

# Investigation of Hexavalent Chromium Reduction in Strong Saline and Acidic Nitro-Phosphate Solutions

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## Abstract

Phosphorus fertilizers from less pure sedimentary sources become increasingly important, due to depletion of phosphorus from igneous rock of high quality. Consequently, robust methods with potential to remove various types of hazardous elements are required. Among such impurities, hexavalent chromium (Cr(VI)) is very likely to become a future challenge. Different industrial ways to treat phosphate rock are currently being practised, and we have here studied how chromium behaves when using the nitro-phosphate process. The reduction mechanism of Cr (VI) in nitric acid and phosphoric acid solutions was investigated by measuring redox potential and UV-VIS spectra. The results show that Cr (VI) is not stable in strong nitric acid solutions. Reduction of Cr (VI) species decreased with decreasing temperature, NO<sub>2</sub> concentration, ionic strength and absence of light. These findings support the proposed reduction reaction:  $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{NO}_2 + 2\text{H}^+(\text{aq}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + \text{H}_2\text{O} + 6\text{NO}_3^-(\text{aq})$ . The reduction rate was observed proportional to the nitric acid decomposition:

$$\text{Rate Cr(III)} \propto k_1 \cdot [\text{HNO}_3]^2 \cdot [\text{Cr(VI)}] / (k_2 + k_3 \cdot [\text{H}_2\text{O}])$$

## Keywords

Nitro-Phosphate Fertilizers, Chromium (VI) Reduction, Chromium Speciation, Ultraviolet-Visible Spectroscopy

## 1. Introduction

One of the largest challenges of the twenty-first century is to address future global food demands in a sustainable way. While the world population continues

to grow the high quality phosphorus reserves become systematically scarce [1]. Phosphorus (P) is an essential element for all living beings, and therefore remains a critical component of fertilizers to sustain the global level food production. Most of the P is primarily supplied from phosphate rock (P rock), which is a finite resource, and is expected to be depleted within the next 100 years [2]. Phosphate rock occur mainly either as sedimentary deposits or igneous ores associated with alkaline rocks. In contrast to sedimentary rocks, igneous rocks offer high-quality phosphates with minor concentration of contaminants. On the other hand, sedimentary rocks account for a significant proportion of the world's phosphate production (90%), while igneous rocks account for 10% and the rest comes from secondary sources [3]. However, a characteristic of sedimentary rocks and other secondary sources is their lower purity and levels of toxic impurities such as chromium in its hexavalent state (Cr (VI)).

Chromium in nature occurs predominantly in trivalent form (Cr (III)), but the extensive use of chromium compounds results in progressive built-up of Cr (VI) leading to environmental contamination [4]. In aqueous media, chromium exists mainly as Cr (III) and Cr (VI) [5]. Cr (III) is rather inert and it is considered as an essential nutrient in human diet [6], although there are contrasting studies showing no significant health benefits [7]. In comparison, Cr (VI) is proven to be a toxic, human carcinogenic with high solubility and mobility [8]. Because of these differences between Cr (III) and Cr (VI), determination of total Cr does not provide satisfactory information about health hazard of a fertilizer product. Therefore, guideline values for Cr (III) and Cr (VI) should be different, taking the health effects in consideration. Nevertheless, if a product contains chromium there will always be a risk of having Cr (VI) depending on the conditions prevailing in the medium wherein chromium is released. However, the detection limits for Cr speciation with the current analytical methods and the varying of Cr species due to changing conditions of its media (e.g. pH, redox potential) make it difficult to evaluate the potential risks [9] [10] [11] [12]. Hence, maximum allowed total chromium concentration in drinking water is 0.05 mg/L [13].

This study attempts to improve our understanding of Cr speciation under high saline and acidic nitro-phosphate process solutions. Cr (VI) reduction by hydrochloric acid has been known since the discovery of the element and Cr (VI) reduction in acidic media with changing acid and initial Cr (VI) concentration has been reported [14] [15] [16] [17]. Arcunda *et al.* worked on Cr (VI) reduction in nitric acid solutions and showed that increasing acid concentration will increase the reduction rate. Pezzin *et al.* showed that Cr (VI) is not stable in acidic media by using different oxidizing acids. Armstrong *et al.* found that Cr (VI) reduction in nitric acid is greatly influenced by bubbling of NO<sub>2</sub> and NO gases [18]. Hasegawa *et al.* studied redox behaviour of Cr in nitric acid solutions and found that NO<sub>x</sub> has a great influence on the oxidation state of Cr [19]. Although the Cr (VI) reduction in strong oxidizing acids has been reported, there has not been a satisfactory reduction mechanism proposed. It is worth noting

that HNO<sub>3</sub> is a strong oxidizing acid, where Cr (VI) reduction is not expected from redox potential analysis. It is a very well-known phenomena that nitric acid decomposes into NO<sub>2</sub> (or N<sub>2</sub>O<sub>4</sub>) and O<sub>2</sub> (Equation (1)), and our main hypothesis is that the NO<sub>2</sub> is contributing to Cr (VI) reduction in acidic nitrate solutions.



In this study, reduction of Cr (VI) in acidic nitrate and nitro-phosphate solutions was investigated by measuring redox potential and UV-VIS spectra.

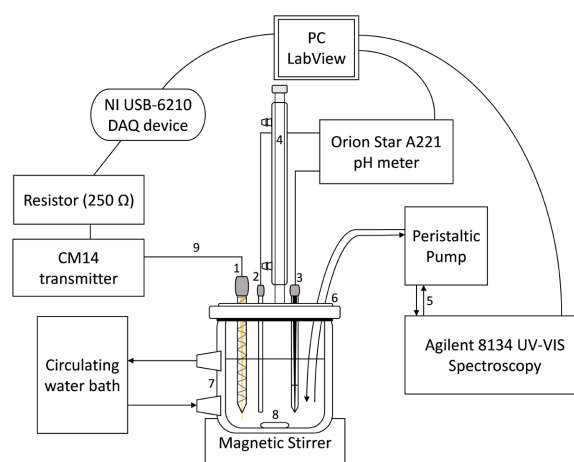
## 2. Materials and Methods

### 2.1. Materials

K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (99.1%) from J.T. Baker, HNO<sub>3</sub> (70%) from VWR, H<sub>3</sub>PO<sub>4</sub> (85%) and Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (99%) from Merck were used without further purification. Type 2 water was used for preparation of all aqueous solutions. 20 mL Cr (VI) stock solution (3000 ppm) was prepared and used for each reduction experiments. HNO<sub>3</sub> (70%) was used without further preparation, and synthetic Pregnant Leach Solution (PLS) was prepared by mixing 70% HNO<sub>3</sub>, 85% H<sub>3</sub>PO<sub>4</sub> and Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O where the final concentrations were 5.45 M, 5.05 M and 2.25 M respectively.

A thermostatic reactor of 250 mL from Diehm was used with custom-made PTFE lid. Redox potentials were measured with Endress + Hauser (E + H) gold electrode combined with a transmitter CM14 and Memosens cable CYK10. Orion star A211 benchtop pH meter was used to measure pH and temperature. Agilent 8134 UV-VIS was used to measure activities of Cr species with flow-through cells from Hellma. A peristaltic pump was used to collect samples from the reactor. Viton O-rings were used to seal the reactor from the air. LabVIEW software from National Instruments was used to record all the measurements.

**Figure 1** provides a schematic view of the set-up.



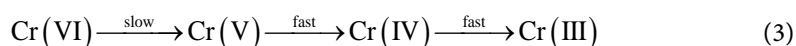
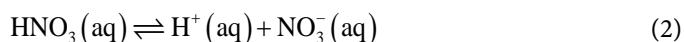
**Figure 1.** Schematic diagram of the reduction experiments. 1: Au electrode CPS12D (Endress + Hauser), 2: Temperature, 3: pH electrode, 4: Condenser, 5: Flow through cell (0.1 mm and 10 mm), 6: PTFE lid (DN 100) with completing Viton O-rings, 7: 250 mL Thermostatic Reactor (DN 100), 8: Stirring bar, 9: Memosensor cable CYK10.

## 2.2. Methods

Aqueous nitric acid solutions with volume of 200 mL were added to the reactor at a predetermined and fixed temperature. Recording started when temperature reached 65 °C ( $\pm 2$  °C) unless specified differently to represent nitro-phosphate process conditions. 20 mL Cr (VI) stock solutions were added to the reactor and stirring kept slow. The reduction system is sensitive to light, temperature, and air. In order to reduce errors, the present work was conducted using a sealed batch type reactor, where all measurements were made without opening the PTFE lid during the reduction process (Table 1). No sparging with argon to remove dissolved gas in the solution was applied due to preliminary results which showed that sparging the solution before adding and mixing Cr (VI), would inhibit the reduction rate, as no reduction was observed.

### 2.2.1. Reduction Reaction

It is well known that HNO<sub>3</sub> decomposes (Equation (1)) and dissociates (Equation (2)) depending on the acidity and presence of light and temperature [20] [21] [22]. In aqueous nitric acid solutions, different nitrogen species exist [23] [24]. However, for this study only the effect of NO<sub>2</sub> gas is considered for the redox potential analysis for Cr (VI) reduction. Cr (VI) may exist in different forms in aqueous solutions depending on the pH and total Cr (VI) concentration. In our experimental conditions, we would expect to have H<sub>2</sub>CrO<sub>4</sub>, HCr<sub>2</sub>O<sub>7</sub><sup>-</sup> and HCrO<sub>4</sub><sup>-</sup> in the acidic solution after mixing [25]. However, in this study equilibrium between Cr (VI) species was not considered since it was not impacting the reduction mechanism. Cr (VI) reduction to Cr (III) is a multistep reaction, where three electrons must be transferred (Equation (3)).



The presence of NO<sub>2</sub> in aqueous nitric acid solutions can provide the necessary electrons for Cr (VI) reduction to Cr (III) (Table 2). The standard redox potentials ( $E_0$ ) were obtained from CRC Handbook of Chemistry and Physics, 95<sup>th</sup> edition. When we apply Nernst equation (Equation 4) for this reaction we can conclude that the reaction goes to the Cr (III) side:

**Table 1.** Summary of the experimental conditions.

#	Different conditions	Temp [°C]	HNO <sub>3</sub> [M]	H <sub>3</sub> PO <sub>4</sub> [M]	Ca(NO <sub>3</sub> ) <sub>2</sub> [M]	Light presence	Reactor	Figures
a	HNO <sub>3</sub>	65	15.7	0	0	Daylight	Closed	Figure 2 Figure 3
b	PLS	65	5.45	5.05	2.25	Daylight	Closed	Figure 4
c	PLS-Reactor open to air	65	5.45	5.05	2.25	Daylight	Open	Figure 5
d	PLS-Lower temperature	45	5.45	5.05	2.25	Daylight	Closed	Figure 6
e	PLS-Absence of light	65	5.45	5.05	2.25	Dark	Closed	Figure 7

**Table 2.** Redox reactions and proposed reduction reaction for dichromate.

	Reaction equilibrium	E <sub>o</sub> [V]
Reduction reaction	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}$	1.36
Oxidation reaction	$2\text{NO}_2 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{NO}_3^- + 4\text{H}^+ + 2\text{e}^-$	0.803
Our proposed reduction reaction	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{NO}_2 + 2\text{H}^+(\text{aq}) \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + \text{H}_2\text{O} + 6\text{NO}_3^-(\text{aq})$	0.56

$$\Delta E = \Delta E_0 - \frac{RT}{n\mathcal{J}} \ln Q \quad (4)$$

$$\Delta E = 0.56\text{V} - \frac{8.3151 \frac{\text{J}}{\text{Kmol}} \times T}{6 \times 96485 \frac{\text{C}}{\text{mol}}} \times \ln \left( \frac{[\text{Cr}^{3+}]^2 \cdot [\text{NO}_3^-]^6}{[\text{Cr}_2\text{O}_7^{2-}] \cdot [\text{NO}_2]^6 \cdot [\text{H}^+]^2} \right) \quad (5)$$

At equilibrium,  $\Delta E = 0$ :

$$K_{eq} = \frac{[\text{Cr}^{3+}]^2 \cdot [\text{NO}_3^-]^6}{[\text{Cr}_2\text{O}_7^{2-}] \cdot [\text{NO}_2]^6 \cdot [\text{H}^+]^2} = e^{\frac{0.56\text{V} \times 6 \times 96485 \frac{\text{C}}{\text{mol}}}{8.3151 \frac{\text{J}}{\text{Kmol}} \times 338.15\text{K}}} = e^{0.56 \times 205.89} \gg 1 \quad (6)$$

In Equations (5) and (6) the bracket parentheses denote activity. We note the strong dependence of the activity of  $\text{NO}_2$ . In our work, the nitrate and  $\text{H}^+$  activities are almost constant since the concentration of the chromium species are minute compared to the nitric acid.

For our experimental conditions Cr (VI) reduction to Cr (III) reaction should take place (Equation (6)). However, the rate determining reaction is the  $\text{NO}_2$  formation. Hence, the changes in  $\text{NO}_2$  concentration affect the reduction rate drastically.

### 2.2.2. UV-VIS Measurements

To characterize the products of the reaction, UV-VIS spectra were recorded at appropriate time intervals. Measurements continued until a complete reduction was achieved. Flow-through cells with different path lengths were selected considering the absorbance properties of the chromium species. We used 0.1 mm path-length cell for measuring Cr (VI) at 350 nm and  $\text{NO}_3^-$  at 300 nm. A 10 mm path-length cell was used to measure Cr (III) at 575 nm. Due to the high nitrate concentrations, Cr (VI) absorbances at 257 nm and 350 nm were not possible to measure. However, the Cr (VI) spectrum has a shoulder at about 430 nm which was measurable with the 10 mm path-length flow-through cell. It is important to mention that a wavelength shift in the spectra of Cr (III) was observed for the PLS solutions. This might be due to ligand(s) replacing the water molecule(s) in the Cr (III) complex [26], or increase in ionic strength which may decrease the water activity in the Cr (III) complex. The detection was limited for Cr (III)- and Cr (VI)-concentrations below 10 ppm.

### 2.2.3. Redox Potential Measurements

An E + H Au electrode was applied for redox potential measurements. CM14 transmitter and 250  $\Omega$  resistor was used to connect the Au electrode to National Instruments unit where all the results were recorded simultaneously by the software LabVIEW. Redox-calibration solution from ZoBell was used to control the redox electrode to be within  $\pm 10$  mV through all the experiments. Measurements were recorded until there was no potential difference ( $\Delta E = 0$ ), then the complete reduction was considered achieved.

## 3. Results and Discussion

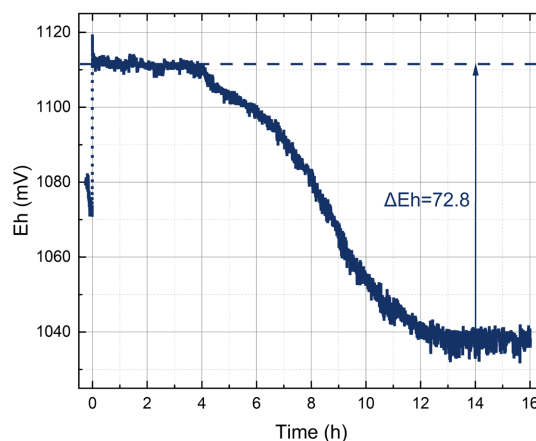
We investigated the rate of Cr (VI) reduction by measuring the concentration of Cr (III) and Cr (VI) in a pregnant leach solution (PLS) and in nitric acid solutions. A summary of the experimental conditions is given in **Table 1** and the summary of the results are given in **Table 3**.

### 3.1. Cr (VI) Reduction in HNO<sub>3</sub>

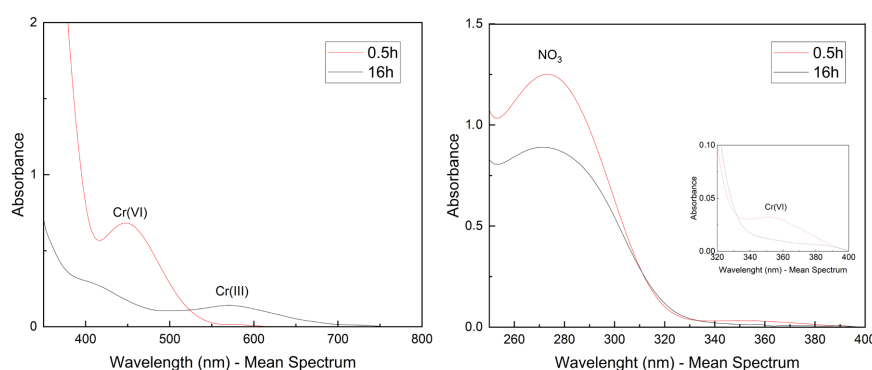
In a closed batch type reactor 70% nitric acid was heated to 65°C and 5.25 mM Cr (VI) was administered and mixed in at  $t = 0$ . Redox potential of aqueous nitric acid was 1.07 V and increased to 1.11 V as soon as Cr (VI) was introduced. The potential started decreasing after 4 hours and reached stability at 1.04 V after 13 hours. Hasegawa *et al.* investigated rest potential of Cr in 8 M nitric acid solution and determined it to be 1.11 - 1.14 V, which is similar to our results [19]. The change in redox potential was 72.8 mV (**Figure 2**). We are not able to determine the  $\Delta E$  due to very high and very low concentrations in the reduction reaction, which is outside the area of ideal solution. However, we can see when the redox reaction has ended. Due to high acid concentration and very low Cr-concentration (15.7 M HNO<sub>3</sub> and 5.25 mM Cr (VI)), a corresponding small change in consumption of H<sup>+</sup> was not possible to measure. However, at equilibrium, it is evident that the concentrations of products are much greater than the reactants (Equation (6)). Also from the UV-VIS measurements it can be seen that Cr (III) was slowly formed while Cr (VI) was reduced (**Figure 3**). These results are in agreement with the literature, but lower acid and lower initial Cr (VI) concentrations [14] [16] were used in the referenced works than in our case.

**Table 3.** Summary of the results.

#	Different conditions	Nitrate concentration decrease [%]	Potential difference [mV]	Slope	R <sup>2</sup>	Complete Reduction
a	HNO <sub>3</sub>	28.4	72.8	NA	NA	13 h
b	PLS	11.3	30	NA	NA	immediate
c	PLS-Reactor open to air	7.4	64.8	0.0335	(0.99789)	20 h
d	PLS-Lower temperature	6.2	40	0.027	(0.99967)	30 h
e	PLS-Absence of light	8.1	62.4	0.020	(0.99775)	40 h



**Figure 2.** Redox potential measurements.



**Figure 3.** UV-VIS measurements (left: 10 mm path-length flow-through cell, right: 0.1 mm path-length flow-through cell).

The nitrate concentration decreased 28.4%. One of the reasons for the decreasing nitrate concentration is the formation of  $\text{NO}_2$  which is subsequently consumed by the indirect reduction of Cr (VI) in the system. Additionally, the decrease in the peak at 275 nm is also affected by the Cr (VI) concentration, since Cr (VI) and  $\text{NO}_3^-$  have an overlapping peak at this wavelength.

### 3.2. Cr (VI) Reduction in PLS

The same experimental conditions were used as in the previous chapter (3.1), apart from using PLS instead of nitric acid solution. We observed an immediate reduction of Cr (VI). Increase in ionic strength had a great influence on the reduction rate. Another factor influencing the reduction rate could be the formation of chromate-phosphate complexes, which might influence the reduction [27]. In 30 minutes, almost all Cr (VI) was reduced to Cr (III). Due to the rapid reduction reaction it was not possible to measure small amounts of Cr (VI). The nitrate concentration decrease varies between  $\text{HNO}_3$  and PLS samples, this might be due to higher ionic strength in PLS resulting lower  $\text{NO}_3^-$  activity. As mentioned earlier, potential differences were not used in calculations. However, it can be seen from **Table 3** that PLS samples have lower potential difference

compared to  $\text{HNO}_3$ .

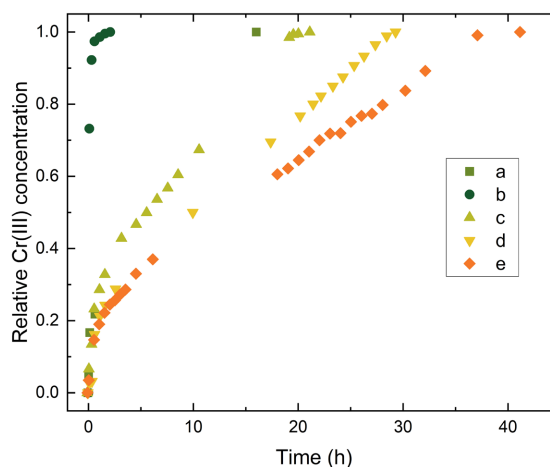
We compared the different conditions qualitatively for Cr (VI) reduction in PLS. Comparison of the reduction rates are giving in **Figure 4** and the variations of Cr (III) and Cr (VI) concentrations over time were plotted against time and results are given in **Table 3**. As can be seen from the graph the Cr (VI) reduction rates varied as  $\text{PLS} > \text{HNO}_3 > \text{PLS-reactor open to air} > \text{PLS-lower temperature} > \text{PLS-absence of light}$ . We obtained the fastest reduction at high ionic strength, high temperature, closed reactor and with presence of daylight.

### 3.2.1. Cr (VI) Reduction in PLS-Reactor Open to Air

The same experimental conditions were used as previous chapter 3.2, apart from the reactor was kept open during the reaction instead of being closed. Complete reduction was reached after 20 hours (**Figure 5**). As expected, in an open type of reactor  $\text{NO}_2$  concentration in the solution was decreased due to evaporation. Thus, the imperative presence of  $\text{NO}_2$  activity was reduced; hence the reduction rate of Cr (VI) decreased. This corresponds to our results where we could not record any reduction in the case where we used sparging. Moreover when the reactor was closed we reached higher Cr (VI) reduction rate. Armstrong *et al.* and Hasegawa *et al.* studied Cr (III) oxidation to Cr (VI) where they conclude that  $\text{NO}_x$  gas has a great influence on the Cr (VI) reduction [18] [19]. It is important to emphasize that partial pressure of  $\text{NO}_2$  can vary depending on the size of the reactor and the setup. Therefore, to investigate the effect of  $\text{NO}_2$  concentration,  $\text{NO}_2$  sparging with varying flow rates needs to be further studied.

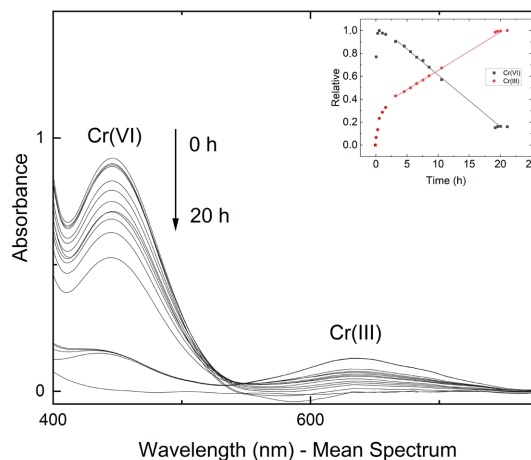
### 3.2.2. Cr(VI) Reduction in PLS-Lower Temperature

The same experimental conditions were used as in previous chapter 3.2, apart from the temperature was fixed at  $45^\circ\text{C}$  instead of  $65^\circ\text{C}$ . Complete reduction was reached after 30 hours (**Figure 6**). As expected, decrease in temperature effects thermal decomposition of nitric acid [28], which decreases the  $\text{NO}_2$  formation,

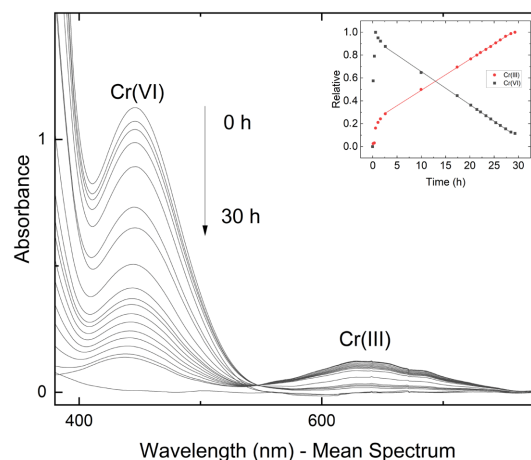


**Figure 4.** UV-VIS measurements of Cr (VI) reduction in acidic nitro-phosphate solutions (a:  $\text{HNO}_3$ , b: PLS, c: PLS-reactor open to air, d: PLS-lower temperature, e: PLS-absence of daylight).





**Figure 5.** UV-VIS measurements of Cr (VI) reduction in acidic nitro-phosphate solution—reactor open to air (slope = 0.0335 ( $R^2 = 0.99789$ )).

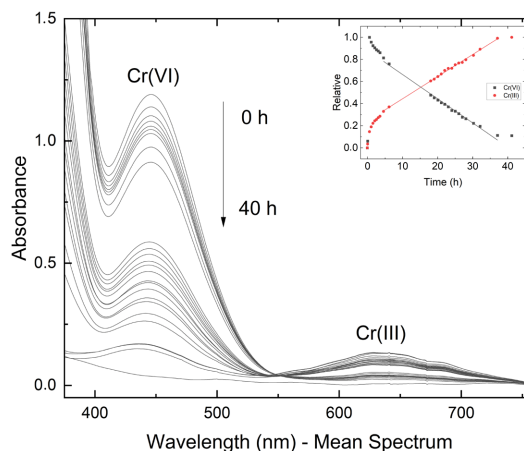


**Figure 6.** UV-VIS measurements of Cr (VI) reduction in acidic nitro-phosphate solution—at 45°C (slope = 0.027 ( $R^2 = 0.99967$ )).

hence the reduction rate of Cr (VI) decreases. Cr (VI) reduction rate will also follow Arrhenius' law, indicating that a 20°C decrease in the temperature will reduce the rate by nearly threefold. However, we observed much higher decrease in the reaction rate, which indicates decrease in  $\text{NO}_2$  formation has a higher impact. To have a better understanding on the effect of temperature on the Cr (VI) reduction rate, varying temperatures can be further investigated.

### 3.2.3. Cr (VI) Reduction in PLS-Absence of Light

The same experimental conditions were applied as in previous chapter 3.2, apart from the reaction conducted without any light presence. Complete reduction was reached after 40 hours (Figure 7). As expected, decrease in light presence decreases the photo decomposition of nitric acid [20], which decreases the  $\text{NO}_2$  formation, hence the reduction rate of Cr (VI) decreases. Additionally, the presence of light might also enhance the oxidative capacity of Cr (VI) [29]. It is evident that light has great effect on the Cr (VI) reduction rate, and this can be



**Figure 7.** UV-VIS measurements of Cr (VI) reduction in acidic nitro-phosphate solution—absence of light (slope = 0.020 ( $R^2 = 0.99775$ )).

further studied with varying wavelengths to see the effect of light.

### 3.3. Reaction Kinetics of Cr (VI) Reduction in PLS

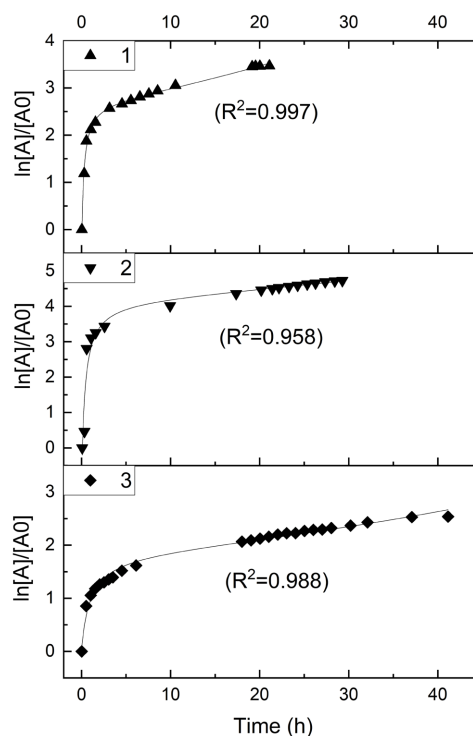
At the outset of these results certain assumptions were made regarding the Cr (VI) reduction reaction kinetics. First assumption was that the reduction kinetics would depend on concentration of Cr (VI),  $\text{HNO}_3$  and  $\text{H}_2\text{O}$ , and the reduction rate is proportional to nitric acid decomposition (Equation (7)) [22]. This agrees with our experimental results, where reduction rate increases with increasing ionic strength. Although the opposite effect has been observed for Cr (VI) reduction rate [30], for our experimental conditions decrease in water activity increased the Cr (III) production, as can be seen from the Equation (7), decrease in water activity will increase the Cr(III) activity. Arbitrary  $k$  values are used in order to represent the decomposition of  $\text{HNO}_3$ .

$$\text{Rate Cr(III)} \propto \frac{k_1 \cdot [\text{HNO}_3]^2 \cdot [\text{Cr(VI)}]}{(k_2 + k_3 \cdot [\text{H}_2\text{O}])} \quad (7)$$

Cr (VI) reduction in PLS was shown to predominantly follow pseudo-first-order kinetic model, while the same trend was not observed in the beginning of the reaction (Figure 8). This might be due to already existing  $\text{NO}_2$  in the solution causing fast reduction where we observed rapid increase in Cr (III) concentration. Another explanation can be that there is more than one type of higher degree reactions occurring before reaching first degree reaction.

## 4. Conclusion

This study compares different conditions effecting the Cr (VI) reduction rate in high saline and acidic nitro-phosphate solutions. The results show that Cr (VI) is not stable in these acidic nitrate solutions, and it is found that Cr (VI) was reduced to Cr (III), and oxidation of Cr (III) to Cr (VI) was not observed under these experimental conditions. It is important to note that Cr (III) is nutrient at



**Figure 8.** Cr (VI) reduction reaction rate non-linear curve fit:  $y = (x+a)/(b_0+b_1(x+a)+b_2(x+a)^2)$  (1: PLS-reactor open to air, 2: PLS-lower temperature, 3: PLS-absence of light).

trace amounts, and it is not considered as a toxic impurity in fertilizers. We also found that the reduction rate of Cr (VI) decreased with decreasing ionic strength, temperature,  $\text{NO}_2$  concentration and absence of light. These findings support the idea that the reduction is depending on the  $\text{NO}_2$  activity, *i.e.* the rate of decomposition of nitric acid. Cr (VI) reduction rates were found highest for  $\text{PLS} > \text{HNO}_3 > \text{PLS-reactor open to air} > \text{PLS-lower temperature} > \text{PLS-absence of light}$ . In order to understand the reduction mechanism extensively, future studies should focus on investigating the kinetics of the individual effects of changing temperature, wavelength of light and initial  $\text{NO}_2$ ,  $\text{H}^+$ ,  $\text{NO}_3^-$ , Cr(VI) concentrations.

### Acknowledgements

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### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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