



## Simultaneous Studies of Redox Reaction of Chromium(VI) and Arsenic(III) in Aqueous Phase: A Kinetic and Mechanistic Approach

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### Authors' contributions

This work was carried out in collaboration among all authors. Author ITB designed the study, performed the kinetic studies and wrote the first draft of the manuscript. Author WAR managed the analyses of the study. Author YGS contributed greatly in the mechanism of the reaction. All authors read and approved the final manuscript.

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### ABSTRACT

A kinetic and mechanistic approach was used to simultaneously study the oxidation of As(III) and reduction of Cr(VI) in aqueous phase, and in the presence of Fe(III). Reactions were monitored by UV-visible spectrophotometry. The stoichiometry of the reaction was 1: 3 ( $\text{Cr}_2\text{O}_7^{2-}$  to  $\text{AsO}_2^-$ ). The rate equation for the reaction is proposed as  $-\text{d}[\text{Cr}_2\text{O}_7^{2-}]/\text{dt} = k_2[\text{Cr}_2\text{O}_7^{2-}][\text{AsO}_2^-]$  where  $k_2$  is the second order rate constant. The reaction was not affected by Fe(III) ions within the studied concentration range of  $0.001 - 0.009 \text{ mol L}^{-1}$ . From the reaction between  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$ , a plausible mechanism involving an ester formation by the reactants leading to the eventual formation of As(V) and Cr(III) was proposed.

Keywords: Oxidation-reduction; arsenic(III); chromium(VI); kinetics; mechanism.

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## 1. INTRODUCTION

A large number of industries process waste streams that get in to the environment and may contain potentially toxic metals at concentrations above the acceptable limits (since there is increase in human needs and changes in civilization) [1]. Environmental contamination can also occur through metal corrosion, atmospheric deposition, soil erosion of metal ions and leaching of heavy metals, sediment re-suspension and metal evaporation from water resources to soil and ground water. Natural phenomena such as weathering and volcanic eruptions have also been reported to significantly contribute to heavy metal pollution [2]. Industrial sources include metal processing in refineries (mining operations), coal burning in power plants, petroleum combustion, electronic device manufacturing units, nuclear power stations and high tension lines, metal-plating facilities, plastics, textiles, tanneries, microelectronics, wood preservation and paper processing plants [3]. The waste streams from the industrial plants contain toxic heavy metals and are not easily removed without specialized or advanced treatment [1].

Among the priority metals that are of great public health significance are arsenic and chromium which are toxic to humans and animals. Chromium is released into the environment by various industries including electro-plating, chromate manufacturing, leather tanning and wood preservation. In the environment, Chromium exists primarily as Cr(VI) and Cr(III), with Cr(VI) being of significant concern due to its carcinogenicity [4]. Another metal is arsenic which is ubiquitous in the earth's crust, and elevated arsenic in the environment is primarily attributed to anthropogenic sources, including industrial waste products, agricultural pesticides and wood preservatives. The predominant inorganic forms of arsenic in the environment are As (V) and As(III). As (V) is mainly present in the environment as  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$  as most soluble forms and most likely partially as  $\text{H}_3\text{AsO}_4$  or  $\text{AsO}_4^{3-}$ , while As(III) dominates in sediments as  $\text{H}_3\text{AsO}_3$  at pH below 9.2 and in some cases as  $\text{AsO}_2^-$  [5]. As (III) is more toxic and mobile than As (V) in the environment. In Schimatari's water supply for instance, As concentrations up to  $34 \mu\text{gL}^{-1}$  along with Cr (VI) levels up to  $40 \mu\text{gL}^{-1}$  were detected. In the Asopos River, total chromium values were up to  $13 \mu\text{gL}^{-1}$ , hexavalent chromium was less than  $5 \mu\text{gL}^{-1}$  and other toxic elements were relatively low [6].

Based on the composition of natural waters, and also the presence of oxygen, iron can occur in the form of di- or trivalent compounds. Due to oxidation and reduction, processes that depend on the ambient oxygen conditions, the electrode potential and the pH of the water, zones of occurrence of iron compounds can be established in deep bodies of standing water. Near the bottom, where reduction processes occur, iron(II) is prevalent, but closer to the surface, where there are larger amounts of oxygen dissolved in the water, iron(III) is dominant [7]. It's therefore expected that, the presence of iron species and other redox couples in water bodies could affect the rates of other redox reactions. From the above, Cr(VI) reduction and As(III) oxidation are desirable to reduce their adverse impact on the environment [8].

## 2. MATERIALS AND METHODS

### 2.1 Chemicals, Reagents and Apparatus

Potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$  (JHD<sup>AR</sup>), chromium(VI) oxide,  $\text{CrO}_3$  (LOBA<sup>AR</sup> CHEMIE PVT Ltd), chromium(III) oxide,  $\text{Cr}_2\text{O}_3$  (LOBA<sup>AR</sup> CHEMIE PVT Ltd), sodium arsenite,  $\text{NaAsO}_2$  (LOBA<sup>AR</sup> CHEMIE PVT Ltd), nitric acid,  $\text{HNO}_3$  (BDH<sup>AR</sup>), sodium nitrate,  $\text{NaNO}_3$  (Fenxichun<sup>AR</sup>), Iron(III) chloride,  $\text{FeCl}_3$  (LOBA<sup>AR</sup> CHEMIE PVT Ltd), acrylamide (JHD<sup>AR</sup>), methanol (99.9 % Fisher Chemical<sup>AR</sup>), distilled water, thermostatic water bath (Clifton unstirred bath model 92498), UV-visible spectrophotometer (Unico<sup>R</sup> 2800P), pH meter (Hanna Instrument H19024), analytical balance (aeADAM PW 184, AE 437531) and normal laboratory glasswares.

### 2.2 Determination of UV-visible Spectrum of the Cr (VI) and Cr(III)

Solutions of the salts of  $\text{CrO}_3$  and  $\text{Cr}_2\text{O}_3$  were prepared (with  $0.009 \text{ molL}^{-1}$ ) and the absorbances of the solutions taken in the wavelength range (300 - 750 nm) with a UV-visible spectrophotometer [9]. The wavelengths of maximum absorption were obtained by plot of absorbances versus wavelengths.

### 2.3 Stoichiometric Studies

The Stoichiometry of the reaction was determined by UV-visible spectrophotometric titration. Here, reaction mixtures containing fixed volume 10.00 mL ( $6.0 \times 10^{-5} \text{ molL}^{-1}$ ) of As(III) and varying volumes 2, 4, 6, 8 and 10 mL (concentrations;  $1.0 \times 10^{-3}$  -  $1.4 \times 10^{-2} \text{ molL}^{-1}$ ) of

Cr(VI) at constant ionic strength (I) of 0.1 molL<sup>-1</sup> NaNO<sub>3</sub>, T = ambient (297 – 300 K) and pH = 6 were allowed to reach completion. The absorbances of the solutions were taken at the wavelength of maximum absorbance of the Cr(VI) metal salt. The equivalent point was obtained from the plots of absorbances of the solutions against their concentrations [10].

## 2.4 Kinetic Studies

All rate measurements were made using UV-visible spectrophotometer at the wavelengths of maximum absorptions. The reaction rates were monitored at the wavelength by noting the decrease in absorbances of the reaction mixtures with time. The results were interpreted based on the fact that, Beer's law is additive for a multi component sample, Equations 1 and 2.

$$(A)\lambda_1 = (\epsilon_{Cr(VI)})\lambda_1 C_{Cr(VI)} + (\epsilon_{Cr(III)})\lambda_1 C_{Cr(III)} \quad (1)$$

$$(A)\lambda_2 = (\epsilon_{Cr(VI)})\lambda_2 C_{Cr(VI)} + (\epsilon_{Cr(III)})\lambda_2 C_{Cr(III)} \quad (2)$$

where A is the absorbances of the mixtures,  $\lambda_1$  and  $\lambda_2$  are wavelengths at which the absorbances were measured,  $\epsilon_{Cr(VI)}$  and  $\epsilon_{Cr(III)}$  are the molar absorptivities,  $C_{Cr(VI)}$  and  $C_{Cr(III)}$  are the concentrations and l is the path length [11].

All kinetic measurements were made under pseudo-first order conditions with the concentrations of AsO<sub>2</sub><sup>-</sup> at least 60 times greater than that of the Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> or Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> at least 60 times greater than that of the AsO<sub>2</sub><sup>-</sup> [9].

The pseudo-first order rate constants,  $k_{obs}$ , were obtained from the plots of  $\ln(A_t - A_\infty / A_0 - A_\infty)$  against time (where  $A_t$ ,  $A_0$  and  $A_\infty$  are the absorbances of the reaction mixtures at times t, zero time and infinite time respectively). Plots of  $\log k_{obs}$  vs.  $\log [AsO_2^-]$  and  $\log k_{obs}$  vs.  $\log [Cr_2O_7^{2-}]$  have been determined, with  $[AsO_2^-] = 2.00, 4.00, 6.00, 8.00$  and  $10.00 (x 10^{-2} \text{ molL}^{-1})$  and  $[Cr_2O_7^{2-}] = 2.00, 4.00, 6.00, 8.00$  and  $10.00 (x 10^{-2} \text{ molL}^{-1})$ . The temperature was kept constant at ambient (297 – 300 K), pH = 6 and I = 0.1 molL<sup>-1</sup>.

## 2.5 Presence of Fe(III) ions

The pseudo first order rate constants,  $k_{obs}$  for the As(III)/Cr(VI) reaction was determined in the presence of another redox material namely Fe(III) with the concentration range of 0.001-0.009 molL<sup>-1</sup> FeCl<sub>3</sub>.

## 2.6 pH Dependence Studies

The pseudo first order rate constants,  $k_{pH}$  for the oxidation-reduction reaction involving As(III) and Cr(VI) were determined at pH in the range of 2 – 10 (using HNO<sub>3</sub> and NaOH).

## 2.7 Temperature Dependence Studies

The temperature dependence rate study for the oxidation-reduction reaction involving As(III) and Cr(VI) were carried out over the temperature range of 288 K - 305 K. Kinetic activation parameters (activation energy,  $E_a$ , entropy change,  $\Delta S$ , and enthalpy change,  $\Delta H$ ) were obtained from Arrhenius and Eyring plots [12-14].

## 2.8 Ionic Strength Effect

The effect of ionic strength changes on rate of the oxidation-reduction reaction involving As(III) and Cr(VI) have been studied over the range of 0.001 - 0.021 molL<sup>-1</sup> concentrations of NaNO<sub>3</sub> salt.

## 3. RESULTS AND DISCUSSION

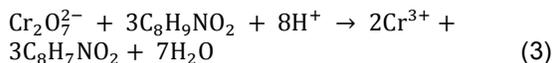
### 3.1 Spectra Consideration of the Solutions used

In Fig. 1 the bands correspond to the d – d transitions; the redistribution of electrons among orbitals that are mainly localized on the metal atoms or charge-transfer (CT) transitions involving the metal d-orbitals. Typically, the bands above 300 nm and below 850 nm, involve the motion of electrons from an essentially ligand-based orbital to an essentially metal-based, or vice versa. This makes charge to be transferred from one atom to another. In general, it is referred to as ligand – to – metal charge – transfer (LMCT). CT bands are observed if the energies of empty and filled ligand- and metal-centered orbitals are similar. It occurs within the visible or near UV region of the spectrum [9,11]. Thus the kinetic studies were done using UV-visible spectrophotometry and at the established wavelengths of maximum absorbances of the solutions used.

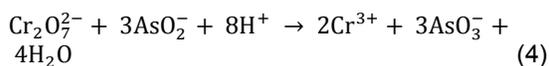
### 3.2 Reaction Stoichiometry

The calculation of the concentrations at the equivalence point of the UV-visible

spectrophotometric titration (as shown in Fig. 2) gave the stoichiometry of the reaction as 1: 3 ( $\text{Cr}_2\text{O}_7^{2-} : \text{AsO}_2^-$ ). Similar stoichiometry has been reported for the reaction between paracetamol and dichromate ion [9,14].



The equation for the reaction between  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{AsO}_2^-$  ions can be given as;



### 3.3 Test for Free Radicals

Addition of acrylamide to the partially oxidized/reduced reaction mixture of As(III)/Cr(VI), at pH = 6, T = ambient (298 – 300 K) and I = 0.1 molL<sup>-1</sup>, showed no gel formation on addition of excess methanol to the reaction mixture. Therefore, free radicals may not have been produced as intermediates in the reaction [15].

### 3.4 Effect of the Initial Concentration on the Reaction Rate

In considering the effects of the concentration on the reactions rate, varying amounts of  $\text{AsO}_2^-$  ions (0.02, 0.04, 0.06, 0.08 and 0.10 molL<sup>-1</sup>) were used against a fixed  $\text{Cr}_2\text{O}_7^{2-}$  ion (0.009 molL<sup>-1</sup>) concentration and varying amounts of  $\text{Cr}_2\text{O}_7^{2-}$  ions (0.02, 0.04, 0.06, 0.08 and 0.10 molL<sup>-1</sup>) were used against a fixed  $\text{AsO}_2^-$  ion (0.009 molL<sup>-1</sup>) concentration. These reactions were monitored using UV-visible spectrophotometer at ambient temperature (298 – 300 K), ionic

strength of 0.1 molL<sup>-1</sup> NaNO<sub>3</sub>, pH of 6 and time intervals of 15, 30, 45, 60 and 75 seconds for each amount of the substance. Pseudo-first order plots of  $\ln[A_t - A_\infty / A_0 - A_\infty]$  versus time were made from the reactions involving  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions. From these plots; the oxidation-reduction reactions (of  $\text{AsO}_2^-$  with  $\text{Cr}_2\text{O}_7^{2-}$ ) are linear to more than 70% extent of the reactions as shown in Fig. 3 and 4 having regression values,  $r^2$  in the range of 0.940 – 0.996. The linearity of the plots suggests that the reaction is first order in both  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions. Table 1 summarizes the values of  $k_{\text{obs}}$  for the oxidation-reduction reaction involving  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions and the results show an increase in  $k_{\text{obs}}$  values with increase in concentration in both cases. Also, plots of  $\log k_{\text{obs}}$  versus  $\log [\text{AsO}_2^-]$  and  $\log k_{\text{obs}}$  versus  $\log [\text{Cr}_2\text{O}_7^{2-}]$  showed a linear relationship (having regression of 0.989 and 0.957 respectively) with the slopes of approximately 1.00; implying that the reaction is first order in both  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions. Hence, the reaction is second order overall, which is in agreement with the studies of oxidation-reduction reaction of chromium(VI) and iron(III) with paracetamol: kinetics and mechanistic studies as observed by Adejo et al. 2014 [9]. Therefore the rate equation for the reaction is as follows:

$$-\frac{d[\text{Cr}_2\text{O}_7^{2-}]}{dt} = k_2[\text{Cr}_2\text{O}_7^{2-}][\text{AsO}_2^-] \quad (5)$$

The results of oxidation-reduction reactions of  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  showed rapid rates with the reactions completing almost before the 75 seconds maximum time for our studies and the reactions increased with increase in both  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions concentrations. These reactions (or observations) are possible because of the

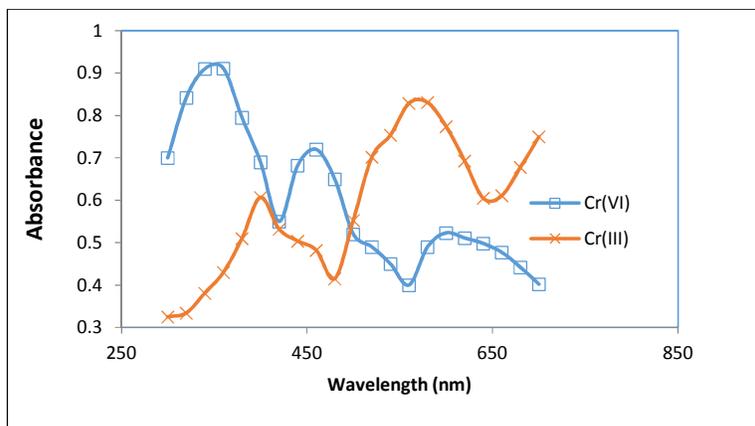
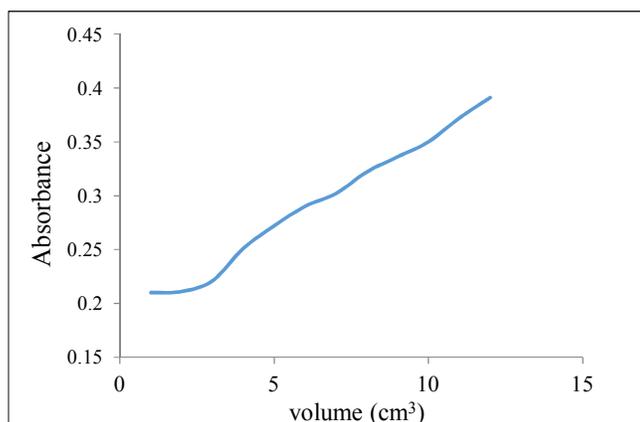


Fig. 1. Determination of  $\lambda_{\text{max}}$  for Cr (VI) and Cr (III) ions



**Fig. 2. UV-visible spectrophotometric titration for the reaction between  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$**

wide variation in the electrode potential of the ions (redox couple) involved;  $\text{Cr}_2\text{O}_7^{2-}/\text{Cr(III)}$  (+1.38 V) and  $\text{AsO}_2^-/\text{As(V)}$  (-0.56 V) [16,17]. Also, the reactions rates increase with increase in the concentrations of both  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{AsO}_2^-$  ions, as most reactions are faster at higher concentrations because of the resulting more effective collisions from the molecular collisions of the molecules in solution with one another [16].

From Table 1 it can be seen that, the  $k_{\text{obs}}$  values are higher at varying  $\text{Cr}_2\text{O}_7^{2-}$  ion concentrations than for  $\text{AsO}_2^-$  ion concentrations. This may be because of the higher electrode potential of  $\text{Cr}_2\text{O}_7^{2-}$  over  $\text{AsO}_2^-$  or because of the fact that the pH at which the studies were conducted favoured the  $\text{Cr}_2\text{O}_7^{2-}$  over  $\text{AsO}_2^-$  [16-18]. Again, the reactions were conducted at pH = 6 (about the pH of natural waters) and the concentrations of these ions are pH dependent as  $\text{Cr}_2\text{O}_7^{2-}$  ion is prevalent in the solution as  $\text{HCrO}_4^-$  ion at this pH and strongly oxidizing. Thus, at such pHs, high concentrations of  $\text{HCrO}_4^-$  together with high electrode potential made the  $k_{\text{obs}}$  values at varying  $\text{Cr}_2\text{O}_7^{2-}$  concentrations to be higher than those of the  $\text{AsO}_2^-$  [17,19,20]. Moreover,  $\text{AsO}_2^-$  dominates in the form of  $\text{H}_2\text{AsO}_3^-$  at alkaline pHs with low electrode potential which might lead to low reaction rates ( $k_{\text{obs}}$  values) [21,22].

### 3.5 Effect of Fe(III) ions on the Reaction Between $\text{AsO}_2^-$ and $\text{Cr}_2\text{O}_7^{2-}$

The oxidation-reduction reaction of  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  was monitored in the presence of Fe(III) ions. From Fig. 5 and Table 2, the rate of the reaction was considered and it can be seen that rate was unaffected within the concentrations

range of 0.001 - 0.009 molL<sup>-1</sup> Fe (III) ions solution. This seems to agree with the fact that, Fe (III) ions have lower oxidizing potential ( $E^\circ = +0.77$  V, Fe (III)/Fe(II)) than the  $\text{Cr}_2\text{O}_7^{2-}$  ( $E^\circ = +1.33$  V, Cr(VI)/Cr(III)) [16,17]. Again, the concentrations range may not have been enough to overcome the oxidizing capacity of the  $\text{Cr}_2\text{O}_7^{2-}$  ions, hence the redox process was as though there were no Fe (III) ions present in solution.

### 3.6 Effect of pH on the Reaction Rate

Examining the conditions under which the oxidation-reduction reaction of  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions may occur in nature is relevant, as these would give good informations on Cr and As speciation in the environment and on the applications of the experimental results that have been obtained. The pH of soil and ground water generally have values between 5 and 9. From Fig. 6 and Table 3, it can be seen that rate decreases with the increase of pH in the acidic range and increases with increase in pH of the alkaline range between pH range of 8 - 10. Reactions generally increase with concentration, as more reactant molecules mean more effective collisions which give rise to higher proportion of molecules that can overcome the energy barrier to give the products [16]. And the availability of  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions in an aqueous environment is dependent on pH as shown in Figs. 7 and 8 [18,17]. That is,  $\text{AsO}_2^-$  exist in aqueous solution at pH's above 8 and below 13 (with dominance as  $\text{H}_2\text{AsO}_3^-$ ) especially at low concentrations, and as the pH increases more of the  $\text{H}_2\text{AsO}_3^-$  ions are present in solution giving rise to greater effective collisions which results to more  $\text{Cr}_2\text{O}_7^{2-}$  ions combining (or accepting

electrons to become reduced) with  $\text{AsO}_2^-$  to give the product hence the higher  $k_{\text{pH}}$  at very basic pH. On the other hand, Cr(VI) exhibits varying ionic species in solution as the pH changed; the dominant forms include  $\text{HCrO}_4^-$  at pH 1 - 6 and  $\text{CrO}_4^{2-}$  at pH >6. Moreover, other forms are also possible,  $\text{HCr}_2\text{O}_7^-$  and  $\text{Cr}_2\text{O}_7^{2-}$ , with their formation requiring Cr(VI) concentration to be greater than  $0.1 \text{ mol L}^{-1}$  [23]. This is however dependent on the nature of the acid used, as HCl results to the formation of chlorochromate ion,  $\text{CrO}_3\text{Cl}^-$ , while sulphuric acid gives a sulfato complex,  $\text{CrO}_3(\text{OSO}_3)^{2-}$ , hence the choice of  $\text{HNO}_3$  acid for this research [23]. The ease of reduction of the Cr (VI) species is of the order  $\text{HCrO}_4^- > \text{CrO}_4^{2-} > \text{HCr}_2\text{O}_7^- > \text{Cr}_2\text{O}_7^{2-}$ , thus the decrease in the reaction rate with increase in pH can be attributable to the presence of  $\text{HCrO}_4^-$  ions at lower pH, which is more reducing than  $\text{CrO}_4^{2-}$ . Moreover, the increase in rate constant with increasing  $[\text{H}^+]$  or decrease in pH seems to suggest the protonation of  $\text{Cr}_2\text{O}_7^{2-}$  to give  $\text{H}_2\text{CrO}_4$  or  $\text{HCrO}_4^-$  [9,23,24].

### 3.7 Effects of Ionic Strength change on the Reaction Rate

Effects of Ionic Strength on the rate of oxidation-reduction reaction between  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions were investigated over the range  $0.001 - 0.021 \text{ mol L}^{-1} \text{ NaNO}_3$ . The results as presented in Fig. 9 and Table 3 which showed that, the reaction rate increase with increase in ionic charge of the solution. This seems to agree with the Kumar, P. 2013 and Hughes-Jones, N. C. et al. 1964 in terms of favourable interactions between the reactants and activated complex and the ionic atmosphere of oppositely charged ions which surround them in solution. Here, the charges on  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions have the same sign, thus, the activated complex may be more highly charged than the reactants ( $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$ ). Increasing the ionic strength of the reaction solution therefore stabilized the activated complex more than the reactants, and thus increase the rate constant by lowering the effective activation energy [21,25].

**Table 1. Pseudo-first order,  $k_{\text{obs}}$  rate data for the oxidation-reduction reaction between  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$**

$[\text{AsO}_2^-]/[\text{Cr}_2\text{O}_7^{2-}] \text{ mol L}^{-1}$	$I \text{ mol L}^{-1}$	$k_{\text{obs}}/10^2 \text{ (s}^{-1}\text{)}$	
		at varying $[\text{AsO}_2^-]$	at varying $[\text{Cr}_2\text{O}_7^{2-}]$
0.10	0.10	22.00	24.00
0.08	0.10	16.00	17.00
0.06	0.10	12.00	13.00
0.04	0.10	9.00	11.00
0.02	0.10	5.00	7.00

**Table 2. Pseudo-first order,  $k_{\text{obs}}$  data for the oxidation-reduction reaction between  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ion in the presence of Fe (III) at  $[\text{AsO}_2^-] = 0.08 \text{ mol L}^{-1}$**

$[\text{Fe(III)}]/10^2 \text{ mol L}^{-1}$	$I \text{ mol L}^{-1}$	$k_{\text{obs}}/10^2 \text{ s}^{-1}$
1.00	0.10	16.00
3.00	0.10	16.00
5.00	0.10	16.00
7.00	0.10	15.00
9.00	0.10	15.00

**Table 3. Effects of variation of pH, ionic strength and temperature on the rate oxidation-reduction reactions between  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$**

pH	$k_{\text{pH}} \text{ s}^{-1}$	$I \text{ mol L}^{-1}$	$k_{\text{I}} \text{ s}^{-1}$	TK	$k_{\text{T}} \text{ s}^{-1}$
2	0.018	0.005	0.015	288	0.006
4	0.016	0.009	0.015	293	0.008
6	0.016	0.013	0.016	298	0.015
8	0.012	0.017	0.017	303	0.020
10	0.013	0.021	0.018	308	0.022

Key;  $k_{\text{pH}}$  = pseudo first order rate constant for the redox reaction at varying pH

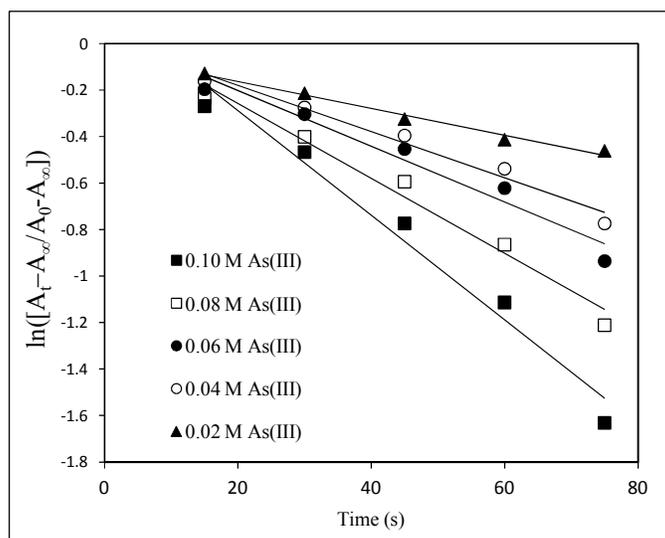


Fig. 3. Effects of initial concentration on the rate of reaction of  $\text{AsO}_2^-$  with  $\text{Cr}_2\text{O}_7^{2-}$

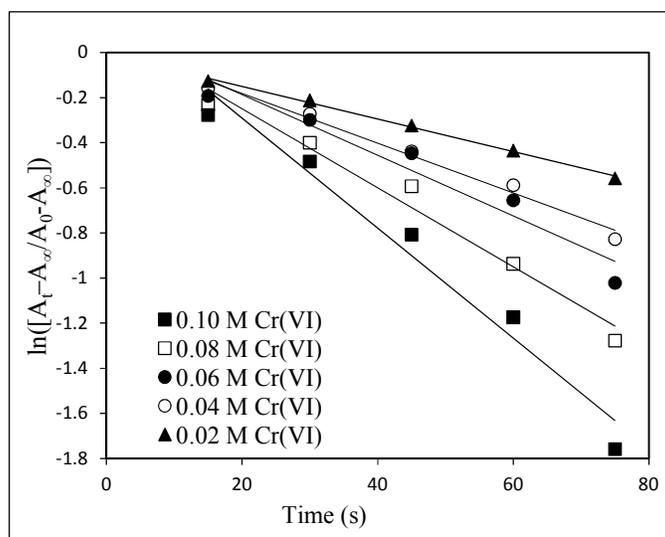


Fig. 4. Effects of initial concentration on the rate of reaction of  $\text{Cr}_2\text{O}_7^{2-}$  with  $\text{AsO}_2^-$

### 3.8 Effect of Temperature on the Reaction Rate

The results of temperature dependence studies for the oxidation-reduction reaction between  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions showed that as the temperature increased, the reaction rates increased as shown in Fig. 10 and Table 3. The values of activation energy ( $E_a$ ), enthalpy change,  $\Delta H$  and entropy change,  $\Delta S$  were calculated from Arrhenius and Eyring's plots respectively and shown Table 4. A high  $E_a$  value signifies that the rate constant depends strongly

on temperature [24] and that a slow reaction would have a higher energy of activation [22]. In our studies, it is evident the high  $E_a$  value for the oxidation-reduction reaction between  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions ( $E_a = 52.01 \text{ kJmol}^{-1}$ , Table 4) with a low  $k_{\text{obs}}$  value ( $0.006 \text{ s}^{-1}$  at 288 K, Table 3). The negative  $\Delta H$  values of these reactions are indicative of the exothermic nature of the oxidation-reduction reactions considered which conforms to the low temperature requirement of these reactions in nature [26]. The values of enthalpy and entropy of activation together give us free energy,  $\Delta G$  for the reactions indicative of

the spontaneity of these  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  oxidation-reduction reactions [11,26].

On the basis of our findings, the following mechanism is proposed for the oxidation-reduction reaction between  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions. In the reaction scheme which involves the oxidation of  $\text{AsO}_2^-$  ion by  $\text{Cr}_2\text{O}_7^{2-}$  ion, the reactive

species of the metals combine to form an inorganic acid ester; chromate ester (rate determining step) [9]. The ester undergoes oxidative decomposition in the next step, leading to the formation of an intermediate and Cr(IV). The proposed mechanism is further supported by the change in colour of the  $\text{Cr}_2\text{O}_7^{2-}$  ion from yellow of Cr(VI) to green of Cr(III).

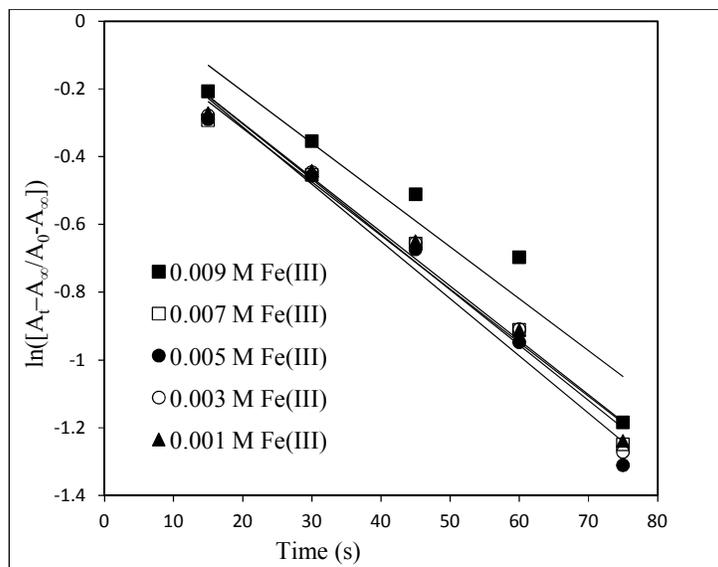


Fig. 5. Effects of Fe (III) ( $\text{molL}^{-1}$ ) on the rate of reaction of  $\text{AsO}_2^-$  with  $\text{Cr}_2\text{O}_7^{2-}$

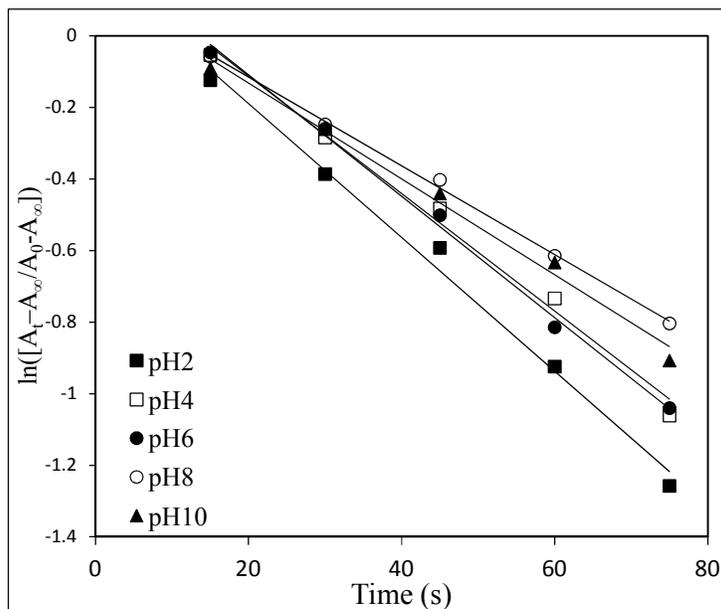
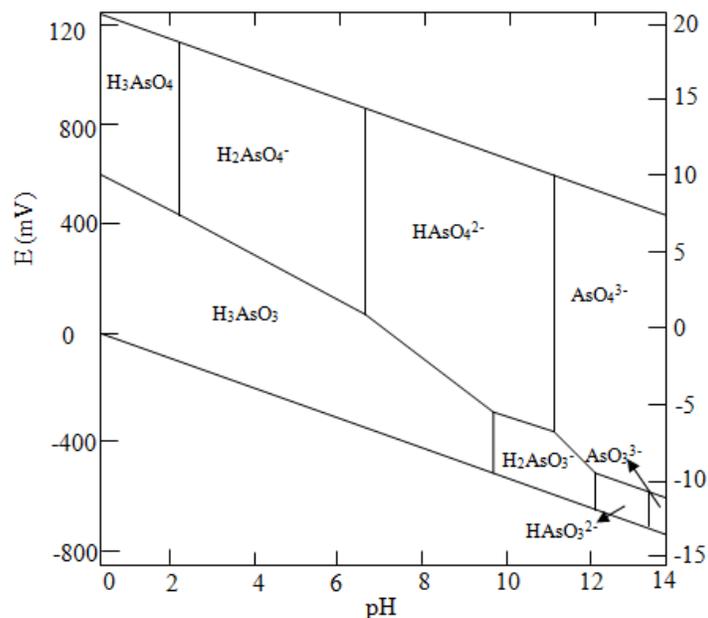


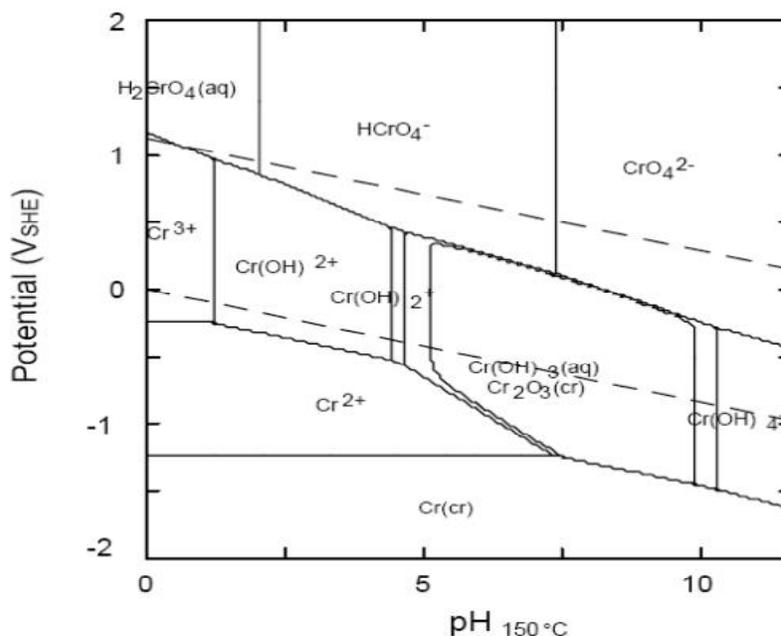
Fig. 6. Effects of pH variation on the rate of reaction of  $\text{AsO}_2^-$  with  $\text{Cr}_2\text{O}_7^{2-}$

**Table 4. Activation parameters (Activation energy, enthalpy change and entropy change) of the oxidation-reduction reactions between  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$**

Nature of reaction	Activation energy, $E_a$ $\text{KJmol}^{-1}$	Enthalpy change, $\Delta H$ $\text{kJmol}^{-1}$	Entropy change, $\Delta S$ $\text{Jmol}^{-1}\text{K}^{-1}$
$\text{AsO}_2^-/\text{Cr}_2\text{O}_7^{2-}$	52.01	-49.54	-114.92



**Fig. 7. E-pH diagram for As in an aqueous environment at 25°C and 1 bar total pressure [18,17]**



**Fig. 8. A simplified Pourbaix diagram for Cr species at 150°C and  $[\text{Cr}(\text{aq})]_{\text{tot}} = 10^{-8}$  [17]**

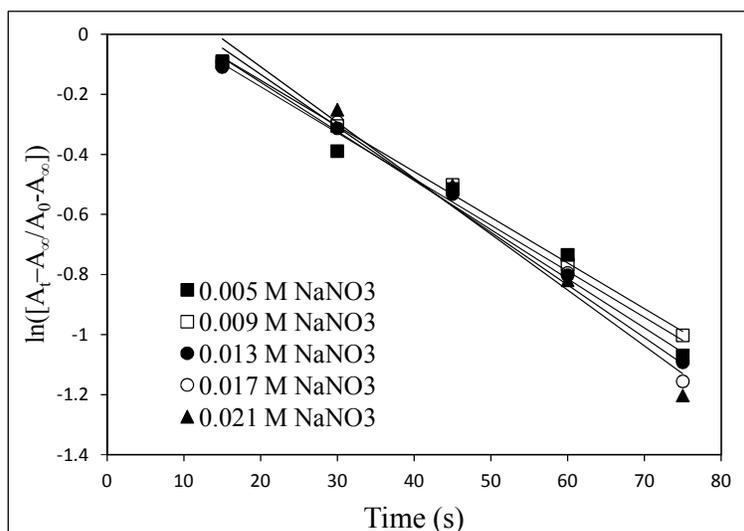


Fig. 9. Effects of ionic strength ( $\text{molL}^{-1}$ ) variation on the rate of reaction of  $\text{AsO}_2^-$  with  $\text{Cr}_2\text{O}_7^{2-}$

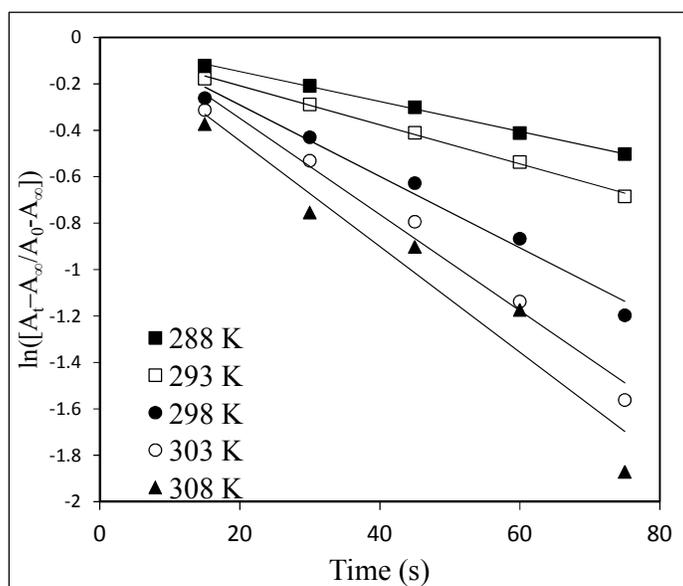
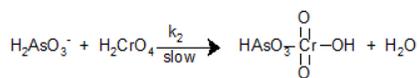
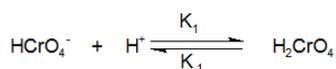
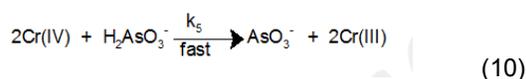
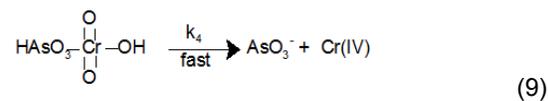
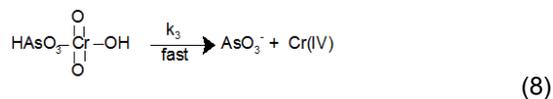


Fig. 10. Effects of temperature (K) variation on the rate of reaction between  $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$   
 $k_I$  = pseudo first order rate constant for the redox reaction at varying ionic strength  
 $k_T$  = pseudo first order rate constant for the redox reaction at varying temperature

### 3.9 Proposed Mechanism for the $\text{AsO}_2^-$ – $\text{Cr}_2\text{O}_7^{2-}$ Reaction



Chromate ester



But,

$$rate = -k_2[H_2AsO_3^-][H_2CrO_4^-] \quad (11)$$

And

$$K_1 = \frac{[H_2CrO_4]}{[HCrO_4^-][H^+]}$$

Also,

$$[H_2CrO_4] = K_1[HCrO_4^-][H^+] \quad (12)$$

Substituting equation (12) into (11) gives

$$rate = k_2K_1[H_2AsO_3^-][H_2CrO_4][H^+] \quad (13)$$

$$= k[H_2AsO_3^-][HCrO_4^-][H^+] \quad (14)$$

Where,

$$k = k_2K_1$$

#### 4. CONCLUSION

The oxidation of arsenic (III) and reduction of chromium(VI) in aqueous medium is reported and from this study, the metal ions evidently changed in their oxidation states. The reactions are first order in both  $AsO_2^-$  and  $Cr_2O_7^{2-}$  and second order overall. The  $k_{obs}$  values are higher for  $Cr_2O_7^{2-}$  than for  $AsO_2^-$  and unaffected by Fe(III) ions which may be because, Fe(III) ions have lower oxidizing potential than the  $Cr_2O_7^{2-}$  or the concentrations range for which the reaction took place were too low. The results of activation parameters, particularly entropy change and ionic strength effect indicate the involvement of a binuclear complex at the activated complex, and the mechanisms were proposed to involve an inorganic ester formation by the reactants and the subsequent formation of products.

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#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

#### REFERENCES

- Ramakrishnaiah CR, Prathima B. Hexavalent chromium removal from industrial wastewater by chemical precipitation method. *International Journal of Engineering Research and Applications (IJERA)*. 2012;2(2):599-603.
- Duffus JH. Heavy metals-a meaningless term? *International Union of Pure and applied Chemistry*, 2002;74(5):793-807.
- Arruti A, Fernández-Olmo I, Irabien A. Evaluation of the contribution of local sources to trace metals levels in urban PM2.5 and PM10 in the Cantabria region (Northern Spain). *Journal of environmental monitoring*, 2010;12(7):1451-1458.
- Dönmez G, Aksu Z. Removal of chromium (VI) from saline wastewaters by Dunaliella species. *Research Journal of Environmental Toxicology*, 2002;38(5):751-762.
- Wilkie JA, Hering JG. Rapid oxidation of geothermal arsenic (III) in stream waters of the Eastern Sierra Nevada, *Environmental Science and Technology*. 1998;32:657-662.
- Charalampos V, Ifigenia M, Economou-Eliopoulos M, Loannis M. Hexavalent chromium and other toxic elements in natural waters in the Thiva – Tanagra – Malakasa Basin, Greece. *Hellenic Journal of Geosciences*. 2008;43:57-56.
- Namiesńska J, Rabajczyk A. The speciation and physico-chemical forms of metals in surface waters and sediments, *Chemical Speciation and Bioavailability*. 2010;22(1):1-25
- Xiaoling D, Lena Q, Mab JG, Willie H, Yuncong L. Enhanced Cr (VI) reduction and As (III) oxidation in ice phase: Important role of dissolved organic matter from biochar. *Journal of Hazardous Materials*, 2014;267:62-70.
- Adejo SO, Yiase SG, Ukoha PO, Iorhuna BT, Gbertyo JA. Oxidation-reduction reaction of chromium(VI) and iron(III) with paracetamol: Kinetics and mechanistic studies. *Archives of Applied Science Research*. 2014;6(5):56-67.
- Verma RM. Analytical chemistry, theory and practice. CBS publishers and distributors PVT Ltd, India. 2010;358-61.
- Amira HK, Samah FE, Sherin FH. A review on UV spectrophotometric methods for simultaneous multicomponent analysis, *European Journal of Pharmaceutical and Medical Research*. 2016;3(2):348-360.
- Dionisio B, Diego G, Jaqueline LP, Juliane RO, Karina GA, Rodolfo LC. Kinetic and thermodynamic parameters of biodiesel oxidation with synthetic antioxidants:

- simplex centroid mixture design, Journal of Brazilian Chemical Society. 2014;25(11): 32-40.
13. Ong LK, Kurniawan A, Suwandi AC, Lin CX, Zhao XS, Ismadji S. Transesterification of leather tanning waste to biodiesel at supercritical condition: Kinetics and thermodynamics studies, The Journal of Supercritical Fluids. 2013;75: 11–20.
  14. Cheong-Song C, Jin-Woo K, Cheol-Jin J, Huiyong K, Ki-Pung Y. Transesterification kinetics of palm olein oil using supercritical methanol. The Journal of Supercritical Fluids. 2011;58(3):365–370.
  15. Iyun JF, Shehu AR. Kinetics and mechanism of the oxidation of ethanol and propanol by chromium(VI) in acidic medium. Chemclass Journal. 2004;12:55-58.
  16. Ajmal M, Nomani AA, Ahmad A. Acute toxicity of chrome electroplating wastes to microorganisms: adsorption of chromate and chromium(VI) on a mixture of clay and sand, Water, Air, and Soil Pollution. 1984;23(2):119–127.
  17. Brookins DG. E-pH Diagrams for Geochemistry. Springer-Verlag, Berlin, Germany; 1988.
  18. Atkins P, De paula J. Physical Chemistry, 7<sup>th</sup> ed. Oxford University Press. New Delhi. 2000;960-62.
  19. Smedley PL, Kinniburgh DG. A review of the source, behavior and distribution of arsenic in natural waters, Applied Geochemistry. 2002;17:517-568.
  20. Schroeder DC, Lee GF. Potential transformation of chromium in natural waters, Water, Air and Soil Pollution. 1975; 4:355–365.
  21. Hughes-Jones NC, Gardner B, Telford B. the Effect of pH and Ionic Strength on the Reaction between Anti-D and Erythrocytes, Immunology. 1964;7:72-81.
  22. Cantu Y, Remes A, Reyna A, Martinez D, Villarreal J, Ramos H, et al. Thermodynamics, kinetics and activation energy studies of the sorption of chromium(III) and chromium(VI) to a Mn<sub>3</sub>O<sub>4</sub> nanomaterials. Chemical Engineering Journal. 2014;254(15):374-383.
  23. Cotton FA, Wilkison G. Advanced inorganic chemistry; A comprehensive text. 3<sup>rd</sup> Ed. Wiley Eastern Ltd, New Delhi. 1978;818-870.
  24. Pacyna JM, Pacyna EG. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide, Environmental Review. 2001;9(4):269-298.
  25. Kumar P. Study of effect of variation of ionic strength of the medium on velocity constant of Ru(III) catalyzed oxidation of hydroxyl benzoic acids by chloramine-T in acidic medium. Oriental Journal of Chemistry, 2013;29(4):23-28.
  26. Attia AA, Khedr SA, Elkholy SA. Adsorption of chromium ion (VI) by acid activated carbon, Brazilian Journal of Chemical Engineering. 2010;27(1):45-59.

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