acid digestion followed by filtration. Unexpectedly, it has also demonstrated that mercuric sulfate is not necessary as a masking agent in the spectrophotometric method of testing for COD which uses a closed-tube digestion set-up. It is, however, important in the more conventional method of open-tube digestion followed by titration.

In turn, the output of this research is significant in five respects: (1) it supports the continued use of a relatively simple and inexpensive method for monitoring environmental pollution and, therefore, contributes to the promotion of a cleaner environment; (2) it does the above without introducing toxic testing substances to the environment through a simple method of detoxification and recovery that can easily be adopted; (3) it suggests a further simplification of the COD testing through the removal of mercuric sulfate in the test process, thereby, also reducing the hazard level of the spent reagents; (4) it lays down the basis for a mass treatment process for chemical wastes which process points to a significant socio-economic impact; and (5) it does not only innovate a technology for treating chemical

wastes but also leads to a technical refinement of a laboratory testing method.

For further research, environmental and analytical scientists alike are encouraged to study the effects of increasing the amount of iron filings in reducing hexavalent chromium to establish effective Fe^0 concentration for the reduction at shorter time and to study more extensively the extent of oxidation of chloride under the spectrophotometric method of COD determination which requires closed-tube digestion. The following related researches are also suggested, namely, (a) study of the reducing efficiency of other reducing agents for Cr(VI) in COD wastes such as sulfur dioxide, sodium sulfite, sodium bisulfite, and ferrous sulfate, and (b) study of the ability of silver ion (silver sulfate) as masking agent for chloride and catalyst in the digestion of organic matter in the spectrophotometric determination of COD.

5. References

GTZ/BMZ, (1995). Environmental Handbook Volume III: Compendium of Environmental Standards, Deutsche Gesellschaft für Technische Zusammenarbeit (GTZ) GmbH, Germany. Retrieved from <http://www2.gtz.de/uvp/publika/English/vol327.htm>.

NIU Shao-feng, LIU Yong, XU Xin-hua, and LOU Zhang-hua, (2005). Removal of hexavalent chromium from aqueous solution by iron nanoparticles. Retrieved from <http://www.zju.edu.cn/jzus/2005/B0510/B051011.pdf>.

Ponder, S.M., Darab, J.G., and Mallouk, T.E., (2000). Remediation of Cr(VI) and Pb(II) aqueous solution using supported nanoscale zero-valent Iron. Retrieved from <http://research.chem.psu.edu/mallouk/articles/es9911420.pdf>.

Swaddle T.W., (1997). Inorganic chemistry: An Industrial and Environmental Perspective. San Diego, California 92101-4495, USA: Academic Press.

