



Full Length Research

KINETICS, THERMODYNAMICS AND STOICHIOMETRY OF AQUEOUS PHASE DECHROMIFICATION USING FERROUS SULPHATE

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ABSTRACT

Received 5 March, 2016
 Revised on the 10 March, 2016
 Accepted 11 March, 2016

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The aqueous phase reduction of hexavalent chromium, Cr(VI) by ferrous sulphate was followed spectrophotometrically (UV-visible) under operating variables such as temperature (298 – 323 K), pH (3 – 12), and initial reductant concentration (2.63×10^{-5} – 7.9×10^{-5} mM). The reaction rate increased slightly with increase in temperature and followed pseudo first - order kinetics with respect to Cr (VI). The activation entropy obtained from plots of $\ln(k_{obs}/T)$ vs. $1/T$ was $-197.53 \text{ JK}^{-1}\text{mol}^{-1}$, suggesting the formation of a condensed compound through an associative mechanism. The activation enthalpy varied from $(-7.5 \times 10^{-6} - 3.3 \times 10^{-4} \text{ kJmol}^{-1})$ and in most cases was negative, implying the exothermicity of the reaction. Activation energies obtained were 58.87, 60.84, 62.82, 63.80 and 65.78 kJmol^{-1} , respectively at 298, 308, 318, 323 and 333 K. This increase in activation energy with increase in temperature implies that bond breakage and product formation was more favourable at lower temperatures. Stoichiometric studies suggested that the Cr(VI) : FeSO_4 molar ratio was 1: 8.7, consistent with the theoretically obtained result. Overall, the finding show that FeSO_4 could be used for the aqueous phase reductive detoxification of Cr(VI) in polluted areas.

Keywords: Hexavalent chromium, ferrous sulphate, dechromification, redox reaction, kinetics, thermodynamics, stoichiometry

INTRODUCTION

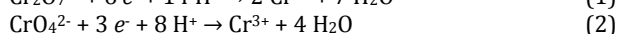
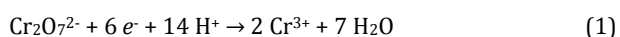
The toxicity of Cr(VI) can never be over emphasized and this is extensively due to the fact that one of the reduction products of Cr(VI) is Cr(V), a known carcinogen which settles on any tissue to form cancerous growths. Cr(V) has also been reported to be a factor leading to premature senility in parts of Russia (Veena *et al.*, 2012). The Cr(VI) ion is a very strong oxidizing agent (therefore very fast in reacting, unlike Cr(III) and likely to form complexes). Cr(VI) is not a very stable state when compared to Cr(III). This can be

further explained by Frost diagram (Shriver *et al.*, 1994; Iorungwa, 2014; Iorungwa *et al.*, 2015) and the standard redox potential (Xu and Gu, 2005; Iorungwa *et al.*, 2014). Chronic inhalation of Cr(VI) compounds increases the risk of lung, nasal and sinus cancer. Severe dermatitis skin ulcer can result from contact with Cr(VI) compounds. It can cause mild to severe liver abnormalities. Cr(VI) compounds are teratogenic to animals (Kimbrough *et al.*, 1999). Effluents from electroplating and tannery industries are a major

source of aquatic pollution in India with high chemical oxygen demand (COD), biological oxygen demand (BOD), and Cr(VI).

Cr(III) on the other hand is an essential element in mammalian metabolism. In addition to insulin, it is used to reduce blood glucose levels and control certain cases of diabetes. It is also responsible for reducing blood cholesterol levels by diminishing the concentration of low density lipoproteins "LDLs" in the blood (Anderson, 1989; Pettine *et al.*, 2002). Various technologies are employed for removing toxic ions from water, which include chemical precipitation, reverse osmosis, ion-flotation, evaporation, ion-exchange and adsorption (Bhatti *et al.*, 2007; Sarin and Pant, 2006).

Most of these methods suffer from drawbacks such as incomplete metal removal, high capital and operational costs, requirements of expensive equipment and monitoring system, high reagent and energy requirements, generation of toxic sludge, other waste products that require disposal, membrane scaling, fouling and blocking (Demirbas *et al.*, 2004; Demiral *et al.*, 2008). Reduction by most electron donors is one effective way of removing toxic ions since it involves precipitation and is also cost effective. The basic reactions describing Cr(VI) reduction in aqueous phase can be presented as follows:



Electrons are donated chemically by a reductant and one of such chemical which readily available is ferrous sulphate (FeSO_4) (Zotter, 1992; Eckenfelder, 2000). The reduction of Cr(VI) by FeSO_4 is favoured under acidic conditions as indicated by the reaction stoichiometry, thus prompting the addition of a suitable mineral acid (Eckenfelder, 2000). For Cr(VI) to be completely reduced, there is need to add the reductant in large excess and once the chemical is reduced, it precipitated as its hydroxide (Iorungwa, 2014).

MATERIALS AND METHODS

MATERIALS

Reagents such as $\text{K}_2\text{Cr}_2\text{O}_7$, FeSO_4 were obtained from BDH with purity of 98 and 96% respectively. All reagents obtained were used without further purification. The analysis was conducted using a Milton and Roy Spectronic 20 UV/Visible spectrophotometer.

Preparation of Solutions

All solutions were prepared using distilled water. All glassware and plastics were washed with distilled water, rinsed with (1:1) HNO_3 and finally with distilled water. Cr(VI) stock solution was prepared from commercially obtained $\text{K}_2\text{Cr}_2\text{O}_7$ (BDH) by dissolving 2.828 g of the salt in 1 L of distilled water. A 2 mg L^{-1} Cr(VI) solution was prepared measuring exactly 2 mL of the stock solution in 1 L of distilled water. FeSO_4 stock solution was prepared by dissolving 1.0 g 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.

Experimental Procedure

Cr(VI) reduction by FeSO_4 was carried out in accordance with methods described elsewhere (Bill *et al.*, 1998; Xu and Gu, 2005; Njoku and Nweze, 2009; Iorungwa *et al.*, 2014a) with slight modifications. A 10 mL portion of $3.85 \times 10^{-2} \text{ mM}$ Cr(VI) was measured into a 250 mL beaker and a 20 mL aliquot of $1.3 \times 10^{-4} \text{ mM}$ FeSO_4 was added and the mixture shaken thoroughly. The pH of the solution was 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 (Milton Roy USA Spectronic 20D) was set at 349 nm and the absorbance of Cr(VI) was read at that wavelength where the absorbance of FeSO_4 was found to be weak. The set up was done in triplicate at temperatures of 298, 308, 318, 323 and 333 K. In order to study the effect of rate 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 and 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: 2.63×10^{-5} , 3.95×10^{-5} , 5.26×10^{-5} , 6.58×10^{-5} and $7.90 \times 10^{-5} \text{ mM}$ to assess the concentration – dependence of the reduction. The reaction was at 298 K and a moderately acidic pH of 5 and an alkaline pH of 9. The initial concentration of Cr(VI) was set at $1.92 \times 10^{-1} \text{ mM}$ and the reaction time was 5 minutes. Equal volumes of 10 mL each of the reductant and Cr(VI) was used for the mixture.

RESULTS AND DISCUSSION

The relationship between the change in concentration of Cr(VI) and time taken at different temperatures are

as presented in Figures 1 to 5 below. From a general stand point, it can be stated that the rate of reduction of Cr(VI) decreases as the pH of the solution was increased and increases as the temperature was increased. This is as shown by the observed rate constants (k_{obs}) obtained from the individual plots.

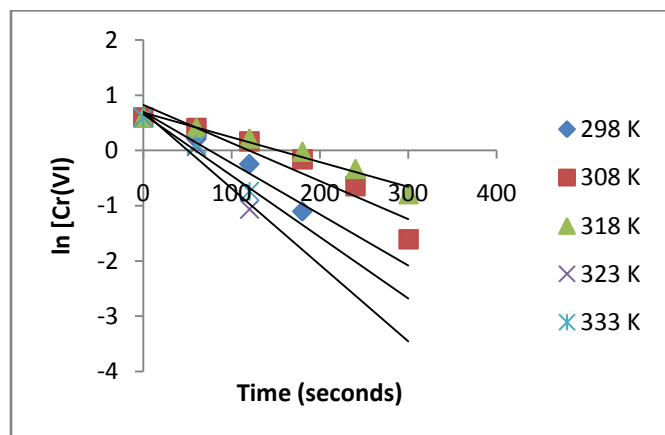


Figure 1: Plot of $\ln [\text{Cr(VI)}]$ against time at pH 3

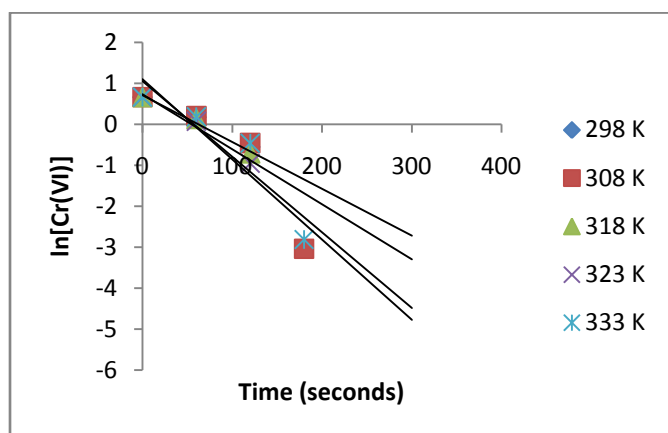


Figure 2: Plot of $\ln [\text{Cr(VI)}]$ against time at pH 5

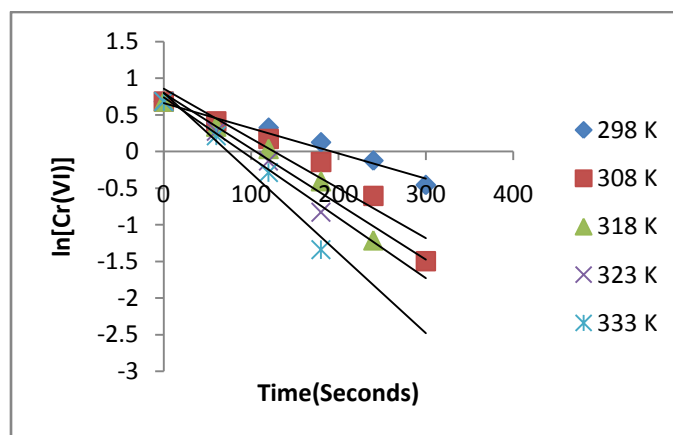


Figure 4: Plot of $\ln [\text{Cr(VI)}]$ against time at pH 9

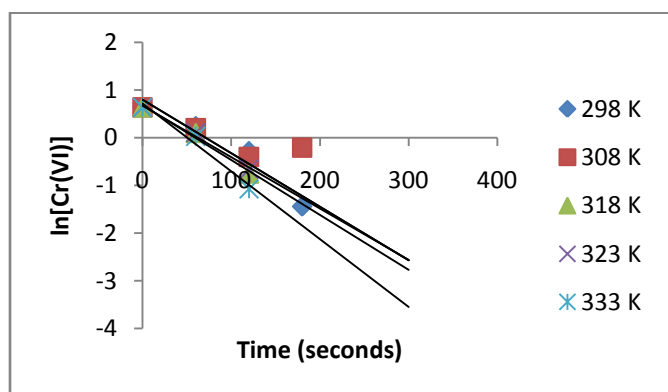


Figure 3: Plot of $\ln [\text{Cr(VI)}]$ against time at pH 7

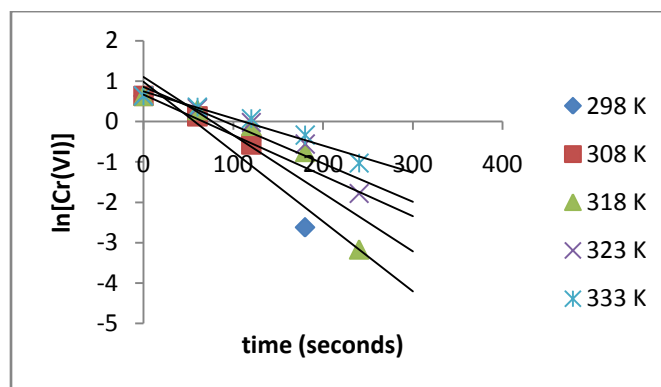


Figure 5: A plot of $\ln [\text{Cr(VI)}]$ against time at pH 12

The k_{obs} obtained when the pH was 3 at a temperature of 298 K was 2.29 s^{-1} and when the temperature was maintained at 308 K, the observed rate constant increased to 2.36 s^{-1} ; temperatures of 318, 323 and 333 K had 2.44, 2.48 and 2.55 s^{-1} respectively. A similar trend but slower pace was observed when the pH was adjusted to 5. Here, the observed rate constant was relatively lower when compared with the outcome at pH 3, the Kelvin temperatures of 298, 308, 318, 323 and 333 had 1.35×10^{-2} , 1.40×10^{-2} , 1.44×10^{-2} , 1.47×10^{-2} and $1.51 \times 10^{-2} \text{ s}^{-1}$. At pH 7, the decrease in the rate of the reaction was also observed with the Kelvin temperature of 298, 308, 318, 323 and 333 registering the observed rate constants of 1.16×10^{-3} , 1.20×10^{-3} , 1.24×10^{-3} , 1.26×10^{-3} and $1.30 \times 10^{-3} \text{ s}^{-1}$ respectively. When the pH was adjusted to 9, the temperatures of 298, 308, 318, 323 and 333 K had 2.82×10^{-3} , 2.91×10^{-3} , 3.01×10^{-3} , 3.05×10^{-3} and $3.15 \times 10^{-3} \text{ s}^{-1}$. The slowest rate recorded when the pH was adjusted to 12; here, 298 K gave an observed rate constant $1.7 \times 10^{-4} \text{ s}^{-1}$, 308, 318, 323 and 333 K had 1.74×10^{-4} , 1.8×10^{-4} , 1.90×10^{-4} and $1.96 \times 10^{-4} \text{ s}^{-1}$.

When a plot of the observed rate constants was made against the individual pH values at all the temperature values under investigation, it observed to decrease steadily with a steep gradient at low pH and flatten at higher values indicating clearly that the rate of reduction was lower at higher pH values. This plot was found to be in agreement with pattern obtained by Nieker *et al.*, 2007. The patterns observed can be ascribed to the fact that the predominant forms of Cr(VI) are HCrO_4^- at pH 1-6 and CrO_4^{2-} at pH > 6, others include HCr_2O_7^- and $\text{Cr}_2\text{O}_7^{2-}$ (Xu and Gu, 2005; Iorungwa, 2014). As the pH increases, there is a conversion of the dominant species through a series of products from hydrolysis such as CrOH^{2+} , $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3^0$, $\text{Cr}(\text{OH})_4^-$, (Rai *et al.*, 1987). Species like $\text{Cr}(\text{OH})_2^{4+}$ and $\text{Cr}_3(\text{OH})_4^{5+}$ are produced at slightly acidic to neutral pH with the concentration of Cr(III) being moderate. With organic moieties, Cr(III) forms strong complexes and these are also used as reductants. When they are formed, there is a slow inner sphere exchange of the ligands around Cr(III) and this may persist in conditions where the Cr(III) – organic ligand are unstable thermodynamically. This explains why at almost neutral pH, there is high level of organic substances in effluents from tanning (Li and Xue, 2001). The redox potential of different oxidation states of Cr in both acidic and alkaline was studied else where it was found that the reduction of Cr(VI) was more spontaneous at lower pH (Cotton and Wilkinson, 1980; Shriver *et al.*, 1994 ; Xu and Gu, 2005).

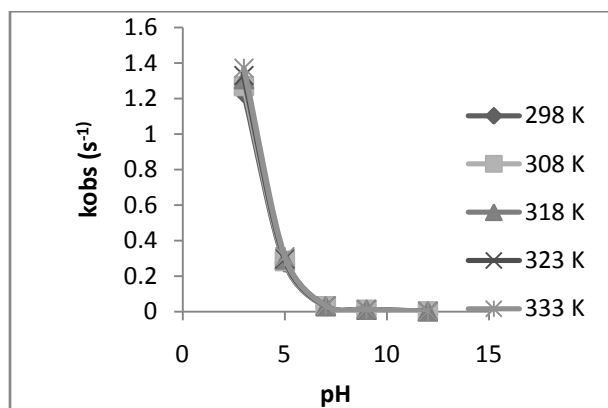


Figure 6: A plot of observed rate constants against pH at different temperature values

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

$$\ln\left(\frac{kh}{k_bT}\right) = \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (3)$$

where:

ΔH^\ddagger = the activation enthalpy (J mol⁻¹)

ΔS^\ddagger = the activation entropy (J K⁻¹)

R = the gas constant (8.314 J K⁻¹mol⁻¹)

T = the absolute temperature (Kelvin)

k = the rate constant (s⁻¹)

h = the Planck constant (6.63 × 10⁻³⁴ Js)

k_B = the Boltzmann constant (1.38 × 10⁻²³ J K⁻¹)

The Eyring's equation was used to make a plot of

$$\ln\left(\frac{k_{obs}}{T}\right) \text{ vs } \frac{1}{T}$$

as seen in Figure 7 and the activated entropy (ΔS^\ddagger) was obtained at the intercept of the plot while the activated enthalpy (ΔH^\ddagger) was obtained from the slope. The results obtained from the plots revealed that the activated entropy was a large negative value of -197.5321 JK⁻¹ and the activated enthalpy had the lowest value of -8.31x10⁻⁶ J mol⁻¹ and 4.157 x 10⁻⁴ J mol⁻¹ as the highest value. The implication of the large negative value of the ΔS^\ddagger is that the reaction followed an associative mechanistic pathway (Xu and Gu, 2005; Iorungwa *et al.*, 2014a; Iorungwa *et al.*, 2014b).

The activation energy was calculated from the relationship $E_a = T\Delta S$ (4)

E_a (kJmol⁻¹) is an operationally defined expression of the dependence of rate constant on temperature according to equation 5.

$$E_a = RT^2 \left(\ln \frac{k}{T} \right) \quad (5)$$

$$\text{Where } k = A \exp^{-E_a/RT} \quad (6)$$

The E_a were 58.8646, 60.8400, 62.8153, 63.8029 and 65.7783 kJmol⁻¹ for 298, 308, 318 323 and 333 K respectively. When these values were compared with the results obtained elsewhere (Xu and Gu, 2005), it was observed that the E_a of organic reductants were relatively higher those obtained when using FeSO_4 as a model reductant indicating that the reaction was more favoured (Xu and Gu, 2005).

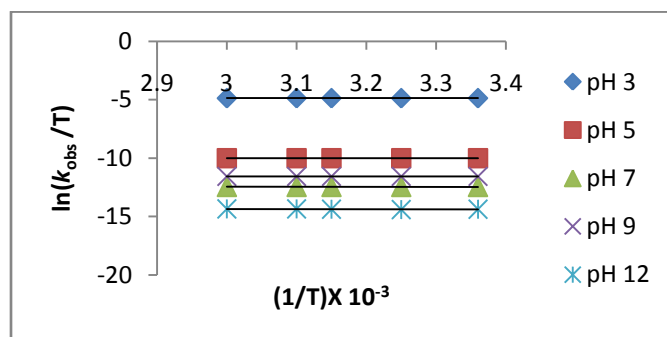
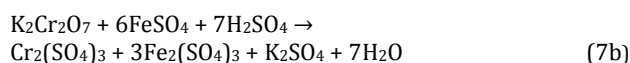
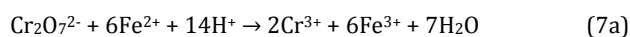


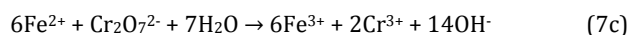
Figure 7: The Eyring's plot for the reduction of Cr(VI) by Ferrous sulphate at different pH values.

In an attempt to establish the stoichiometry of the reaction, different concentrations of FeSO_4 were prepared viz: 2.6×10^{-5} , 3.95×10^{-5} , 6.58×10^{-5} and 7.9×10^{-5} mM while the concentration of Cr(VI) was maintained at 6.58×10^{-5} mM. After reacting, it was observed that 2.63×10^{-5} mM of FeSO_4 consumed exactly 9.31×10^{-6} mM giving a $\text{Cr(VI)} : \text{FeSO}_4$ of 1:8 and when the concentration of FeSO_4 was further increased to 3.95×10^{-5} mM, the amount of Cr(VI) consumed increased to 1.31×10^{-5} mM maintaining about the same ratio and similar trends were observed when the concentration of FeSO_4 was varied to 5.26×10^{-5} , 6.58×10^{-5} and 7.9×10^{-5} mM and the ratio was maintained. When the experiment was conducted in alkaline media, the ratio did not change as seen in Table 1. This observation clearly implied that stoichiometry was not affected by changes in the pH of the medium.

When Cr(VI) is reduced, the species generated has been established to be Cr(III) (Richard and Bourg, 1991; Shriver *et al.*, 1994; Deng and Stone, 1995; Ball and Nordstrom, 1998). The reaction between Cr(VI) and FeSO_4 in acidic medium as reported by Iorungwa, (2014) could be expressed in the equations below:



In alkaline medium the reaction is represented as follows



The $\text{Cr(VI)} : \text{FeSO}_4$ ratio obtained from experiment was found to be 1: 8 and 1: 6 for $\text{Cr}_2\text{O}_7^{2-} : \text{FeSO}_4$ both in acidic and alkaline media. The values are stoichiometric and in agreement with theoretically obtained values.

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Table 1: showing the amount of Cr(VI) consumed as the concentration of FeSO_4 was varied at different pH

Medium	Conc. FeSO_4 (mM)	Residual Cr(VI) (mM)	Consumed Cr(VI) (mM)
Acidic	2.63×10^{-5}	$1.83 \times 10^{-4} \pm 0.11$	$9.31 \times 10^{-6} \pm 0.11$
	3.95×10^{-5}	$1.79 \times 10^{-4} \pm 0.00$	$1.31 \times 10^{-5} \pm 0.00$
	5.26×10^{-5}	$1.74 \times 10^{-4} \pm 0.11$	$1.83 \times 10^{-5} \pm 0.11$
	6.58×10^{-5}	$1.7 \times 10^{-4} \pm 0.17$	$2.26 \times 10^{-5} \pm 0.17$
	7.9×10^{-5}	$1.66 \times 10^{-4} \pm 0.02$	$2.69 \times 10^{-5} \pm 0.02$
Alkaline	2.63×10^{-5}	$1.84 \times 10^{-4} \pm 0.12$	$8.62 \times 10^{-6} \pm 0.11$
	3.95×10^{-5}	$1.79 \times 10^{-4} \pm 0.10$	$1.31 \times 10^{-5} \pm 0.00$
	5.26×10^{-5}	$1.75 \times 10^{-4} \pm 0.11$	$1.75 \times 10^{-5} \pm 0.11$
	6.58×10^{-5}	$1.7 \times 10^{-4} \pm 0.17$	$2.19 \times 10^{-5} \pm 0.17$
	7.9×10^{-5}	$1.66 \times 10^{-4} \pm 0.02$	$2.63 \times 10^{-5} \pm 0.02$

CONCLUSION

This research has demonstrated that FeSO_4 reduced Cr(VI) in aqueous phase, the rate of reduction decreased as the pH increased and the activation entropy (ΔS) of the reduction was largely negative with a relatively small value of the activation enthalpy (ΔH). This resulted in 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, FeSO_4 reduced Cr(VI) with a lower energy of activation meaning that FeSO_4 is a better reductant which can be used for cleanup and will complete the process in shorter time. The reduction process further showed that the stoichiometry does not depend on pH.

CONFLICT OF INTEREST

None declared.

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Article's citation

Iorungwa MS, Wuana RA, Yiasse SG and Tor-Anyiin TA (2016). Kinetics, thermodynamics and stoichiometry of aqueous phase dechromification using ferrous sulphate. *Ew J Chem Kinet* 1(1): 10-15.