

A Kinetic, Thermodynamic and Stoichiometric Study on the Reductive Detoxification of Cr(VI) in Aqueous Phase by Sodium Metabisulphite

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Abstract

In this study $\text{Na}_2\text{S}_2\text{O}_5$, was assessed as an inorganic reductant of Cr(VI) in aqueous phase. The absorbance of Cr(VI) was monitored at 349 nm using a Milton Roy Spectronic 20D UV/Visible spectrophotometer at different temperatures (298 – 323 K) to study the effect of temperature on reduction while, the effect of pH was studied at pH 3, 5, 7, 9 and 12. The effect of concentration was also considered by varying the concentrations of the reductants (i.e. 4, 6, 8, 10 and 12 mg/L) over a pH of 5, 298 K and 5 minutes with concentration of Cr(VI) set at 10mg/L. The temperature effect showed that the reaction rate increased slightly with increase in temperature. It was found that there was a logarithmic increase in time required to reach a certain percentage reduction of the $[\text{Cr(VI)}]_{\text{initial}}$, as the pH was increased. The kinetic results showed that the reaction was first – order with respect to Cr(VI) with the rate equation of $-\frac{d[\text{Cr(VI)}]}{dt} = k[\text{Cr(VI)}]$. The activation entropy obtained from plots of $\ln(k_{\text{obs}}/T)$ vs. $1/T$ was $-197.53 \text{ J.K}^{-1}.\text{mol}^{-1}$ agreeing with the formation of a condensed compound. The activation enthalpy varied from $(-7.5 \times 10^{-6} - 3.3 \times 10^{-4} \text{ kJmol}^{-1})$ and most cases it was negative showing that the reaction was rather exothermic. The activation energies obtained were 58.87, 60.84, 62.82, 63.80 and 65.78 kJmol^{-1} for the respective Kelvin temperatures of 298, 308, 318, 323 and 333. This increase in activation energy with increasing temperature implied that bond breakage and product formation was more favourable at lower temperature. The stoichiometry suggests that the Cr(VI) : $\text{Na}_2\text{S}_2\text{O}_5$ ratio was 1 Cr(VI) : 1.36 $\text{Na}_2\text{S}_2\text{O}_5$, this value was found to be in agreement with the theoretically obtained result for both acidic and alkaline regimes. The findings from the research show that $\text{Na}_2\text{S}_2\text{O}_5$ could be used for the reductive detoxification of Cr(VI) in polluted areas.

1. INTRODUCTION

Chromium is one of the abundant elements in the earth's crust with an average concentration of 100 mg L^{-1} (Emsley, 2001). The concentration range of Cr in rivers and lakes is usually from 0.026 to $5.2 \mu\text{g L}^{-1}$, in sea water from 0.005 to $0.8 \mu\text{g L}^{-1}$, in soil between 1 and 3000 mg g^{-1} , in air from 0.005 to 10 ng m^{-3} (Kotas and Stasicka, 2000). Cr is the only elemental solid which shows antiferromagnetic ordering at or below room temperature (Fawcett, 1988). It has also high corrosion resistance and hardness. Many of its compounds are intensely coloured. Because of its unique characters, Cr was widely used in electroplating, tanning, pigments, dyes, industrial water cooling, metal finishing, magnetic tapes, paper pulp producing, photographic film, automotive parts, chemical manufacturing, wood protection, ore and petroleum refining, metallurgical and refractory producing, and other industrial activities (Babel and Opiso, 2007; Pandey *et al.*, 2010). Due to these industries and other anthropogenic activities (e.g. disposal of products or chemicals containing Cr, or burning of fossil fuels), huge amounts of Cr compounds were discharged into the environment, including air, soil, and water (Liu, *et al.*, 2012).

Among the two stable forms of Chromium available in the aquatic systems, Cr (VI) and Cr (III), trivalent chromium is less dangerous. Hexavalent chromium is a priority metal pollutant introduced into natural water from these processes. Hexavalent chromium compounds are highly toxic when ingested or inhaled. Carcinogenesis caused by hexavalent chromium may result from the formation of mutagenic oxidative DNA lesions following intracellular reduction to the trivalent form. Consequently any hexavalent chromium present in wastewater should be reduced to Cr (III) before discharge into the sewer. The treatment procedure of Cr(VI)-bearing wastewater often comprise reduction of Cr(VI) and any of the after treatments such as coagulation-precipitation, active carbon adsorption, ion-exchange or membrane separation (Wang *et al.*, 2010; Huang and Logan, 2011 and El – Shazly, 2005). The objectives of our research was to detoxify Cr(VI) by reduction using sodium metabisulphite, determine the rate of reduction and also obtain some thermodynamic parameters of the reduction process.

The two environmentally stable oxidation states, Cr(III) and Cr(VI), exhibit very different toxicities and mobilities. Cr(III) is relatively insoluble in aqueous systems, and exhibits little or no toxicity. In contrast, Cr(VI) usually occurs as the highly soluble and toxic chromate anion, and is the suspected carcinogen and mutagen (Costa, 2003).

Chromium(VI) is a thermodynamically stable form in aerobic systems while chromium(III) is a stable form in anaerobic systems. The fact that both Cr forms are often found in aerobic and anaerobic environments is due to the slow kinetics of Cr(VI)/Cr(III) redox reactions (Hu *et al.*, 2010). Thus, chromium speciation in the environment may reflect the kinetics of its redox transformations and not the equilibrium state. Dramatic differences have been noted in mobility, uptake and toxicity of both chromium oxidation states.

The U.S. Environmental Protection Agency (USEPA) has approved several chemical reductants for in situ treatment of Cr (VI) these include; sodium dithionite, ferrous sulphate, sodium metabisulphite, calcium polysulphide, nano - zero valent Iron. All agents operate on the same principle by providing additional electron donors to address the high amount of Cr(VI) (Guertin *et al.*, 2005).

2 MATERIALS AND METHODS

2.1 Materials

All solutions were prepared using distilled water. All glassware and plastics were washed with distilled water, rinsed with (1:1) HNO₃ and finally with distilled water. Chromium (VI) stock solution was prepared from K₂Cr₂O₇ (BDH) by dissolving 2.828g of the salt in 1 litre of distilled water. A 2 mgL⁻¹ Cr(VI) solution was prepared measuring exactly 2mL of the stock solution in 1 L of distilled water. Na₂S₂O₅ stock solution was prepared by dissolving 1.0g of the salt in a litre of distilled water. Interferences were avoided by adding diphenyl carbazide to Cr(VI) before adjusting the pH of the solution.

2.2 Experimental Procedures.

The reduction of Cr(VI) by Na₂S₂O₅ was conducted in accordance with the method described by Njoku and Nweze (2009) with slight modifications. A 10 mL portion of 2.0 mg/L Cr(VI) was measured into a 250mL beaker. Next, a 20-mL aliquot of 20.0 mg/L Na₂S₂O₅ was added and the mixture shaken thoroughly. The pH of the solution was adjusted using 1.0 M H₂SO₄ in the acidic region and 1.0 M NaOH in the alkaline region before they were made to come in contact. The UV/Visible spectrophotometer (Milton Roy USA Spectronic 20D) was set at 349 nm and the absorbance of Cr(VI) was read at that wavelength. The absorbance of Na₂S₂O₅ was found to be weak at this wavelength. The set up was done in triplicate at temperatures of 298, 308, 318, 323 and 333 K. In order to study the effect of reaction time on Cr(VI) reduction, separate set ups of the above mixture was made and each monitored for different time intervals of 0, 1, 2, 3, 4,5 minutes to minimize interference due to withdrawal of samples. The reaction was done for the initial pH values of 3, 5, 7, 9 and 12.

The stoichiometric study was conducted using five concentrations of the reductants: 4, 6, 8, 10 and 12 mg/L to assess the concentration – dependence of the reduction. The reaction was at 298 K and a moderately acidic pH of 5. The initial concentration of Cr(VI) was set at about 10.0 mg/L and the reaction time was 5 minutes. Equal volumes of 10mL each of the reductant and Cr(VI) was used for the mixture.

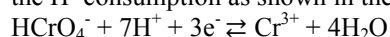
3. Results and Discussion

3.1 Effect of pH

Table 1 presents the results of the reduction of Cr(VI) by Na₂S₂O₅ at different temperature and pH conditions in aqueous phase. A first glance observation was that the reaction was fast with more than half of the concentration reduced at 300 seconds. The rate of reduction was basically increasing with decrease in pH. The rate of reduction was also slightly affected by increase in temperature with most reaction reaching completion at 180 seconds when the initial temperature was increased to 308 K. The rate in acidic and neutral solutions was faster than in basic solution. This observation agreed with that of Bill *et al.*, (1998) where an in situ kinetic reduction of Cr(VI) by ferrous iron in solid phase was studied. The findings of the present study are also to be consistent with those of Wittbrodt and Palmer, (1996) and Elovitz and Fish, (1994).

The rate of reduction depends on the speciation of chromium in a given pH range as this is shown in the Pourbaix diagram (figure 2). In order to explain the increase in reaction rate with decreasing pH, one needs to take into account the speciation of both Cr(VI) and the reductants under these conditions. The Eh-pH diagram shown (Fig. 2) provides a generalized depiction of the major aqueous chromium species and redox stabilities under conditions of chemical equilibrium. The dominant Cr(VI) species are HCrO₄⁻ at pH 1-6 and CrO₄²⁻ at pH > 6. Cr(VI) also forms other species, such as HCr₂O₇⁻ and Cr₂O₇²⁻. However, their formation requires Cr(VI) concentrations > 10⁻² mol·dm⁻³. The increase in reaction rate with decreasing pH can therefore probably be attributed to HCrO₄⁻ which is reduced more easily than CrO₄²⁻ (Cotton and Wilkinson, 1988).

In acidic solution Cr(VI) demonstrates a very high positive redox potential (E^o within 1.33 and 1.38 V, Figure 1) (Greenwood and Earnshaw, 1984; Shriver *et al.* 1994, Ball and Nordstrom 1998) which denotes that it is strongly oxidizing and unstable in the presence of electron donors. As the HCrO₄⁻ reduction is accompanied by the H⁺ consumption as shown in the equation below:



In more basic solution the reduction of CrO₄²⁻, generates OH⁻ against a gradient as shown in the equation below

(Nieboer and Jusys 1988). The reduction potential of chromate to Cr(III) hydroxide is -0.13 V in basic medium.
 $\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \rightleftharpoons \text{Cr}(\text{OH})_3 + 5\text{OH}^-$

When a plot of the logarithm of time taken to attain 50% reduction against was made against the pH, it was found that there was a linear logarithm relationship between pH and the time taken given by

$$\log(t_{0.5}) \propto \log\left(\frac{1}{[\text{H}^+]}\right) = \text{pH}$$

and the relationship showed that the Cr(VI) – Na₂S₂O₅ reaction system rate law has first – order dependence on [H⁺]. This observation was in agreement with findings obtained elsewhere (Beukes *et al.*, 1999; Sweitlik, 2002; Niekerk, *et al.*, 2007 and Iorungwa, 2014).

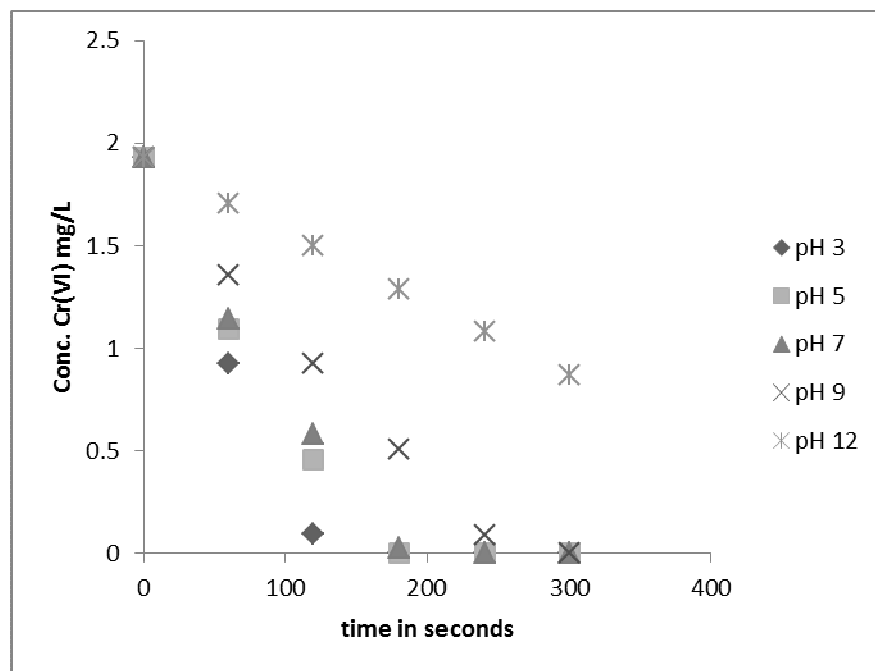


Fig.1. A plot of Concentration of Cr(VI) vs time (secs) for various pH at 298 K

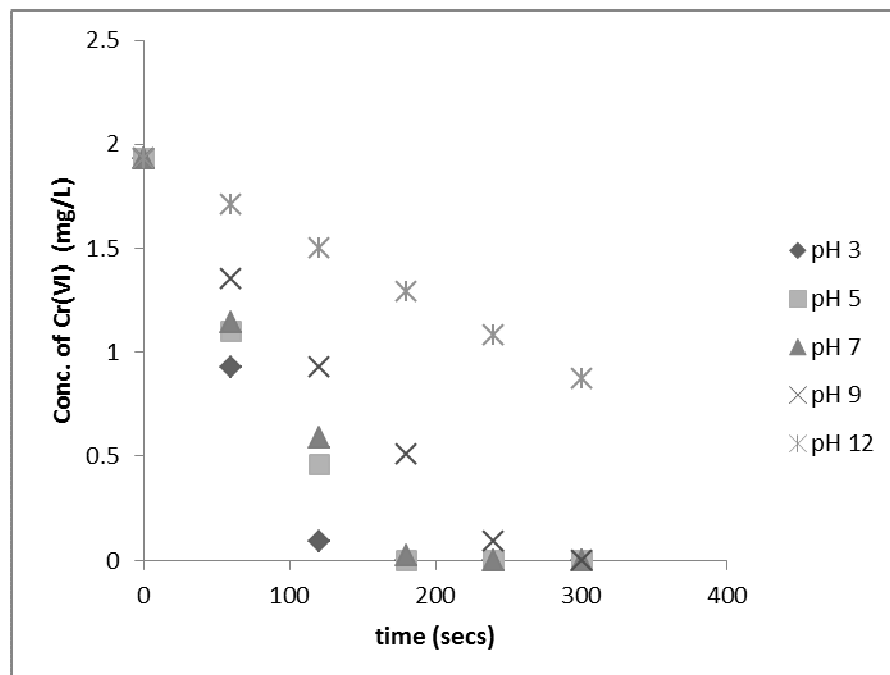


Fig.2. A plot of Concentration of Cr(VI) vs time (secs) for various pH at 308 K

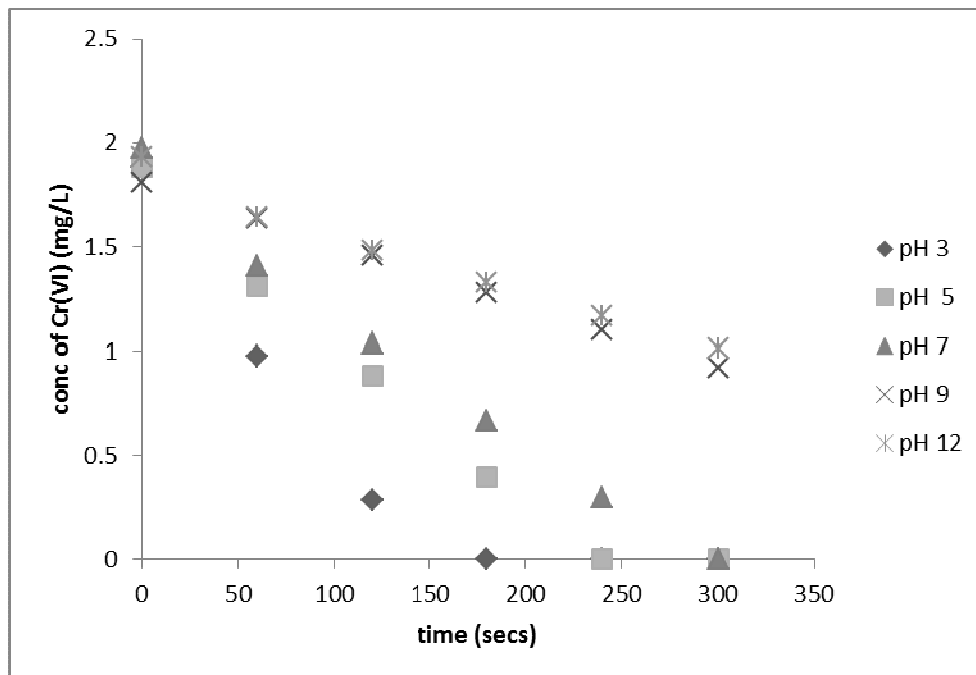


Fig.3. A plot of Concentration of Cr(VI) vs time (secs) for various pH at 318 K

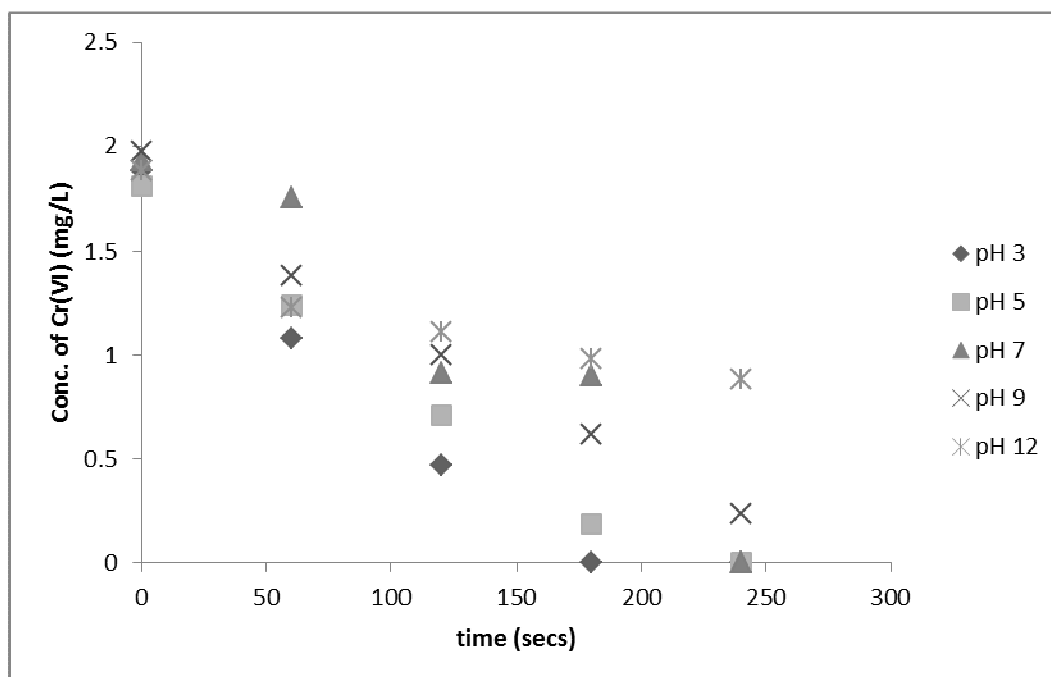


Fig.4. A plot of Concentration of Cr(VI) vs time (secs) for various pH at 323 K

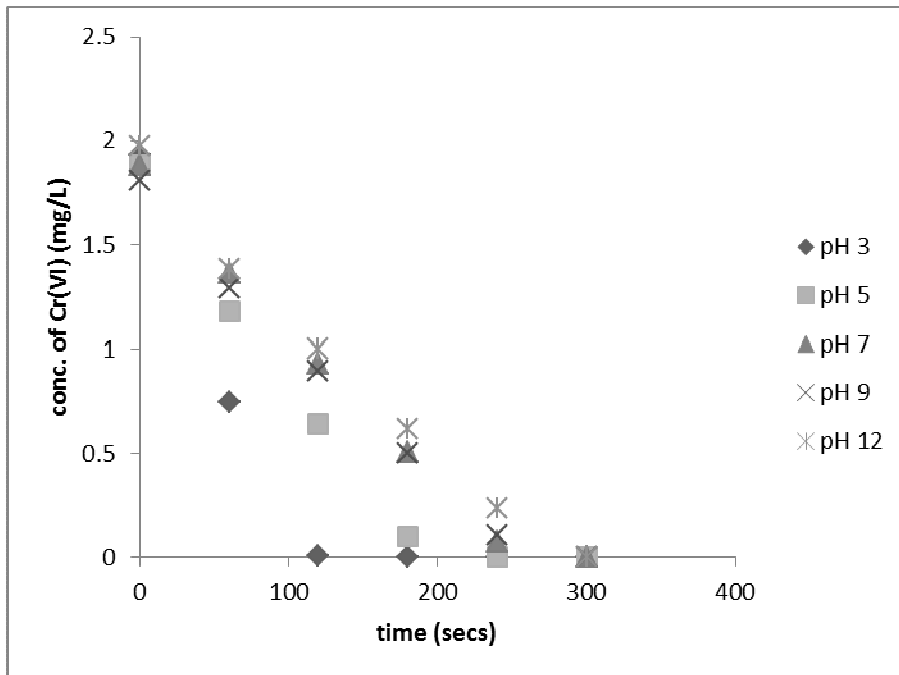


Fig. 5. A plot of Concentration of Cr(VI) vs time (secs) for various pH at 333 K

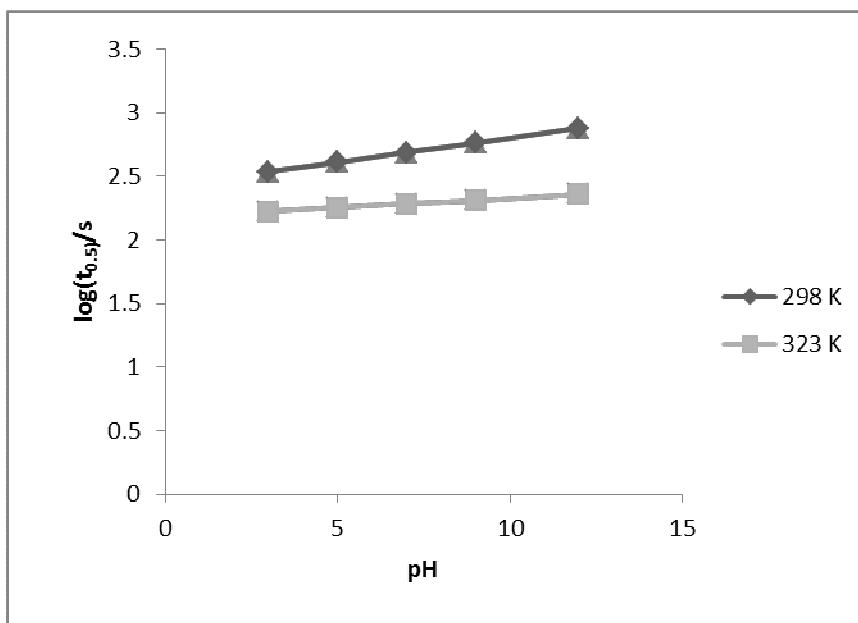


Fig. 6. A plot of Time required to reach 50% reduction of the initial [Cr(VI)] $t_{(0.5)}$ at 298 and 323 K against pH.

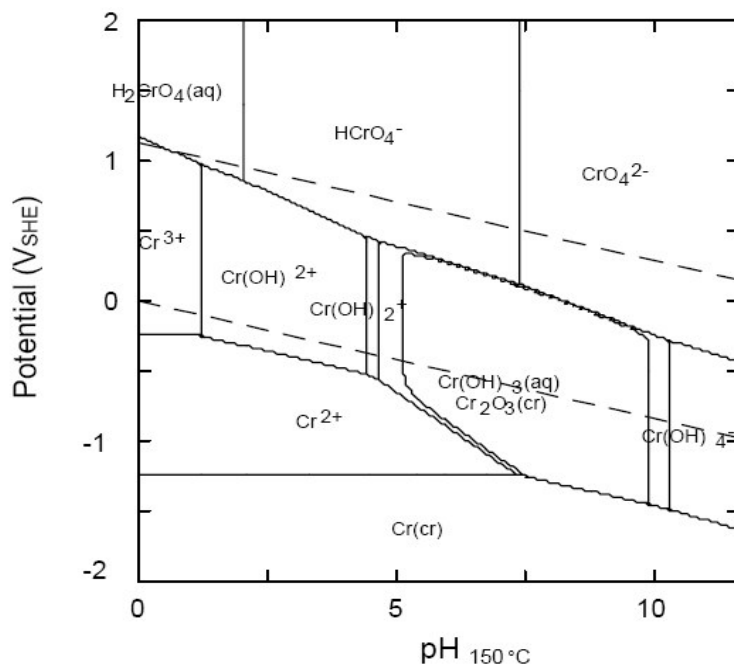


Fig. 7 A simplified Pourbaix diagram for chromium species at 150 °C and $[Cr(aq)]_{tot} = 10^{-8} M$ (Source: Ball and Nordstrom 1998, Richard and Bourg 1991, Nieboer and Jusys 1988)

3.2 Kinetic study

After monitoring the reactions at physiological temperature (298 K), the reactions were further considered at higher initial temperatures of 308, 318, 323 and 333 K. The reactions were observed to be faster as the temperature of the reaction was increased most of the reaction were completed at a temperature of about 308 K and at a time of 180 seconds. A plot of $\ln[Cr(VI)]$ against time was made (figures 8 – 12) and it showed that the reaction had a first – order dependence on Cr(VI). The observed rate constants k_{obs} was obtained from the slopes of the plots.

For each pH and reductant, another plot of $\ln(k_{obs}/T)$ against $1/T$ was made, this was in accordance with the Elovitz and Fish, (1994). The graph was found to be linear with very nice regression coefficients of $0.987 \geq r^2 \leq 0.960$. The observed rate constant was found to be highest at a pH of 3 and this also increased as the temperature was increased. For example, the k_{obs} for the reduction of Cr(VI) by $Na_2S_2O_5$ was found to $1.227 s^{-1}$ at 298 K and when the temperature was increased to 308K, the k_{obs} also increased to $1.269 s^{-1}$. And as the temperature was raised to 318, 323 and 333 K, the k_{obs} , there was a correspondent increase of 1.310, 1.330 and $1.370 s^{-1}$ respectively. When the pH was increased to 5, it was observed that the reaction became slower but the rate still increased as the temperature was increased. It was seen that the k_{obs} at 298 K was $0.276 s^{-1}$ and other temperatures such as 308, 318, 323 and 333 K had 0.286, 0.295, 0.299 and $0.3088 s^{-1}$ respectively. This shows that the reaction is slower at a higher pH and faster at higher temperature. The higher k_{obs} values at lower pH can be attributed to the fact that there are so many protons at lower pH that deplete the electrons thereby causing reduction at a higher rate. Increased temperature increases the rate of interaction between reacting species; this is why the k_{obs} increased when the temperature was increased. The trend was also observed at hyper alkaline region regions of pH and 12. At pH 9, the rate of reduction was significantly slow; this could be seen for the decrease in the k_{obs} values. At a temperature of 298 K, the value was found to be $0.011 s^{-1}$ but rose to $0.0115 s^{-1}$ when the temperature was increased to 308 K and for 318, 323 and 333 K, the observed rate constants became 0.0118, 0.012 and $0.0124 s^{-1}$ respectively. The slow rate observed at the high pH values can be attributed to the formation of other species as seen in figure 3 or the complete depletion of Cr(VI) in the solution. This observation agrees with the assertions of Beukes *et. al*, (1999).

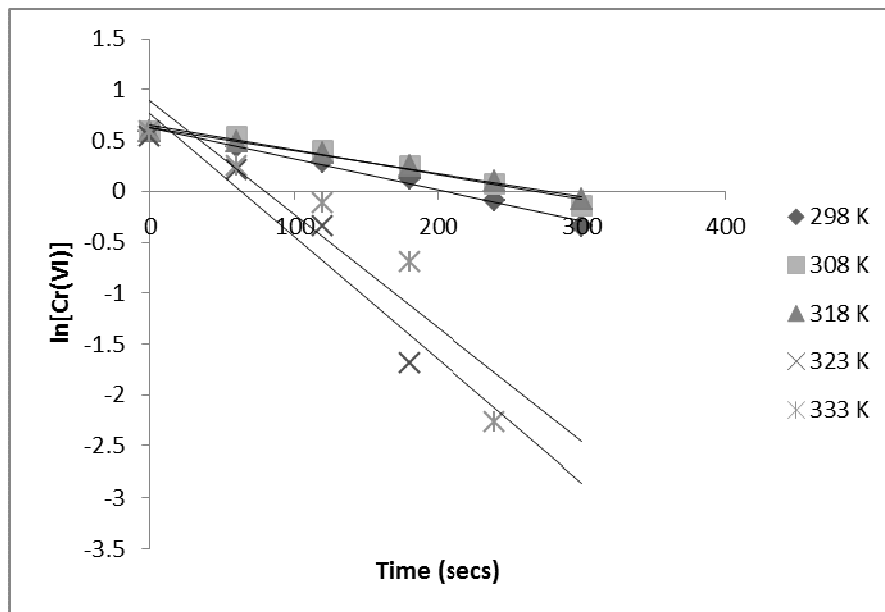


Fig. 8. A plot of natural logarithm of $[Cr(VI)]$ against time (secs) at pH 3

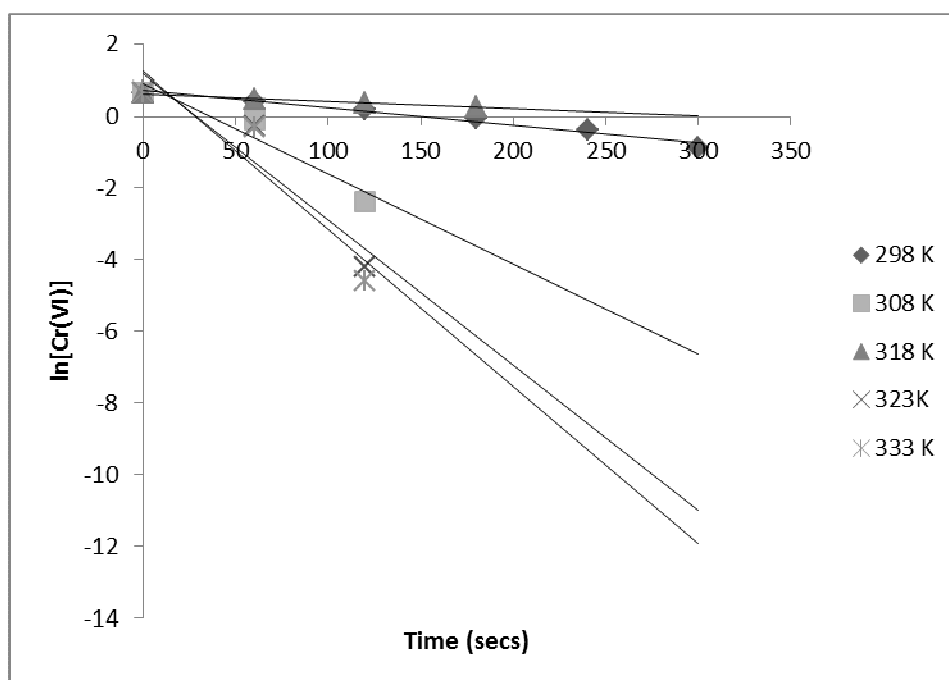


Fig. 9. A plot of natural logarithm of $[Cr(VI)]$ against time (secs) at pH 5

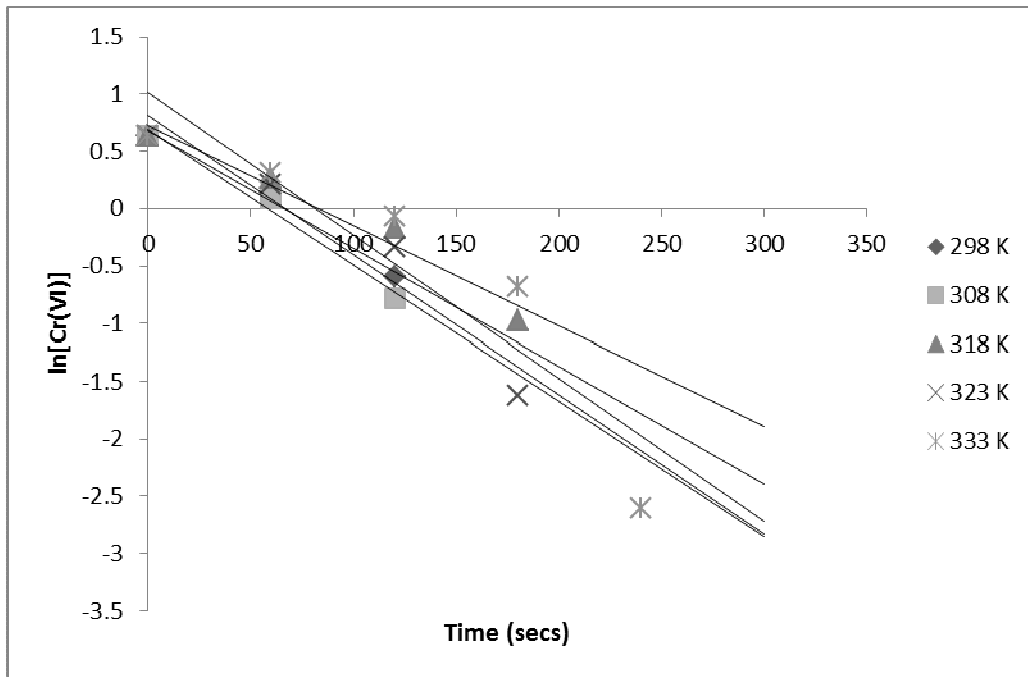


Fig.10 A plot of natural logarithm of $[Cr(VI)]$ against time (secs) at pH 7

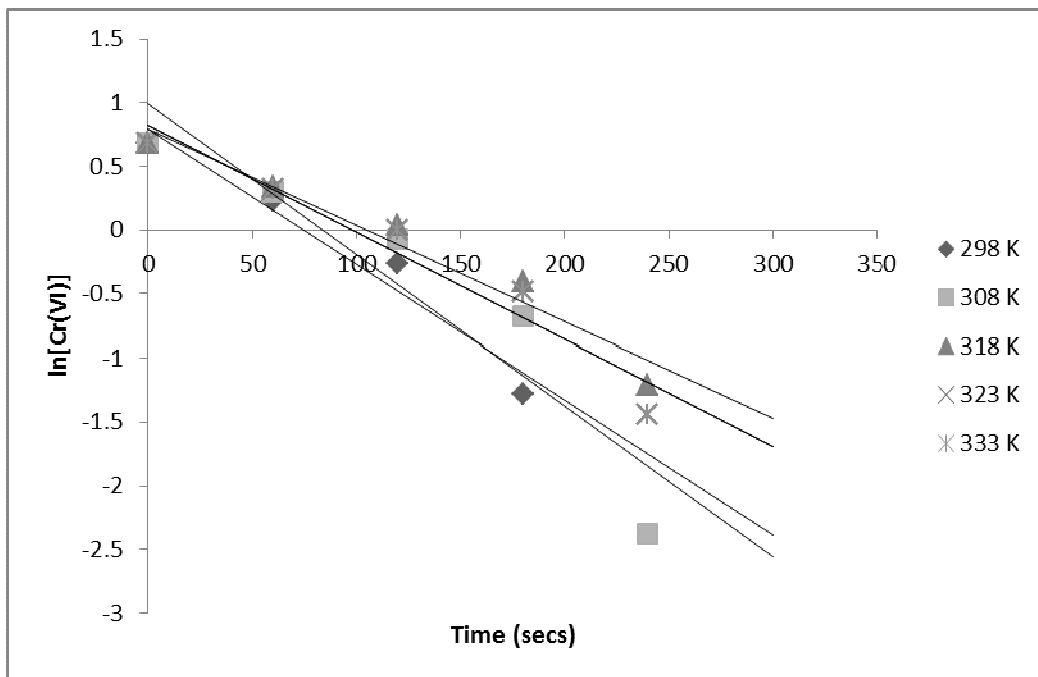


Fig. 11. A plot of natural logarithm of $[Cr(VI)]$ against time (secs) at pH 9

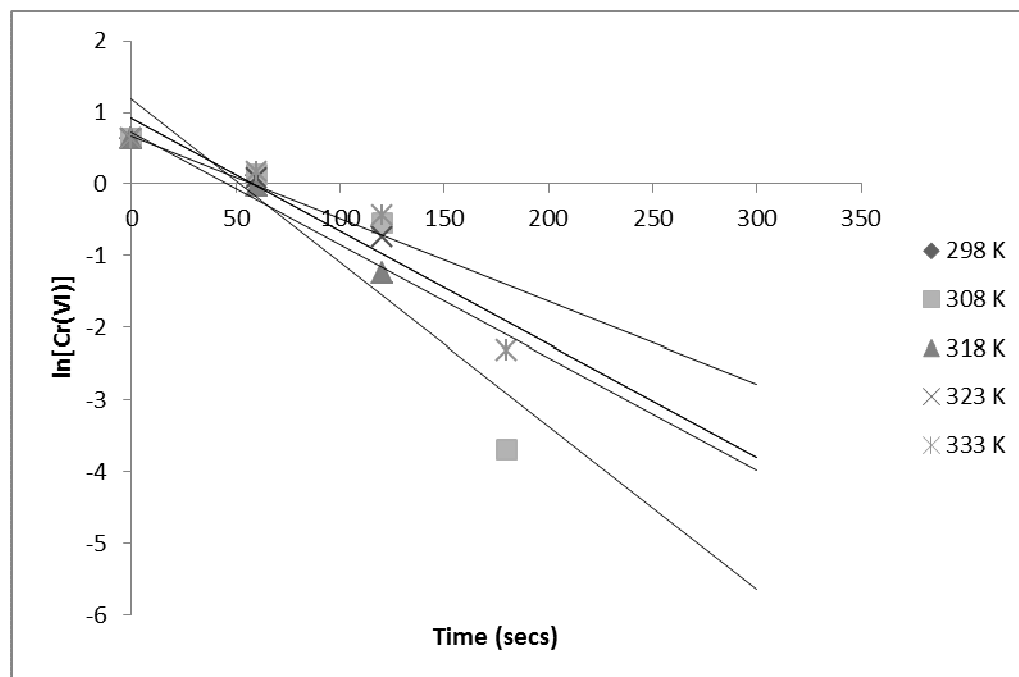


Fig. 12: A plot of natural logarithm of $[Cr(VI)]$ against time (secs) at pH 12

The activation enthalpies and entropies (ΔH^\ddagger and ΔS^\ddagger) was obtained from the slopes and intercepts of another plot of $\ln(k_{obs}/T)$ against $1/T$. This is in accordance with the Elovitz and Fish (1994) equation

$$\ln\left(\frac{k_{obs}}{T}\right) = \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

where

T is the temperature in Kelvin,

k_b is Boltzman's constant (1.38×10^{-23} J/K),

h is Planck's constant (6.63×10^{-34} Js), and

R is the gas constant (8.314 J/K/mol).

The activation energies was therefore computed from the relationship:

$$E_a = \Delta H - T\Delta S$$

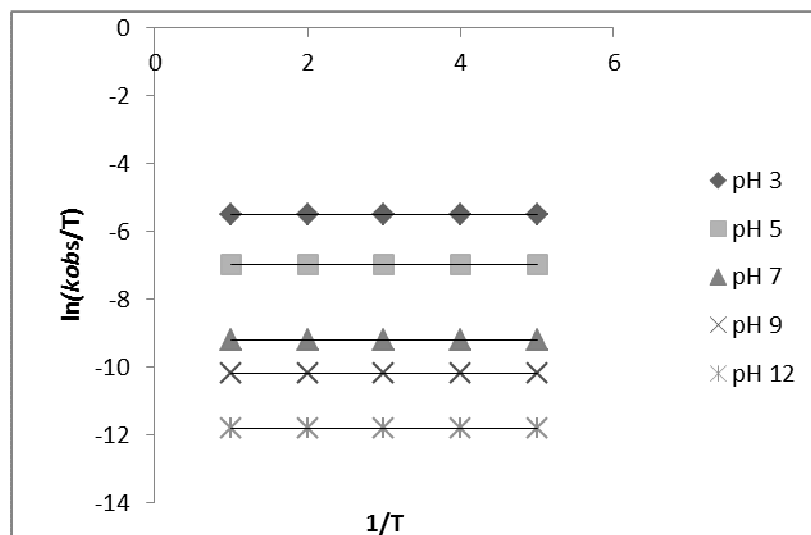


Fig. 13: A plot of $\ln(k_{obs}/T)$ vs $1/T$ for the reduction of $Cr(VI)$ by $Na_2S_2O_5$

Because of the empirical manner in which the rate coefficients were derived, the activation parameters ΔH^\ddagger and ΔS^\ddagger must be taken as composite values for all reactions prior to and including the rate-limiting step. The activation entropy (ΔS^\ddagger) is often used as an indicator of the configuration of the activated complex. A large

negative number indicates that the reactant molecules are separated by short bonds, thus the decrease in entropy is large and the pre-exponential factor $[(k_b T/h) \exp(\Delta S^\ddagger/R)]$ is small. The values of the activation energy obtained when compared with that of some organic compounds used in chromium reduction was relatively lower at 298 K. The values also revealed that $\text{Na}_2\text{S}_2\text{O}_5$ activation energies that are almost the same at a given temperature and pH. For example, activation energy (E_a) of 58.8645, 60.8395, 62.8153, 63.8029 and 65.7783 kJmol^{-1} was obtained at 298, 308, 318, 323 and 333°K at pH 3 to 12. The activation enthalpy (ΔH) of the reduction was found to vary with pH but remained constant with change in temperature. For example, it maintained a value of $-7.4 \times 10^{-6} \text{ kJmol}^{-1}$ at pH 3 but for pH 5, 7, 9 and 12, the values became 3.3×10^{-6} , -2.1×10^{-4} - 6.7×10^{-5} and $3.3 \times 10^{-4} \text{ kJmol}^{-1}$ respectively while the activation entropy (ΔS) was $-197.5323 \text{ J.K}^{-1}\text{mol}^{-1}$ for all pH and temperature. The action data was compared with the values obtained by Xu, (2005) at 298 K (table 1) and it was clearly seen that the ΔH^\ddagger obtained when $\text{Na}_2\text{S}_2\text{O}_5$ was adopted as model reductant was lower than the ones obtained by Xu, 2005. This is the same when the ΔS^\ddagger obtained was compared as it was $-197.5323 \text{ j.K}^{-1}\text{mol}^{-1}$ against the higher values obtained for the organic reductants.

Table 1. Activation data for Cr(VI) reduction by organic compounds at 25 °C

Reductant	ΔH^\ddagger (KJ/mol)	$-\Delta S^\ddagger$ (J/K/mol)	E_a (KJ/mol)
Vitamin C	42.4	71.0	63.5
Ethanol	49.0	120.2	84.8
Isopropyl alcohol	53.2	107.7	85.3
Benzyl alcohol	26.6	180.8	80.5
Triphenylcarbinol	49.4	105.0	80.7
Benzhydrol	24.7	155.2	70.9

source: Xu, (2005).

3.3 Reaction Stoichiometry

While it is known that the reduction of Cr(VI) results in the production of Cr(III) species (Deng, 1995), the reaction with $\text{Na}_2\text{S}_2\text{O}_5$ generates a theoretical stoichiometric equation (Iorungwa, 2014):

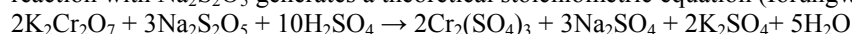


Table 2 below shows the amount (mg/L) of Cr(VI) consumed when the concentration of $\text{Na}_2\text{S}_2\text{O}_5$ was varied. Here, it was observed that the 4 mg/L of $\text{Na}_2\text{S}_2\text{O}_5$ consumed exactly 2.94 mg/L of Cr(VI) giving a stoichiometric mass balance Cr(VI)/ $\text{Na}_2\text{S}_2\text{O}_5$ ratio of 1:1.4. This ratio was maintained when the concentration of $\text{Na}_2\text{S}_2\text{O}_5$ was varied from 4 to 12 mg/L and the result obtained from the experiment was in agreement with the theoretical ratio obtained elsewhere (Iorungwa, 2014).

TABLE 2: Showing the amount of Cr(VI) consumed as the concentration of $\text{Na}_2\text{S}_2\text{O}_5$ is varied.

Reductant	$\text{Na}_2\text{S}_2\text{O}_5$ (mg/L)	Residual ^(a) Cr(VI)(mg/L)	Consumed Cr(VI)(mg/L)
	4	7.0556±0.01	2.9444±0.01
	6	5.5794 ±0.10	4.4206±0.10
	8	4.1508±0.11	5.8492±0.11
	10	2.6905±0.15	7.3095±0.15
	12	1.2381 ±0.00	8.7619±0.00

(a)Mean value from triplicate determination ± standard deviation

4. Conclusion

This study has demonstrated that whereas $\text{Na}_2\text{S}_2\text{O}_5$ reduced Cr(VI) in aqueous phase, the reduction rate decreased with increasing pH and the activation entropy (ΔS) of the reduction was largely negative with a relatively small value of the activation enthalpy (ΔH). This gave rise to a Gibb's energy of activation that has a smaller value when compared with the activation energy obtained from the reduction of Cr(VI) by some organic compounds under similar experimental conditions. These observations are rather advantageous because, whereas organic compounds reduce Cr(VI) higher energy of activation, $\text{Na}_2\text{S}_2\text{O}_5$ reduced Cr(VI) with a lower energy of activation meaning that $\text{Na}_2\text{S}_2\text{O}_5$ is a better reductant which can be used for cleanup and will complete the process in shorter time.

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