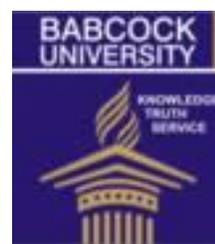




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An aqueous dechromification by hydrazine sulphate: a kinetic, thermodynamic and stoichiometric method

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Abstract

The ability of $N_2H_6SO_4$ to reduce Cr(VI) in aqueous phase was determined spectrophotometrically at different temperatures (298 – 333K) 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 reductant (i.e. 4, 6, 8, 10 and 12mg/L) a pH of 5.4 at 298K for 12 minutes with concentration of Cr(VI) set at 10mg/L. The temperature effect showed that the reaction rate increased with increase in temperature. The kinetic results showed that the reaction was pseudo-first order with respect to Cr(VI). The activation entropy obtained from Eyring's plot was -78.87 J/K/mol which agrees with the formation of a condensed compound. The activation enthalpy was -7.125KJ/mol showing that the reaction was exothermic. The activation energies obtained were 23.50, 24.28, 25.07, 25.47 and 26.26KJ/mol for the respective temperatures of 298, 308, 318, 323, and 333K. This increase in activation energy with increase in temperature implies that bond breakage and product formation was more favourable at lower temperature. The stoichiometry suggested that the Cr(VI) : $N_2H_6SO_4$ molar ratio was 1 Cr(VI) : 1.45 $N_2H_6SO_4$, this value was found to be in agreement with the theoretically obtained result. The results of this study show that $N_2H_6SO_4$ could be use for the reduction of Cr(VI) in polluted environment.

Keywords: Aqueous phase Reduction; Cr (VI); $N_2H_6SO_4$

Introduction

Chromium is a shiny, silvery in colour, hard and brittle metal. It has a high melting point (1875.0°C) and boiling point (2,672.0 °C). Oxidation states from -2 to +6 are known. The most stable oxidation state is +3. The natural isotope for Cr are ⁵⁰Cr (4.3%), ⁵²Cr (83.8%), ⁵³Cr (9.6%), and ⁵⁴Cr (2.4%) (Abbott *et al.*, 1965).

The abundance of Cr in the universe and on earth varies considerably. Chromium (Cr) is found in the universe at 15 parts per million (ppm) by mass, in the sun at 20 ppm and in carbonaceous meteorites at

3.1 parts per thousand by mass. Crustal rocks on the earth contain an average of 140 ppm of Cr, seawater contains 0.6 ppb, stream water has 1 ppb and humans have 30 ppb Cr by mass. (Abbott *et al.* 1965).

Chromium (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, Chromium (Cr) was widely used in photographic film, paper pulp producing, automotive parts, chemical manufacturing, electroplating, tanning, pigments,

dyes, industrial water cooling, metal finishing, magnetic tapes, 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 have been 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. Chromium exhibits a wide range of possible oxidation states where the +3 state is most stable energetically; the +3 and +6 states are most commonly observed in the environment.

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 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 Cr(VI)/Cr(III) redox reactions (Hu *et al.*, 2010, Iorungwa *et al.*, 2014). 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 objectives of our research was to detoxify Cr(VI) by reduction using Hydrazine sulphate, determine the rate of reduction, its stoichiometry and also obtain some thermodynamic parameters of the reduction.

Materials and methods

Materials

All the reagents and chemicals such as diphenylcarbazide (DPC), $K_2Cr_2O_7$, $N_2H_6SO_4$, H_2SO_4 used in the study were of analytical/G.R. grade which were purchased from Merck (Mumbai, India). All solutions were prepared using distilled water. Glasswares and plastics were washed with distilled water, rinsed with (1:1) HNO_3 and finally with distilled water. Chromium (VI) stock solution was prepared from $K_2Cr_2O_7$ by dissolving 2.828g of the salt in 1 litre of distilled water (0.0096mol/L). A 2 mg/L Cr(VI) solution was prepared measuring exactly 2mL of the stock solution in 1 L of distilled water. $N_2H_6SO_4$ stock solution was prepared by dissolving 1.0g of the salt in a litre of distilled water (0.0077mol/L). Interferences were avoided by adding diphenylcarbazide to Cr(VI) before adjusting the pH of the solution.

Methods

The reduction of Cr(VI) by $N_2H_6SO_4$ was conducted in accordance with the method described elsewhere [Njoku and Nweze (2009); Iorungwa *et al.*, (2014)] with slight modifications. A 10 mL portion of 2.0 mg/L Cr(VI) was measured into a 250mL beaker and stirred to make a uniform solution. Next, a 20mL aliquot of 20.0 mg/L $N_2H_6SO_4$ was added and the mixture shaken thoroughly. The pH of these solutions were adjusted using 1.0 M H_2SO_4 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 (Unicom Heyios α UV-Visible spectrophotometer) was set at 372 nm and the absorbance of Cr(VI) was read at that wavelength. The spectrum gave the wavelength in nanometers of the remaining chromium which was thereafter extrapolated from the calibration curve to obtain the concentration in mg/L of the remaining Cr(VI). The experiment 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, 5,6,7,8 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. These are referred to as initial pH values because the pH of the reactions change after the reactions reach completion.

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 5.4. The initial concentration of Cr(VI) was set at about 10.0 mg/L and the reaction time was

10 minutes. Equal volumes of 10mL each of the reductant and Cr(VI) was used for the mixture.

Results and discussion

Kinetic study

Figures 2 and 3 shows the results of the reduction of Cr(VI) by $N_2H_6SO_4$ at different temperatures and pH conditions in aqueous phase. Generally speaking, the result shows that the rate of reduction increased with decrease in pH and increase in temperature.

The rate in acidic and neutral solution was faster than in basic solution. This observation agrees with that of Market *et al* (1998) where an *in situ* kinetic reduction of Cr(VI) by ferrous iron in solid phase was studied. The findings of this study are also consistent with those of Palmer and Wittbrodt, (1996); Elovitz and Fish (1994); Iorungwa, (2014).

The rate of reduction depends on the speciation of Cr(VI) in a given pH range as shown in the pourbaix diagram (Fig.1). To properly explain the increase in reaction rate with decreasing pH, we need to take into consideration the speciation of both Cr(VI) and the reductant under these conditions. The Eh – pH diagram shown in(Fig 1)provides a generalized depiction of the major aqueous chromium species and redox stabilities under conditions of chemical equilibrium. The dominant Cr(VI) species are $HCrO_4^-$ at pH 1-6 and CrO_4^{2-} at pH greater than 6. Cr(VI) also forms other species such as $HCr_2O_7^-$ and $Cr_2O_7^{2-}$.

However, their formation requires Cr(VI) concentrations $> 10^{-2} \text{ mol.dm}^{-3}$. The increase in reaction rate with decreasing pH can therefore probably be attributed to $HCrO_4^-$ which is reduced more easily than CrO_4^{2-} (Wilkinson and Cotton, (1988), Iorungwa *et al* (2014).

In acidic solution, Cr(VI) demonstrates a very high positive redox potential (E^0 within 1.33 and 1.38V) (Iorungwa *et al* 2014, Ball and Nordstrom 1998, Shriver *et al* 1994, Greenwood and Earnshaw, 1984), which denotes that it is strongly oxidizing and unstable in the presence of electron donors. As the $HCrO_4^-$ reduction is accompanied by the H^+ consumption as shown in the equation below:



When a plot of the logarithm of time taken to attain 75% reduction against the pH was done, it was found that there was a linear logarithm relationship between pH and the time taken. This is given by

$$\text{Log}(t_{0.75}) \propto \text{log}(1/H^+) = \text{pH}$$

The relationship showed that the Cr(VI) – $N_2H_6SO_4$ reaction system rate law has first – order dependence on $[H^+]$. This observation was in agreement with findings obtained elsewhere (Beukes *et al*, 1999)

In more basic solution the reduction of CrO_4^{2-} , generates OH^- against a gradient as shown in the

equation below (Iorungwa *et al*. (2014), Nieboer and Jusy 1988). The reduction potential of chromate to Cr(III) hydroxide is -0.13V in basic medium.

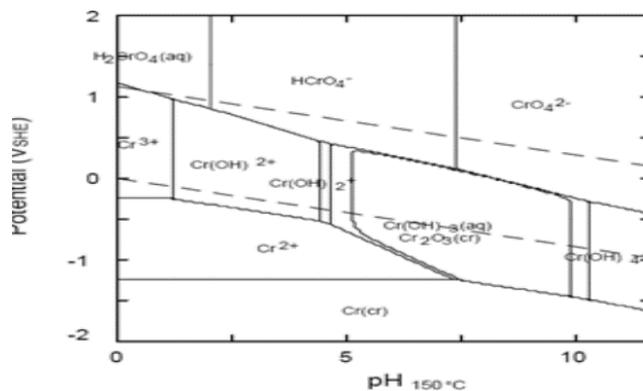
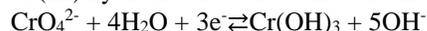


Fig.1. A simplified Pourbaix diagram for Chromium species at 150°C and $[Cr(aq)]_{tot} = 10^{-8} \text{ M}$ (Ball and Nordstrom 1998, Richard and Bourg 1991, Nieboer and Jusys 1988, Iorungwa, *et al.*, 2014)

Monitoring the reaction at physiological temperature (298K), the reactions were further considered at higher initial temperatures of 308K, 318K, 323K, and 333 K. The reactions were observed to be faster as the temperature of the reaction was increased. A plot of natural logarithm of $[Cr(VI)]$ against time was made (Fig 3) and it showed that the reaction had a first-order dependence on Cr(VI). The observed rate constants K_{obs} were determined from the slopes of the plots.

After determining the k_{obs} , another plot of $\ln(k_{obs}/T)$ against $1/T$ was made, this was in accordance with the Elovitz and Fish, (1994), Iorungwa, (2014). The graph was found to be linear with regression coefficient of 0.837. The observed rate constant (K_{obs}) for the reduction of Cr(VI) by $N_2H_6SO_4$ at different temperatures and pH5.4 was found to increase with increase in temperature. For example, k_{obs} was found to be $1.714 \times 10^{-3} \text{ s}^{-1}$ at 298K and when the temperature was increased to 308 K, the k_{obs} increased to $1.768 \times 10^{-3} \text{ s}^{-1}$. As the temperature was raised to 318 K, 323 K, and 333 K, the k_{obs} also increased to, 2.305×10^{-3} , 2.461×10^{-3} and $2.553 \times 10^{-3} \text{ s}^{-1}$ respectively.

The results obtained showed that the reaction is slower at a higher pH and faster at a higher temperature. Increased temperatures increase the rate of interaction between reacting species; this is why the K_{obs} increased when the temperature was increased. The slow rate observed at high pH values can be attributed to the formation of other species as shown in (fig.1 Pourbaix diagram) or the complete depletion of Cr (VI) in the solution. This observation agrees with Iorungwa *et al* (2014), Beukes *et al* (1999).

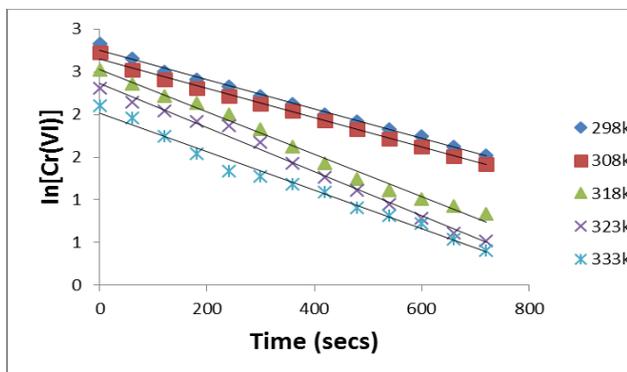


Figure 2: A plot of natural logarithm of Cr(VI) against time (secs) at different temperatures and pH 5.4.

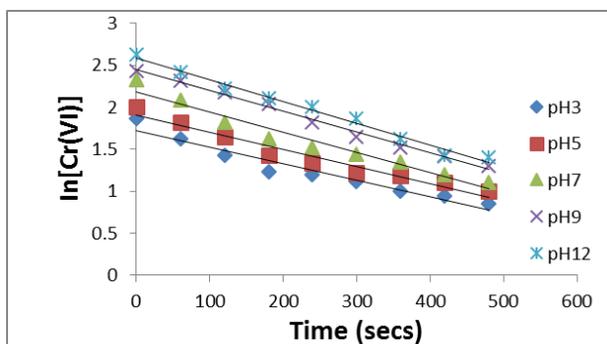


Figure 3: A plot of natural logarithm of Cr(VI) against time (secs) at different pH conditions and physiological temperature (298 K)

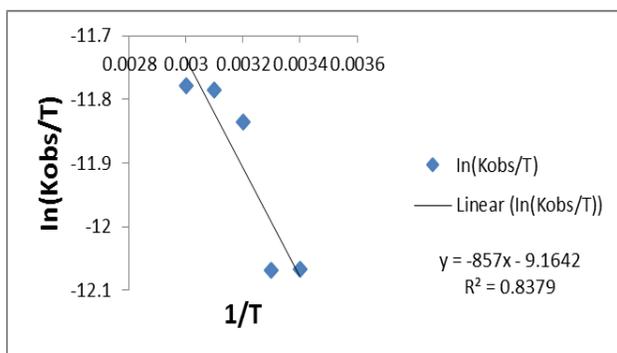


Figure 4: Shows a plot of $\ln(K_{obs}/T)$ against $1/T$ for the reduction of Cr(VI) by $N_2H_6SO_4$

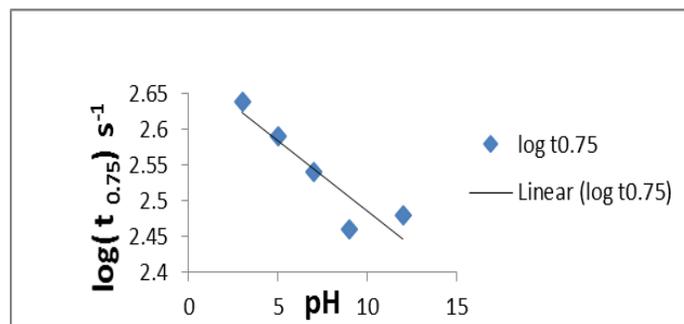


Figure 5: Time required to reach 75% reduction of the initial Cr(VI) ($t_{0.75}$)

Thermodynamic study

To study the thermodynamic activation parameters, the K_{obs} obtained from the plot of $\ln[Cr(VI)]$ against time was divided by temperature and fit into the following Eyring's equation;

$$\ln(K_{obs}/T) = \ln(K_b/h) + \Delta S/R - \Delta H/RT$$

Where;

T=temperature in Kelvin

K_b = Boltzmann's constant (1.38×10^{-23} J/K)

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

R = gas constant (8.314J/K/mol)

The Eyring's equation was used to make a plot of $\ln(K_{obs}/T)$ against $1/T$ as seen in fig.4. The activated entropy (ΔS) was obtained at the intercept of the plot while the activated enthalpy (ΔH) was obtained from the slope. The results obtained from the plots showed that the activated entropy was a negative value of -78.87J/K and the activated enthalpy had a value of -7.125J/mol for all temperatures. The negative enthalpy ($-\Delta H$) indicates that the reduction of Cr(VI) using $N_2H_6SO_4$ is exothermic. The activation entropy (ΔS) 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. The values of the activation energy obtained when compared with that of some organic compounds used in chromium reduction was relatively lower at 298K.

The activation energy was calculated from the relationship:

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

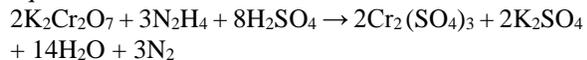
Where, E_a is in KJ/mol.

The E_a obtained were 23.50, 24.28, 25.07, 25.47 and 26.26 KJ/mol for 298, 308, 318, 323 and 333K respectively. When these values were compared with the results obtained by X.R. Xu and J.D. Gu(2005), it was observed that the E_a of organic reductant were higher compared to the result obtained when using $N_2H_6SO_4$ as a model reductant, implying that the

reaction is more favourable when using inorganic reductant than organic.

Stoichiometric study

It has been established that the reduction of Cr(VI) generates Cr(III) compounds [Deng,(1995), Chulsung Kim,(2001), Iorungwa,(2014)], the reaction with $N_2H_6SO_4$ generates a theoretical Stoichiometric equation.



A first glance at Table 4.7 shows that the concentration of Cr(VI) consumed increased steadily as the concentration of $N_2H_6SO_4$ was increased, while that of the residual Cr(VI) decreased steadily with increase in concentration of $N_2H_6SO_4$. It was observed that 4mg/L of $N_2H_6SO_4$ consumed exactly 2.759mg/L of Cr(VI) given a Stoichiometric mass balance Cr(VI)/ $N_2H_6SO_4$ ratio of 1:1.45. This ratio was maintained when the concentration of $N_2H_6SO_4$ was varied from 4 to 12mg/L. The result obtained from the experiment was in agreement with the theoretical ratio obtained elsewhere (Iorungwa, 2014).

Conclusion

This research has demonstrated that $N_2H_6SO_4$ reduced Cr(VI) in aqueous phase, the rate of reduction decreased with increase in pH and the activation entropy (ΔS) of the reduction was negative with relatively small value of the activation enthalpy (ΔH). This gives rise to activation energy that has smaller values when compared with the activation energy obtained from the reduction of Cr(VI) by some organic compounds under similar experimental conditions. These observations are advantageous because, whereas organic compounds reduced Cr(VI) with higher activation energy, $N_2H_6SO_4$ reduced with lower activation energy meaning that $N_2H_6SO_4$ is a better reductant which can cleanup and complete the process in a shorter time.

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