# Validation of Nernst Equation for Hexavalent Chromium Reduction Process

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**Abstract:** Generally, chromium is stable at oxidation number of +3 and +6. Trivalent chromium $Cr^{3+}$ is non-toxic but hexavalent chromium $Cr^{6+}$ is. Hexavalent chromium is also known to be carcinogenic which is highly toxic and does dissolve in water. Among various kinds of treatment methods, reducing hexavalent chromium to trivalent chromium is one of the best and commonly used methods. In the study, synthetic wastewater containing chromium will be titrated by iron (II) sulphate until all chromium ions were fully reduced by iron (II) sulphate. ORP was used as a control parameter to optimize the amount of reducing agent to be added in the process. There were three different methods to monitor the change of OPP value in the reduction process. First, the ORP value is monitored manually. Secondly the ORP readings were monitored online through computer program and finally using an auto titrator (Mettler Toledo DL50). The results have been compared, and we found that the ORP changes given the same trend for all the experiments. It proven that all $Cr^{6+}$ ion was completely reduced when ORP values achieve the peak. This finding was validated by the computer simulation gave the same results as the experimental results. As the conclusion, the chromium reduction process using ferrous sulphate obeyed the Nernst equation. On the other hand, ORP can be used as a sensitive and effective controller to optimize the reducing agent for the hexavelent chromium reduction process

**Keywords:** *Hexavalent chromium; Nernst Equation; controller, optimization*

## 1. Introduction

Generally, chromium exists in ionic form with oxidation number +3 or +6 where $Cr^{3+}$ is relatively more stable then $Cr^{6+}$ on the other hand $Cr^{6+}$ is relatively more soluble in water compared to $Cr^{3+}$. The high solubility of $Cr^{6+}$ in water increase the water pH value, in addition high toxicity of hexavalent chromium will also pollute the water once it dissolves in water. As the acute effect, water polluted by hexavalent chromium will cause skin irritating and certain disease like ulceration. As the chronic effect, hexavalent chromium in water could destroy our liver and kidneys. So, the United States Environmental Protection Agency (EPA) had passed the Safe Drinking Water Act since 1974 stated that the maximum chromium content in our drinking water is at 0.1 ppm.

There is various type of treatment method on chromium polluted water has been discovered. There is chemical reduction, precipitation, ion exchange and electrolysis. Among all these treatment methods, reducing hexavalent chromium to trivalent chromium is one of the best and commonly used methods. According to [2] trivalent chromium has 3 electrons at d orbital which are the higher

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spin in octahedral plane. So, hexavalent chromium tends to be reduced to trivalent chromium which is more stable. The reduction process of hexavalent chromium can be represented with the equation below.

$$Cr^{6+} + 3e^- \rightarrow Cr^{3+} \qquad (1)$$

To reduce hexavalent chromium, a reduction agent is necessary. Iron is one of the cheaper reduction agents which is commonly use in water treatment field. According to [3] metal iron as reduction agent gives slow reaction rate, but iron salt like $FeSO_4.7H_2O$ give a better result where the reaction will complete within 1-2 minutes only. In addition, [4] had reported that the use of iron salt as the reduction agent in water treatment can also remove cyanide ion which is content in the polluted water. So, by using iron salt as reduction agent, the rate equation of the process can be written as below [5].

In this study, ORP value (Oxidation-Reduction Potential) had been chosen to be the control signal on the amount of reduction agent adding into the sample. According to [6] this technique is very accurate and effective to use. Therefore, this technique is still in use until today because it is the only method that can measure the content of hexavalent chromium in low concentration accurately by using the online ORP meter [7].

$$-\frac{d[Cr(VI)]}{dt} = k[Cr(VI)][Fe(II)] \qquad (2)$$

with,
$k = [4.4 \times 10^3 M^2 s^1 (H^+)] + [3.0 \times 10^5 M^3 s^1 (H^+)^2] +$

$[3.0 \times 10^4 M^{-1e} \beta_{FeOH}^+(OH^-)] + [1 \times 10^{8-} M^{-1} s^{1e} \beta_{Fe(OH)2}(OH)_2]$
$^e\beta_{FeOH}^- = 3.16 \times 10^4 M^{-1}$, $^e\beta_{Fe(OH)2} = 3.16 \times 10^7 M^{-2}$ at low ion concentration.

According to [7] ORP is related with the concentration of an oxidizer or a reducer in a solution. It can be a signal for the potential of a solution to oxidize or reduce other particles. In a solution, the existing of oxidation agent increases the ORP value whereby the existing of reduction agent decrease the ORP value. Study by [8] also reported that, at certain pH value, ORP value can detect the end point of a redox reaction. Generally, extra reduction agent will be added into the sample to ensure the reaction is complete. But in water treatment concern, the additional reduction agent in water will also polluting the water. In this case, the amount of reduction agent adding into the water need to be controlled to optimize the cost and to ensure the quality of water [7]. In this paper, ORP value is use as a signal to optimize the adding of reduction agent to reduce hexavalent chromium in water. Theoritically, the reaction is obey to Nernst equation [3-4]

$$E = E_o + \frac{RT}{nF} \ln \frac{[oxidised\ form]^x}{[reduced\ form]^y} \qquad (3)$$

with,

$E$ = electrode potential reading (mV)

$E^o$ = standard electrode potential (mV)

$n$ = number of electron shifted from oxidation

agent to reduction agent

$R$ = gas coefficient (8.314J/°C)

$T$ = absolute temperature (298K)

$F$ = Faraday coefficient (96500 C)

$x, y$ = stoichiometry coefficient for particular ion.

According to this equation, the measurement of redox potential is proportional to the fraction of oxidized material activities to reduced material activities which are in the equilibrium form [7]. So, at the absolute temperature, 298K, Nernst equation can be written as below.

$$E = E^o + \frac{8.314 \times 298 \times 2.303}{z \times 96500}$$
$$\log \frac{[oxidised\ form]^x}{[reduced\ form]^y} \qquad (4)$$

$$E = E^o + \frac{0.0591}{z} \log \frac{[oxidised\ form]^x}{[reduced\ form]^y} \qquad (5)$$

And the overall process can be represented by the partial chemical equations as below.

oxidation: $\quad 3Fe^{2+} \leftrightarrow 3Fe^{3+} + 3e^- \qquad (6)$
reduction: $\quad Cr^{6+} + 3e^- \leftrightarrow Cr^{3+} \qquad (7)$
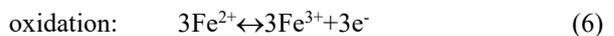
So, if we bring these equations into Nernst equation at the absolute temperature, we get

$$E_1 = E_1^0 + \frac{0.0591}{3} \log \frac{[Fe^{3+}]^3}{[Fe^{2+}]^3} \qquad (8)$$

$$E_2 = E_2^0 + \frac{0.0591}{3} \log \frac{[Cr^{6+}]}{[Cr^{3+}]} \qquad (9)$$

Usually, redox potential is measure by using a galvanized cell which is using standard electrode made by platinum or gold [7]. The measurement is more refer to ratio of total oxidized species to total reduced species that contain in equilibrium state. By this theory, we can write the equation below.

$$E_{cell} \alpha \ln \left[ \frac{\sum_{i=1}^{M} [oxidised \ material]}{\sum_{i=1}^{M} [reduced \ material]} \right] \qquad (10)$$

For the case hexavalent chromium reduced by iron salt, the readings from the ORP meter are more to the ratio written below.

$$ORP \alpha \ \ln \frac{[Cr^{6+}][Fe^{3+}]^3}{[Cr^{3+}][Fe^{2+}]^3} \qquad (11)$$

According to this equation, ratio of [oxidized material]/ [reduced material] for a redox system can be verify by the ORP readings of the system [9]. Hence, by using Matlab or others related computer program, a simulation on ratio of ion concentration can be generated. Both result from computer simulation and laboratory test will be compared to verify the redox reaction is obey to the Nernst equation.

Refer to the previous report by [7] a computer simulation had been done by SIMNON Version 2.04/Regular (SSPA Systems, Sweden). The result of the simulation is given by the graph below. The trend of ORP value change showing that the adding of reduction agent at early reaction, ORP value decreased enormously. ORP value begins to increase once the reaction starts because of the oxidation of ion $Fe^{2+}$ to $Fe^{3+}$. However the rate of ORP value increase become slower and reach a maximum point where most of the $Fe^{3+}$ ion had combined with $Cr^{3+}$ ion to form a precipitate which is known as $(Cr_xFe_{1-x})(OH)_3$. ORP value then decreased again since all the $Cr^{6+}$ ion had finish reacted but iron salt still adding in continuously.

The main objective of this paper is to study the trend of ORP change during the process of reducing hexavalent chromium to trivalent chromium by using iron (II) sulphate as the reduction agent. ORP values are recorded manually and by using computer online reading from ORP meter and by using autotitrator. Finally, the process will relate to the Nernst equation to create a computer simulation by Matlab to validate the reduction process is obey to Nernst equation. In addition, to validate the use of ORP value to be the control signal on the amount of reduction agent adding into the chromium polluted water as presented in Figure 1.0.
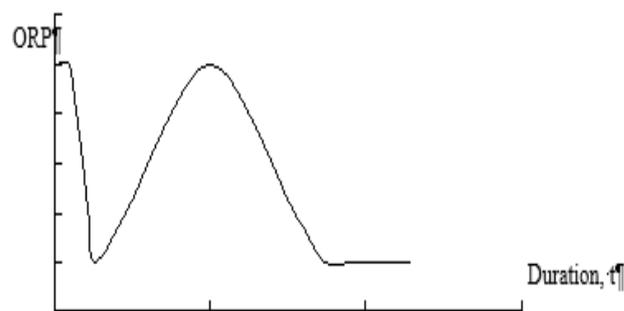


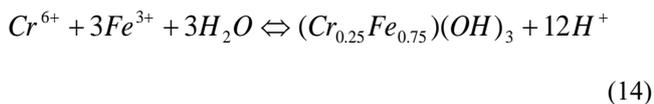Figure 1.0       Graph ORP versus duration

## 2. Materials and Method

Chemical required in this experiment is Potassium Dichromate ($K_2Cr_2O_7$), Iron sulphate ($FeSO_4.7H_2O$), 1,5-diphenylcarbohydrazide which is ChromaVer 3 reagent chromium powder use for detecting the existing of hexavalent chromium by using HACH machine and iron reagent which is used to detect the existing of ion $Fe^{2+}$.First of all, potassium dichromate salt is use as the source of hexavalent chromium ion in the synthetic chromium solution. 5.6577g potassium dichromate diluted in 2L of distillation water to produce chromium stock solution with concentration 100mg/L. Different volume of chromium solution had been diluted to produce chromium solution with different concentration. Iron salt solution which is function as the oxidation agent is prepare by diluting 55.6g $FeSO_4.7H_2O$ in 1 Liter water to produce iron solution in concentration 1mol/Liter. Concentration of stock solution had been tested by using HACH machine by using related reagent in standard method.

There are three types of tests in this study. Firstly, ORP readings for the whole process recorded manually. Chromium aliquots 20mg/L had feed into a 2 Liter beaker which is ready with an ORP probe and pH meter. pH readings is measure by pH Schott Model 672P (Great Lakes Instruments, Portugal) until 2 decimal points. On the other hand, ORP is measure by ORP meter Schott Model 672R (Great Lakes Instruments, US) until 0.01 unit also. By using a burette, the prepared iron solution is titrated into the chromium aliquots. A magnetic stirrer (Snijders Scientific Tilburg, Netherlands) is necessary to ensure the chemical reaction run averagely. pH and ORP readings of the process recorded every 5ml iron salt added. Sample had been taken every 5ml iron salt added to analyze the existing of chromium ion. Ion analysis is analyzed by spectrophotometer HACH DR/2000 Model 44800-00 (Colo, U.S.).

Secondly, ORP readings will be read online through computer. The setting of the instruments remains the same. ORP and pH value of the process is recorded into the computer every second automatically. Finally, the experiment will run by using autotitrator (Mettler Toledo DL50). Stock chromium solution had been diluted to different concentration before the tests begin. Since the

volume of the container provided by the autotitrator is very limited, only 80ml of sample is use for every test. All details and particulars which are necessary keyed into the autotitrator before the test start. Titrant will be titrated into the sample from 0.02ml/unit to 0.2ml/unit depends on the change of ORP value. Ion content in the sample is analyzed at the end of every run of the test.

According to [7] the change of ORP for the system is obey to Nernst equation which is used to represent the change of electrode potential while the redox process. Hence, a computer simulation had been created to verify that the change of ORP value that obtained in the experiment heuristically, online through computer and autotitrator on hexavalent chromium reduction process by using iron sulphate as the reduction agent are obey to the Nernst equation. Generally, the process can be summarized in the equations below. 0.2 had been added on the $Fe^{2+}$ differential equation to represent iron solution is added continuously. All these equations get combined and simulate according to time by Matlab Version 6.01. By solving all the equation stated above, the change of ORP value is successfully be simulated and pH value of the process also can be calculated.

$$3Fe^{3+} \Leftrightarrow 3Fe^{3+} + 3e^- \tag{12}$$

$$Cr^{6+} + 3e^- \Leftrightarrow Cr^{3+} \tag{13}$$

$$Cr^{6+} + 3Fe^{3+} + 3H_2O \Leftrightarrow (Cr_{0.25}Fe_{0.75})(OH)_3 + 12H^+ \tag{14}$$

Every element in the equations is differentiate by time as below.

$$\frac{d[Fe^{2+}]}{dt} = -k_1[Fe^{2+}]^3 + k_2[Fe^{3+}]^3[e^-]^3 + 0.2 \tag{15}$$

$$\frac{d[Fe^{3+}]}{dt} = k_1[Fe^{2+}]^3 - k_2[Fe^{3+}]^3[e^-]^3 - k_5[Cr^{3+}][Fe^{3+}] + k_6[H^+]^{12} \tag{16}$$

$$\frac{d[e^-]}{dt} = k_1[Fe^{2+}]^3 - k_2[Fe^{3+}]^3[e^-]^3 - k_3[Cr^{6+}][e^-]^3 + k_4[Cr^{3+}] \tag{17}$$

$$\frac{d[Cr^{6+}]}{dt} = -k_3[Cr^{6+}][e^-]^3 + k_4[Cr^{3+}] \tag{18}$$

$$\frac{d[Cr^{3+}]}{dt} = k_3[Cr^{6+}][e^-]^3 - k_4[Cr^{3+}] - k_5[Cr^{3+}][Fe^{3+}] + k_6[H^+]^{12} \tag{19}$$

$$\frac{d[H^+]}{dt} = k_5[Cr^{3+}][Fe^{3+}] + k_6[H^+]^{12} \tag{20}$$

$$ORP = \log \frac{[Cr^{6+}][Fe^{3+}]^3}{[Cr^{3+}][Fe^{2+}]^3} \tag{21}$$

$$pH = -\log[H^+] \tag{22}$$

## 3. Results and Discussion

First, ORP value of the process is obtained heuristically through the ORP probe. There are four runs of test had been done by using four different concentration chromium solutions. All the results showed a same pattern of graph ORP versus volume of iron sulphate added. Through the graph, we observe that the ORP value decrease immediately the reduction agent added into the hexavalent chromium.

This is because of the default potential different of $Fe^{3+}/Fe^{2+}$ system in the iron solution with the $Cr^{6+}/Cr^{3+}$ system which represent the chromium solution [7]. While the process begins, ORP reading decrease because of the introduction of reducing agent $Fe^{2+}$. The ORP value begin to increase once the oxidation agent $Cr^{6+}$ started to react and ion $Fe^{2+}$ had been oxidize to $Fe^{3+}$. Refer to what [10], the existing of an oxidation agent increase ORP value meanwhile the reducing agent decrease the ORP value. Perhaps, the rate of increasing of ORP value become slower when most of the $Cr^{3+}$ and $Fe^{3+}$ ion combined to form a complex precipitate which is brown in color $(Cr_{0.25}Fe_{0.75})(OH)_3$. The ORP value of the process increase continuously until it reaches a peak. Here, all the $Cr^{6+}$ which contain in the water had been totally reduce to $Cr^{3+}$ by the reducing agent. This finding is verified by the ion analysis by using spectrophotometer HACH. Hence, the ORP value started to decrease since the reducing agent is still adding continuously into the process. The overall result of the heuristically test on ORP value is showed in Figure 3 to Figure 6.

The second test and the third test are both using the computer online program and the autotitrator (Mettler Toledo DL50) to trace the change of ORP readings for the process. Generally, the results give the similar trend of ORP changed for both tests. The ORP value showed a little decreasing at the beginning of the process and then increase to a maximum value where most of the $Cr^{6+}$ had finished

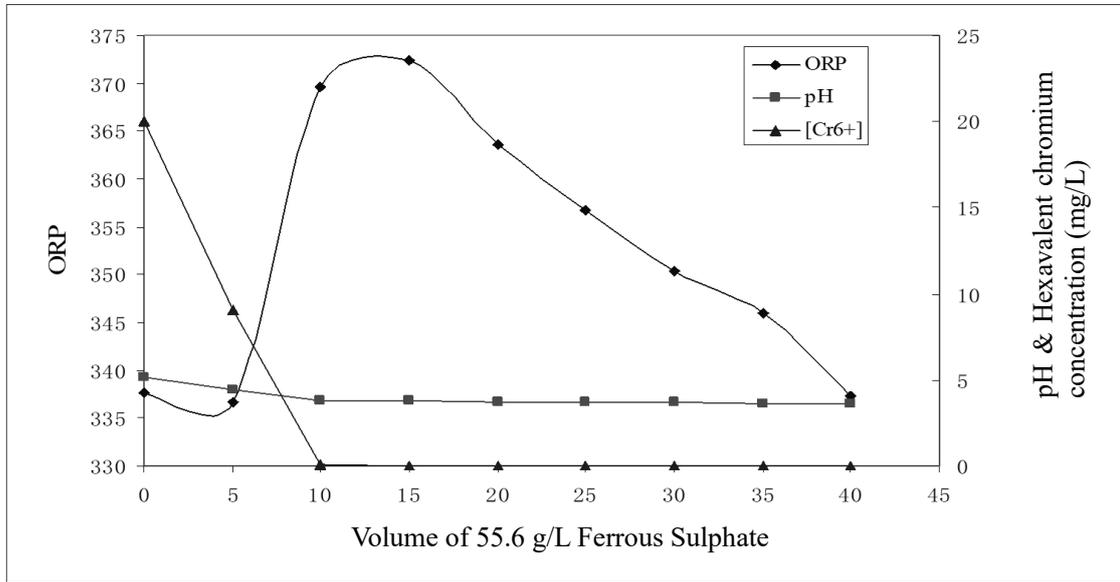reacted with the reduction agent to form a complex precipitate.



Figure 3.0 ORP, pH and $Cr^{6+}$ concentration change versus volume of iron solutionb added into the hexavalent chromium 20 mg/L
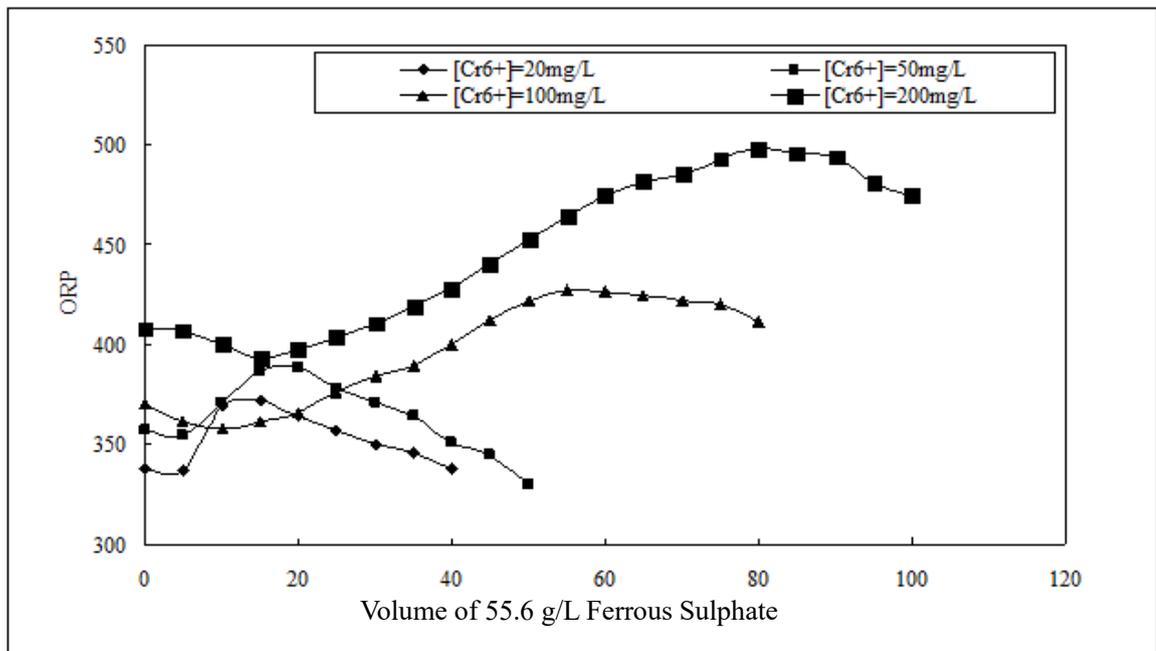


Figure 4.0 ORP change versus volume of iron solutionb added in to the hexavalent chromium
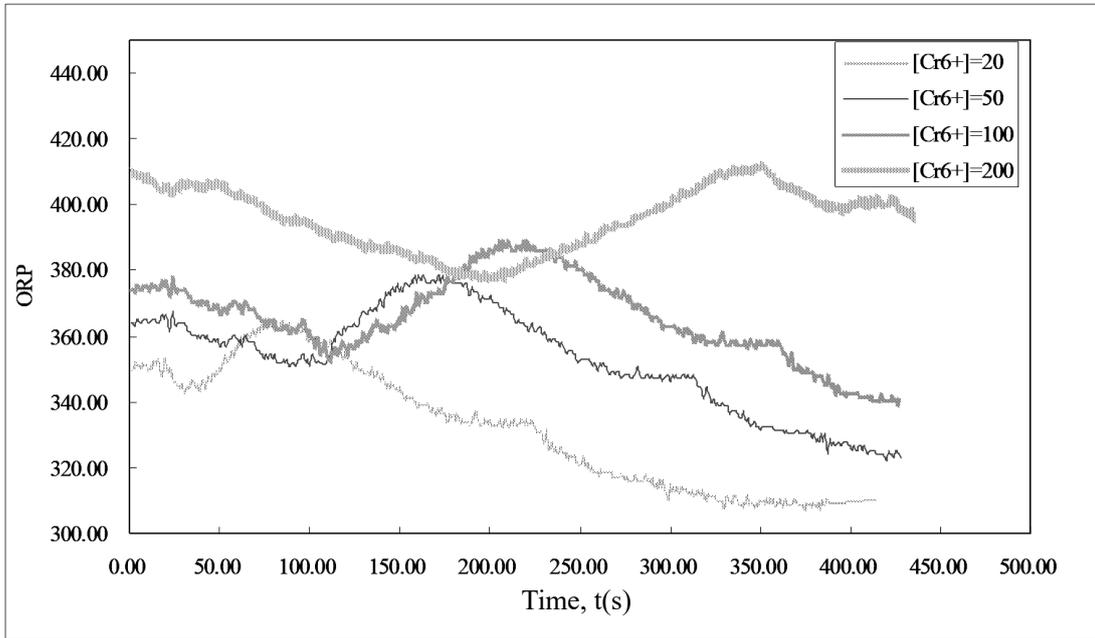
Figure 5.0      ORP change versus volume of ferrous sulphate solution added in to the hexavalent chromium
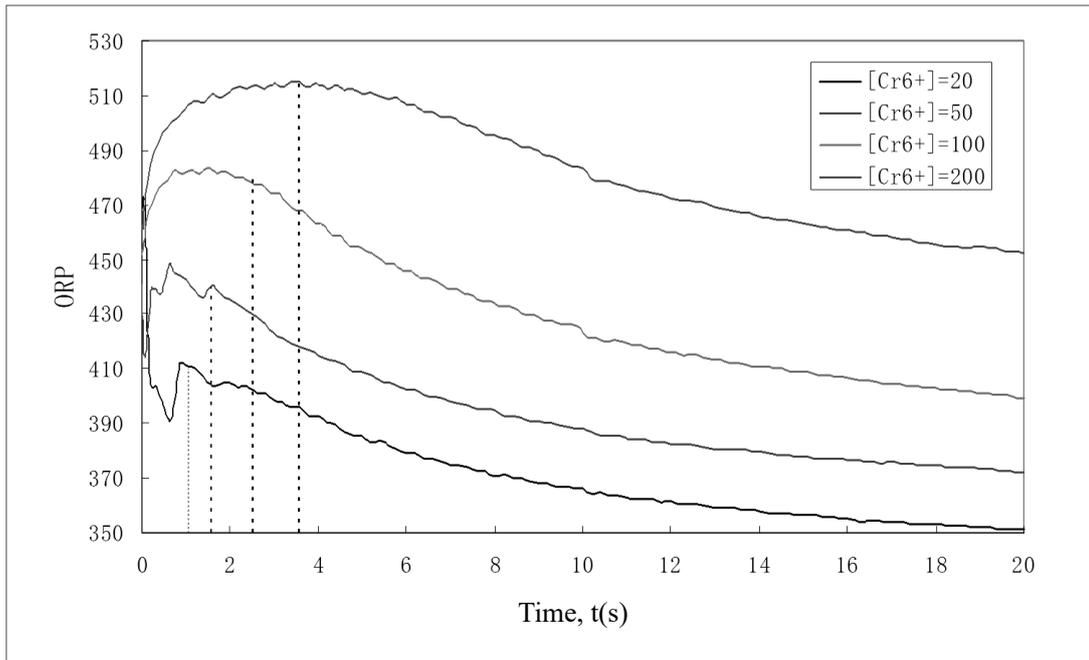


Figure 6.0      ORP change versus volume of ferrous sulphate solution added into the hexavalent chromium
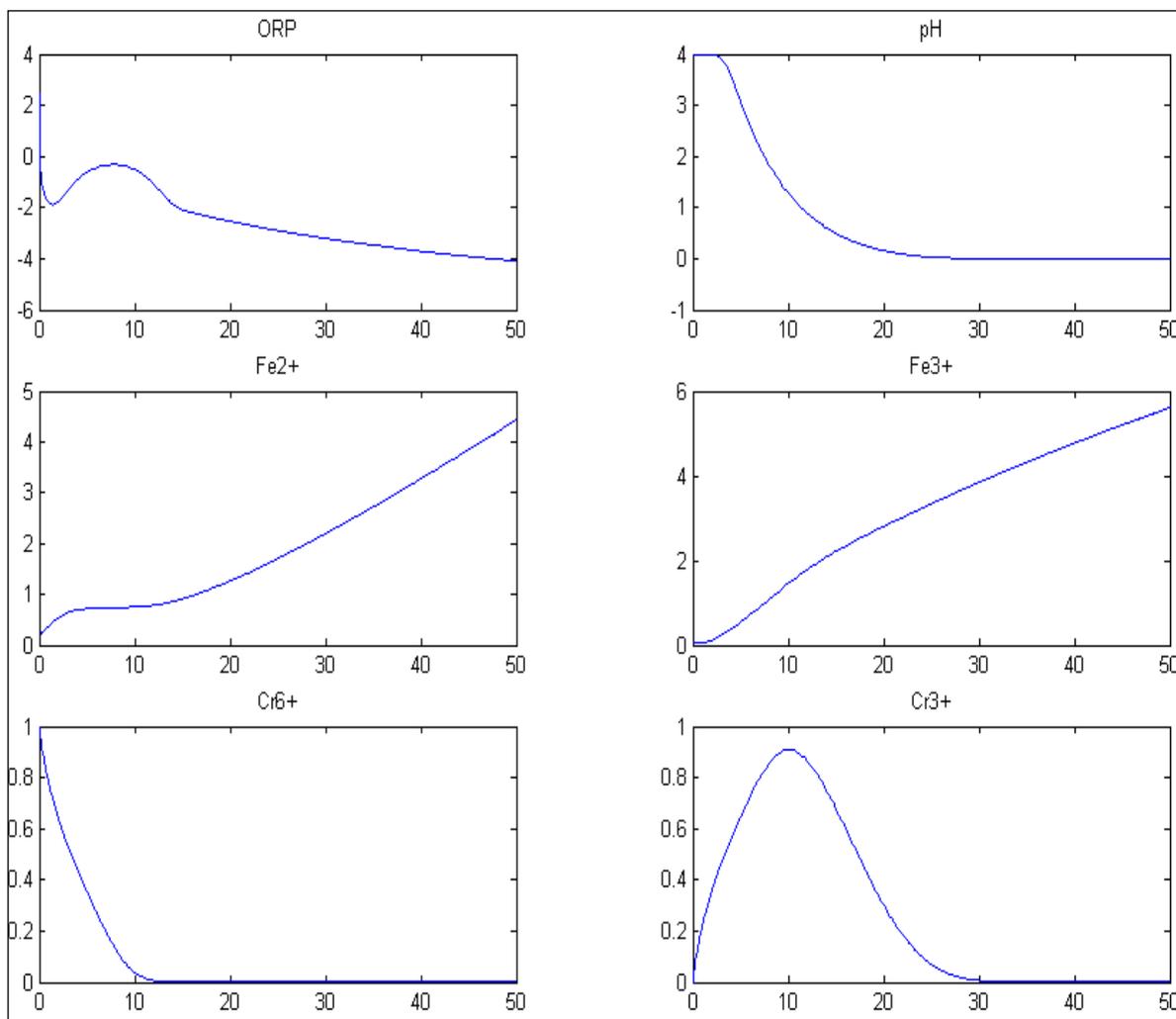
Figure 7.0 ORP change versus volume of iron solutionb added into the hexavalent chromium

Similarly the finding is verified by doing the ion analysis by using HACH spectrophotometer Since the reducing agent keep adding continuously, the ORP value keep decreasing after the peak. The results are showed in the Figure 3 to Figure 6. From all these three diagrams, we notice that the pattern of the graph is shifting to the right when the concentration of chromium solution increase. Hence, it's proven that more reducing agent is required when the chromium contains increase. Finally, the result will be compared with the computer simulation result. The computer simulation is created using Matlab base on Nernst equation. A few simulations had been run based on different initial value. Among all the tests, this is the best set of initial value which can represent the process apparently.

Table 1.0  Rate coefficient and concentration

| Rate Coefficient | | Initial Concentration | |
| --- | --- | --- | --- |
| $k_1$ | 0.5 | $Fe^{2+}$ | 0.2 |
| $k_2$ | 0.001 | $Fe^{3+}$ | 0.05 |
| $k_3$ | 0.1 | $e^-$ | 1.5 |
| $k_4$ | 0.001 | $Cr^{6+}$ | 1 |
| $k_5$ | 0.01 | $Cr^{3+}$ | 0 |
| $k_6$ | 0.00001 | $H^+$ | 0.0001 |

The $Cr^{6+}$ concentration is initially equal to 1. The number 0.2 had been chosen as the initial value for $Fe^{2+}$ concentration because $Fe^{2+}$ is added continuously into the process. Since the fast oxidation rate of $Fe^{2+}$, we let the initial value of $Fe^{3+}$ to be 0.05. Since the whole system is based on an electolide solution, there must be a lot of free electrons contain in the solution. Since the initial pH reading of the system is around 4.0, the concentration of free hydrogen ion is written as

0.0001. Based on equations (13) - (22), the result of simulation is shown in Figure 6.

Here we can see all the trends of change for iron and chromium ion. Similarly, the ORP value change give the same pattern as what had been done in the experiment and most of the chromium are finished reacting at the peak of the ORP value. The simulation successfully verifies the chromium reduction process is obey to Nernst equation and therefore ORP is an efficiency parameter to control the adding of reducing agent into the system to obtain the optimum state of treatment.

## 4. Conclusions

There are three different methods of experiment had been done by using the various concentrations of synthetic hexavalent chromium solutions and the experimental results are verified by the Matlab computer simulation. All the results give a similar trend of ORP change for the process. Through the ion analysis by using HACH spectrophotometer, hexavalent chromium contains in the solution almost finished reduced to $Cr^{3+}$ at the peak of the ORP value. Hence, we can conclude that the ORP is an efficient control parameter in controlling the adding of reducing agent in the water treatment process. Therefore, the computer simulation also verifies the process is obey to Nernst equation. The computer simulation results had strengthen the facts we find in the experiment.

## 5. Acknowledgment

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