



# Hexacyanoferrate(III) oxidation of arsenic and its subsequent removal from the spent reaction mixture

Praveen Kumar Tandon\*, Santosh Bahadur Singh

Department of Chemistry, University of Allahabad, Allahabad 211002, India

## ARTICLE INFO

### Article history:

Received 20 March 2010

Received in revised form 22 July 2010

Accepted 30 September 2010

Available online 7 October 2010

### Keywords:

Hexacyanoferrate(III)

Iridium(III) chloride

Sodium arsenite

Unio Shell ash

## ABSTRACT

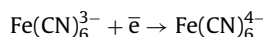
Inorganic arsenic is the most toxic form and has been classified in group 1 as carcinogenic to humans which induces lung, urinary bladder and primary skin cancer. Worldwide concern over its presence in water bodies have prompted much research and policy development focusing on the removal of this chronic human carcinogen. It has been observed that the ash of *Unio (Lamellidens marginalis* – the fresh water mussel) can be used successfully for the removal of arsenic(V) from the aqueous solutions at low pH (~9.0). Initially the kinetics of oxidation of arsenic(III) by alkaline hexacyanoferrate(III), both with and without adding iridium(III) chloride was studied. Subsequently after complete removal of ferrocyanide, the removal of arsenic(V) produced in the spent reaction mixture was taken up. Out of the five ashes obtained from different sources, the ash of *Unio* was found to be the best which results in decreasing arsenic(V) concentration from 1000 ppb to >10 ppb, TDS from 16.9 ppt to 8.5 ppt and conductivity from 33.8 mS to 17.1 mS. Kinetic results show the possibility of graphical separation of the reaction proceeding in the absence of iridium(III) from that proceeding in the presence of iridium(III) chloride.

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## 1. Introduction

Arsenic contamination of groundwater is a global problem. Recent studies reported serious health risks due to arsenic in drinking water. Out of two forms of arsenic existing in water, As(III) is more toxic and mobile than the As(V) species. Additionally As(III) exist in nonionic  $\text{H}_3\text{AsO}_3$  at pH 8, which is not adsorbed efficiently to the mineral surfaces. In comparison As(V) present as anions,  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$  is adsorbed easily to the solid surfaces. Therefore, pre-oxidation of As(III) to As(V) is necessary for its easy removal. Various salts and complexes of iron have been used as oxidants. Recently extensive work has been done on ferrate (iron in +6 oxidation state) [1–3], which has been used in the oxidation of various organic and inorganic substrates and also in the removal of arsenic from water. Hexacyanoferrate(III) has long been used as an oxidant presumably due its cheap availability, less complexity involved in the estimation and its capability to act in acidic and alkaline medium both [4]. Based on the assumption that slight interaction of the electronic levels of oxidant and reductant is sufficient to permit electron transfer hexacyanoferrate(III) functions in the oxidation–reduction reactions as a simple one electron abstracting reagent and oxidation invariably occurs via a direct

charge transfer process.



Recently from our laboratory oxidation of iodide ion by hexacyanoferrate(III) has been reported in the presence of Pd(II), Ru(III), and Ir(III) in the presence of various acids like hydrochloric acid, sulphuric acid and perchloric acid [5–7].

Catalytic activity of transition metal ions is well known in organic reactions but little work using these ions to catalyze the inorganic reactions has been done. Iridium(III) chloride has been reported to catalyze the oxidation of organic compounds in acidic medium [8–11]. To our knowledge, there have been only three uncatalyzed kinetic studies [12–14] of the reaction of arsenic(III) with hexacyanoferrate(III) in aqueous alkaline medium and the catalyzed study of the reaction has not been reported till now which prompted us to investigate the kinetics of this reaction both in the presence as well as in the absence of iridium(III) chloride. Present scenario of arsenic problem in many parts of world including India, further motivated us to extend the work for subsequent removal of arsenic(V) from the spent reaction mixture. The present method of converting arsenic(III) into arsenic(V) and its subsequent removal from water may well be extended for the arsenic problem in drinking water also as the present method apart from removing arsenic contents also appreciably decreases the total dissolved substances and conductivity after the treatment.

Thus, main objective of this study was to investigate the kinetics and mechanism of oxidation of As(III) by hexacyanoferrate(III)

\* Corresponding author. Tel.: +91 9415310943, fax: +91 532 2461236.

E-mail address: [ptandonk@yahoo.co.in](mailto:ptandonk@yahoo.co.in) (P.K. Tandon).

both in the presence and absence of iridium(III) and the subsequent removal of arsenic [as arsenate(V)] from the spent reaction mixture, using the ash obtained from upper shell of dead *Unio (Lamellidens marginalis)*, the fresh water mussel) generally found in fresh water ponds, lakes, streams etc.

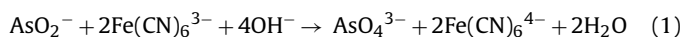
## 2. Experimental

### 2.1. Materials

Analytical grade chemicals were used as such without further purification. Solutions were prepared in doubly distilled water. It was not essential to always prepare a fresh solution of potassium hexacyanoferrate(III) (Qualigen) as spectrum of this solution does not change appreciably for over a period of months, even in diffused daylight. Solutions of sodium arsenite (NaAsO<sub>2</sub>, BDH) were prepared fresh by dissolving the sample in double distilled water. Effects of change of hexacyanoferrate(II) and KCl concentrations on the reaction rate were determined by adding the salts externally. Strength of sodium hexachloroiridate(III) (Johnson Matthey & Co.), prepared by dissolving the sample in minimum amount of A.R. HCl (0.62 × 10<sup>-2</sup> mol dm<sup>-3</sup>) was 3.35 × 10<sup>-3</sup> mol dm<sup>-3</sup>.

### 2.2. Kinetic study and stoichiometry

Reactions were performed at constant temperature with an accuracy of ±0.1 °C. Progress of the reaction was measured at different time intervals by measuring the absorbance of 3.0 ml aliquot of the reaction mixture at 420 nm with the help of a double-beam spectrophotometer (Systronics 2203, India). At this wavelength only hexacyanoferrate(III) absorbs strongly and hexacyanoferrate(II) or other reactants do not absorb. Absorbance values thus are directly proportional to the remaining amount of hexacyanoferrate(III) in the reaction mixture. Total amount of hexacyanoferrate(III) consumed for complete oxidation of one mole of sodium arsenite was determined under the condition when the concentration of hexacyanoferrate(III) ≫ arsenic(III) concentration. Stoichiometry of the reaction may be shown by the following equation



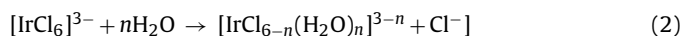
### 2.3. Determination of kinetic orders

Oxidation of sodium arsenite by hexacyanoferrate(III) in aqueous alkaline medium proceeds even in the absence of iridium(III) chloride therefore, the reactions in the presence and absence of iridium(III) chloride were studied separately under similar conditions. Initial slope value for each set, was calculated from the individual graph plotted between the values of absorbance at corresponding time (or log absorbance versus time), Rate of the reaction ( $-dc/dt$ ) was then obtained by dividing the initial slope value with  $\epsilon$  (the molar absorption coefficient). Orders, with respect to various reactants were confirmed by plotting log absorbance versus time (for oxidant variation only), by plotting  $-dc/dt$  values versus concentration of the reactant, by calculating slope of the double logarithmic graphs between rate versus concentration and by calculating the rate constant for molar concentrations. Tables and figures contain initial concentrations of the reactants. Study could not be made at constant ionic strength of the medium ( $\mu$ ) due to large volumes of potassium chloride required to keep the ionic strength constant. However, to find out whether the reaction is taking place between the charged species or one of the reactant is a neutral molecule, the effect of change of ionic strength of the medium on the rate was studied separately with the help of a standard solution of potassium chloride.

## 3. Kinetic results and discussion

### 3.1. Probable species of iridium(III)

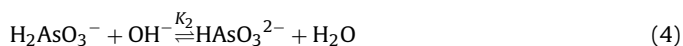
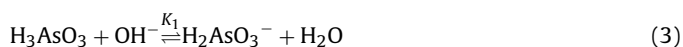
It is known that IrCl<sub>3</sub> in HCl medium gives IrCl<sub>6</sub><sup>3-</sup> species [15,16]. Further the aquation of [IrCl<sub>6</sub>]<sup>3-</sup> gives [IrCl<sub>5</sub>(H<sub>2</sub>O)]<sup>2-</sup>, [IrCl<sub>4</sub>(H<sub>2</sub>O)]<sup>1-</sup>, [IrCl<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>] species [17] as shown by the following equilibrium.



Since positive effect of chloride ion was observed in our studies hence the hydrated species can not be the reactive species as the equilibrium in Eq. (2) will be shifted towards the left hand side. Thus, [IrCl<sub>6</sub>]<sup>3-</sup> has been considered as the reactive species of iridium(III) chloride in the present study.

### 3.2. Reactive species of sodium arsenite in aqueous alkaline medium

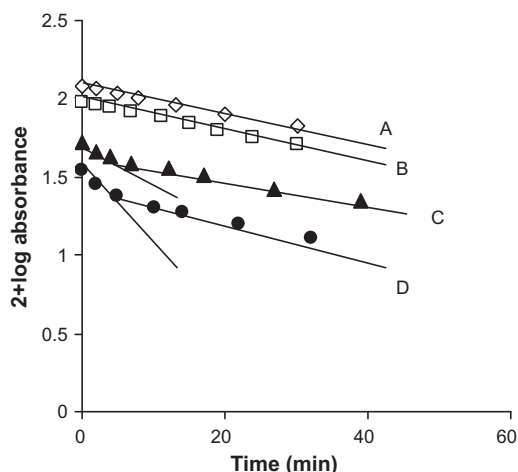
From Raman spectral study Loehr and Plane [18] have reported that predominant forms of arsenic present in hydroxide solutions are As(OH)<sub>3</sub>, AsO(OH)<sub>2</sub><sup>-</sup>, AsO<sub>2</sub>(OH)<sub>2</sub><sup>2-</sup> and AsO<sub>3</sub><sup>3-</sup>. Similar views have been expressed by others [19] too. It has also been reported [20] that the addition of [OH<sup>-</sup>] to As(OH)<sub>3</sub> converts three coordinated As<sup>III</sup> to four coordinated As(OH)<sub>4</sub><sup>-</sup>, which differs only in the degree of hydration and it is difficult to predict the precise form of As<sup>III</sup> in such solutions. Equilibrium Eqs. (3)–(5) have been suggested [13,14] in alkaline solutions of H<sub>3</sub>AsO<sub>3</sub>.



Hexacyanoferrate(III) reacts with all of the species and hydroxide ion dependence shows that the order of reactivity of these species is AsO<sub>3</sub><sup>3-</sup> > HASO<sub>3</sub><sup>2-</sup> > H<sub>2</sub>AsO<sub>3</sub><sup>1-</sup> and that H<sub>3</sub>AsO<sub>3</sub> is either not reactive at all or much less reactive than H<sub>2</sub>AsO<sub>3</sub><sup>1-</sup>.

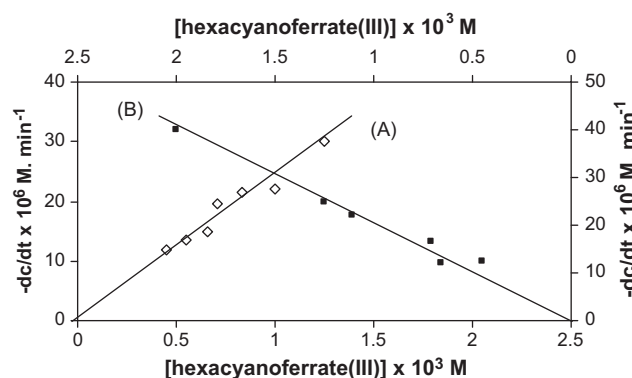
### 3.3. Kinetics of As(III) oxidation

First order plots (log absorbance versus time) show straight lines in major part of the reaction both in the absence (Fig. 1A and B) and in the presence of iridium(III) (Fig. 1C and D). When iridium(III) was present in the reaction mixture it can be seen that the reaction is quite fast in the beginning but after a brief period it slows down. Rate values ( $-dc/dt$ ) increase proportionately with increasing concentration of oxidant (Table 1) both in the presence and absence of iridium(III) and the first order rate constant values for molar concentration ( $k^*$ ) are practically constant among themselves. In the presence of iridium(III) rate constant values, obtained graphically ( $k_{\text{graphical}}$ ) and those obtained by using the standard first order rate equation ( $k_{\text{calculated}}$ ), show fair constancy separately in themselves both for the fast and slow reactions. Constancy in  $k^*$ ,  $k_{\text{graphical}}$  and  $k_{\text{calculated}}$  values is also observed when the reaction takes place in the absence of iridium(III). On plotting rate values ( $-dc/dt$ ) versus concentration of the oxidant, straight lines passing through the origin are obtained in both the cases when reaction takes place in the absence as well as in the presence of iridium(III) (Fig. 2). Finally slope values of 1.00 were obtained on plotting double logarithmic graphs between the rate and the oxidant concentrations in both the cases. All these facts collectively confirm that in the absence as well as in the presence of iridium(III) both, rate of the reaction through out follows first order kinetics with respect to oxidant concentrations. However, possibility of a faster reaction in the beginning can



**Fig. 1.** Sample individual time plots for the consumption of hexacyanoferrate(III) in the oxidation of arsenic(III) at 30 °C.  $[K_3Fe(CN)_6]$  = A –  $1.25 \times 10^{-3} \text{ mol dm}^{-3}$ , B –  $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ , C –  $0.66 \times 10^{-3} \text{ mol dm}^{-3}$  and D –  $0.45 \times 10^{-3} \text{ mol dm}^{-3}$   $[NaOH] = 10.00 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[NaAsO_2] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[IrCl_3] = 6.68 \times 10^{-5} \text{ mol dm}^{-3}$  (reaction with catalyst only) (reaction without catalyst – A and B; reaction with catalyst – C and D).

be seen in when the reaction takes place in the presence of catalyst (Fig. 1C and D). It appears that the reaction starts at a faster rate but subsequently it slows down. It may be presumed that the complex formed between the substrate and catalyst reacts at a much slower rate with oxidant compared to the reaction in which the oxidant directly reacts with the arsenic(III) species. Comparison of the first order rate constant values ( $k_{gr}$  and  $k_{calc}$ ) further confirm the assumption that in the presence of catalyst, rate of the reaction increases to a large extent in the beginning but subsequently



**Fig. 2.** Effect of variation of hexacyanoferrate(III) concentrations on the rate of oxidation of arsenic(III) at 30 °C. A (without catalyst) and B (with catalyst); captions are same as in Fig. 1 (except for  $[K_3Fe(CN)_6]$ ).

it decreases with increasing concentration of the complex formed between the catalyst and the substrate. Association of arsenic with platinum group metals like Pt, Ir, Os is well known at least in the natural deposits [21], which are capable of both entering the major (Fe–Co–Ni) arsenides and forming their own arsenide minerals. Similar products of oxidation in both the cases, whether the reaction takes place in the absence or in presence of catalyst discard the possibility that retarding effect is produced by one of the products. The rate values ( $-dc/dt$ ) increase with increasing concentration of sodium arsenite in both the cases (Table 2), indicating direct proportionality of the rate with respect to the concentrations of sodium arsenite. This trend becomes clear on plotting rate values ( $-dc/dt$ ) versus concentration of sodium arsenite in which a straight line passing through the origin is obtained (Fig. 3). Slope values of 0.80 and 1.0 respectively, were obtained on plotting double logarithmic

**Table 1**  
Effect of variation of hexacyanoferrate(III) concentrations on the rate of oxidation of arsenic(III) at 30 °C.

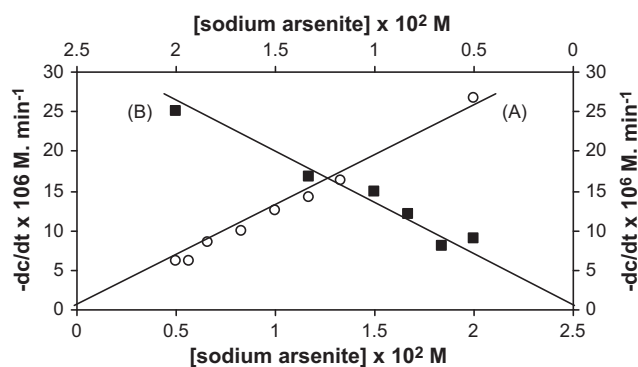
| $[K_3Fe(CN)_6] (\times 10^3 \text{ M})$ | $-dc/dt (\times 10^6 \text{ M min}^{-1})$ |       | $k^* (\times 10^2 \text{ min}^{-1})$ |      | $k_{gr} (\times 10^2 \text{ min}^{-1})$ |      |      | $k_{calc} (\times 10^2 \text{ min}^{-1})$ |      |      |      |      |
|---|---|-------|--------------------------------------|------|---|------|------|---|------|------|------|------|
|   | (A)                                       | (B)   | (A)                                  | (B)  | (A)                                     | (B)  | Fast | Slow                                      | (A)  | (B)  | Fast | Slow |
| 0.45                                    | 12.00                                     | 12.50 | 2.66                                 | 2.27 | 2.30                                    | 6.14 | 1.79 |   | 2.32 | 5.73 | 2.75 |      |
| 0.55                                    | 13.60                                     | –     | 2.47                                 | –    | 2.16                                    | –    | –    |   | 2.34 | –    | –    |      |
| 0.66                                    | 15.00                                     | 12.00 | 2.27                                 | 1.81 | 2.30                                    | 5.11 | 1.53 |   | 2.10 | 4.30 | 2.18 |      |
| 0.71                                    | 19.50                                     | 16.66 | 2.74                                 | 2.34 | 2.42                                    | 3.16 | 1.68 |   | 2.37 | 3.52 | 2.25 |      |
| 0.83                                    | 21.40                                     | –     | 2.57                                 | –    | 2.16                                    | –    | –    |   | 2.08 | –    | –    |      |
| 1.00                                    | 22.20                                     | –     | 2.22                                 | –    | 2.04                                    | –    | –    |   | 2.12 | –    | –    |      |
| 1.11                                    | –   | 22.00 | –                                    | 1.98 | –                                       | 5.11 | 2.30 |   | –    | 3.17 | 2.66 |      |
| 1.25                                    | 30.00                                     | 25.00 | 2.40                                 | 2.00 | 1.84                                    | 3.06 | 1.97 |   | 1.85 | 3.22 | 2.29 |      |
| 2.00                                    | –   | 40.00 | –                                    | 2.00 | –                                       | 2.68 | 1.81 |   | –    | 2.69 | 2.08 |      |

$[NaOH] = 10.00 \times 10^{-2} \text{ M}$  (for both A and B),  $[sodium\ arsenite] = 1.00 \times 10^{-2} \text{ M}$  (for both A and B),  $[IrCl_3] = 6.68 \times 10^{-5} \text{ M}$  (only for B). A for reactions without catalyst and B for reactions with catalyst.  $k^* \frac{-dc/dt}{[K_3Fe(CN)_6]}$

**Table 2**  
Effect of variation of sodium arsenite and hydroxyl ion concentrations on the rate of oxidation of arsenic(III) at 30 °C.

| $[NaAsO_2] (\times 10^2 \text{ M})$ | $-dc/dt (\times 10^6 \text{ M min}^{-1})$ |       | $k^* (\text{M}^{-1} \text{ min}^{-1})$ |      | $[OH^-] (\times 10^2 \text{ M})$ | $-dc/dt (\times 10^6 \text{ M min}^{-1})$ |       | $k^{**} (\text{M}^{-2} \text{ min}^{-1})$ |      |
|-------------------------------------|---|-------|--|------|----------------------------------|---|-------|---|------|
|                                     | (A)                                       | (B)   | (A)                                    | (B)  |                                  | (A)                                       | (B)   | (A)                                       | (B)  |
| 0.50                                | 6.25                                      | 9.00  | 2.27                                   | 3.27 | 3.33                             | 1.80                                      | 1.59  | 2.91                                      | 2.61 |
| 0.57                                | 6.25                                      | –     | 1.99                                   | –    | 4.00                             | 2.85                                      | 1.36  | 2.95                                      | 1.55 |
| 0.66                                | 8.58                                      | 8.12  | 2.36                                   | 2.24 | 5.00                             | 4.00                                      | 3.63  | 2.91                                      | 2.64 |
| 0.83                                | 10.00                                     | 12.00 | 2.19                                   | 2.62 | 6.66                             | 6.66                                      | 7.14  | 2.73                                      | 2.93 |
| 1.00                                | 12.50                                     | 15.00 | 2.27                                   | 2.73 | 8.33                             | 8.00                                      | 17.50 | 2.10                                      | 4.58 |
| 1.17                                | 14.28                                     | –     | 2.22                                   | –    | 10.00                            | 12.50                                     | 12.50 | 2.27                                      | 2.27 |
| 1.33                                | 16.25                                     | 16.66 | 2.22                                   | 2.28 | 14.28                            | 28.00                                     | 26.66 | 2.50                                      | 2.34 |
| 2.00                                | 26.66                                     | 25.00 | 2.42                                   | 2.27 | 20.00                            | 50.00                                     | 55.00 | 2.27                                      | 2.50 |

$[NaAsO_2] = 1.00 \times 10^{-2} \text{ M}$  (for \* only),  $[OH^-] = 10.00 \times 10^{-2} \text{ M}$  (for # only)  $[K_3Fe(CN)_6] = 0.55 \times 10^{-3} \text{ M}$ ,  $[IrCl_3] = 6.68 \times 10^{-5} \text{ M}$  (for B only).  $k^* \frac{-dc/dt}{[K_3Fe(CN)_6][NaAsO_2]}$   $k^{**} \frac{-dc/dt}{[NaOH]^2[K_3Fe(CN)_6]}$

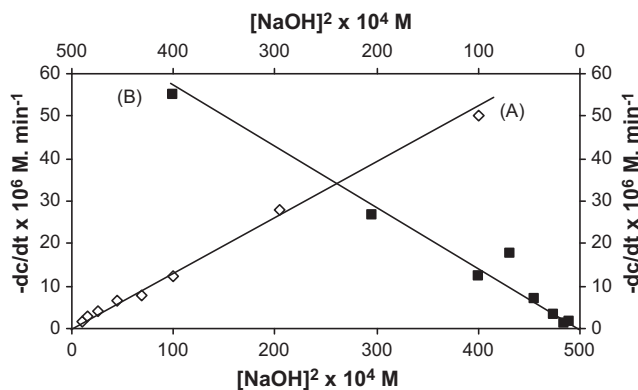


**Fig. 3.** Effect of variation of sodium arsenite concentrations on its oxidation at 30 °C.

$[K_3Fe(CN)_6] = 0.55 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[NaOH] = 10.00 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[IrCl_3] = 6.68 \times 10^{-5} \text{ mol dm}^{-3}$  (only for reactions with catalyst). Captions are same for A (without catalyst) and B (with catalyst).

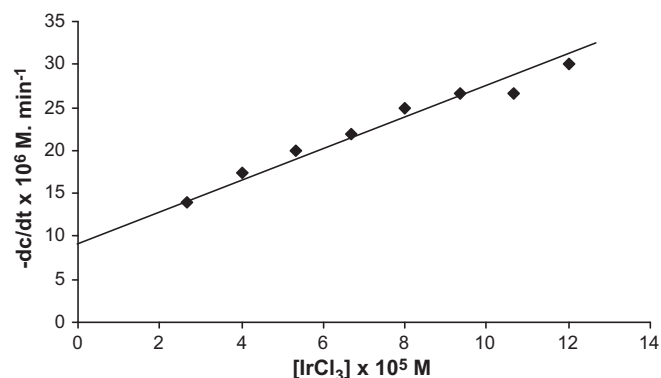
graphs between the rate and inorganic substrate concentrations in the presence and absence of catalyst which finally confirm that order of the reaction with respect to sodium arsenite concentrations is one in both the cases. Rate increases to a large extent on increasing hydroxyl ion concentration. Straight lines passing through the origin were obtained in both the cases on plotting rate against the square of hydroxyl ion concentration (Fig. 4), indicating that the reaction follows second order kinetics with respect to  $OH^-$  ion concentrations. Slope values of 2.15 and 1.80 respectively on plotting double logarithmic plots in the presence and absence of catalyst further confirm that rate of the reaction is proportional to the square of hydroxyl ion concentrations. This nature is contrary to the previously reported results [14]. Interestingly, on plotting  $-dc/dt$  values versus concentration of  $IrCl_3$ , a straight line was obtained with a positive intercept at y-axis (Fig. 5). Slope of this line shows the rate of reaction which takes place after adding iridium(III), while the positive intercept gives the extent of the reaction, which takes place in the absence of the catalyst. Proportionate increase in  $-dc/dt$  values with increasing catalyst concentrations and fair constancy in  $k^*$  values indicate that the reaction follows first order kinetics with respect to iridium(III) chloride concentrations (Table 3).

To find out whether hexacyanoferrate(III) is reduced before the rate determining step or not, concentration of hexacyanoferrate(II) was changed adding the ions externally. Practical constancy in the rate values at  $31.06 \pm 0.01$  and  $28.3 \pm 0.01$  ( $\times 10^{-6} \text{ M min}^{-1}$ )



**Fig. 4.** Effect of variation of hydroxyl ion concentrations on the rate of oxidation of arsenic(III) at 30 °C.

Captions are same for A (without catalyst) and B (with catalyst):  $[K_3Fe(CN)_6] = 0.55 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[NaAsO_2] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[IrCl_3] = 6.68 \times 10^{-5} \text{ mol dm}^{-3}$  (only for reactions with catalyst).



**Fig. 5.** Effect of variation of iridium trichloride concentrations on the rate of oxidation of arsenic(III) at 30 °C.

$[K_3Fe(CN)_6] = 0.83 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[NaAsO_2] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[NaOH] = 10.00 \times 10^{-2} \text{ mol dm}^{-3}$ .

(Table 4) clearly shows that the change in hexacyanoferrate(II) concentrations does not affect the rate of oxidation of arsenic(III) in the absence or in the presence of catalyst. Change in ionic strength of the medium ( $I$ ) with the help of a standard solution of potassium chloride shows that both in the absence and presence of catalyst, rate of reaction increases with increasing ionic strength of the medium (Table 4). Thermodynamic parameters viz. energy of activation, entropy of activation and free energy of activation values were found to be 8.31 kcal and 15.24 kcal,  $-32.34 \text{ e.u.}$  and  $-51.12 \text{ e.u.}$ ,  $18.11 \text{ K cal mol}^{-1}$  and  $30.73 \text{ K cal mol}^{-1}$  respectively for the reactions taking place in the absence and presence of catalyst. These values confirm that formation of activated complex is easier in the case when reaction takes place in the presence of catalyst.

### 3.3.1. Mechanism of reaction in the presence of iridium(III) chloride

Suggested path of oxidation of arsenic(III) by aqueous alkaline hexacyanoferrate(III) in presence of iridium(III) chloride is shown in Scheme 1. Under the experimental conditions shifting of equilibrium towards the left hand side in Eq. (2) results in the formation of reactive species of catalyst in step I. Loehr and Plane have shown that  $H_3AsO_3$ ,  $H_2AsO_3^-$ ,  $HAsO_3^{2-}$  and  $AsO_3^{3-}$  exist in basic solutions. It has been reported [14] that predominant form of  $H_3AsO_3$  is  $H_2AsO_3^-$  when  $[OH^-]/[As^{III}]$  ratio is less than one. In the present work, the above ratio is much more than unity. It is therefore suggested that  $H_2AsO_3^-$  further reacts with  $OH^-$  to give  $[HAsO_3^{2-}]$  species, which is the reactive form of arsenic(III) in the present study. In step II of Scheme 1 these two steps have been shown collectively. In the step III the reactive form of catalyst obtained in step I combines with the reactive form of arsenic obtained in step II giving rise to the activated complex. It appears that a competition for complex formation takes place between hexacyanoferrate(III)

**Table 3**

Effect of variation of iridium trichloride concentrations on the rate of oxidation of arsenic(III) at 30 °C.

| $[IrCl_3] (\times 10^5 \text{ M})$ | $-dc/dt (\times 10^6 \text{ M min}^{-1})$ | $k^* (\text{M}^{-1} \text{ min}^{-1})$ |
|------------------------------------|---|--|
| 2.67                               | 14.00                                     | 6.32                                   |
| 4.00                               | 17.50                                     | 5.27                                   |
| 5.34                               | 20.00                                     | 4.51                                   |
| 6.68                               | 22.00                                     | 3.97                                   |
| 8.01                               | 25.00                                     | 3.76                                   |
| 9.35                               | 26.60                                     | 3.35                                   |
| 10.68                              | 26.60                                     | 3.00                                   |
| 12.02                              | 30.00                                     | 3.01                                   |

$[K_3Fe(CN)_6] = 0.83 \times 10^{-3} \text{ M}$ ;  $[NaAsO_2] = 1.0 \times 10^{-2} \text{ M}$ ;  $[NaOH] = 10.0 \times 10^{-2} \text{ M}$ .  
 $k^* = \frac{-dc/dt}{[K_3Fe(CN)_6][IrCl_3]}$

**Table 4**  
Effect of variation of hexacyanoferrate(II) and chloride ion concentrations on the rate of oxidation of arsenic(III) at 30 °C.

| [K <sub>4</sub> Fe(CN) <sub>6</sub> ] <sup>4-</sup> (×10 <sup>3</sup> M) | -dc/dt (×10 <sup>6</sup> M min <sup>-1</sup> ) |       | [KCl] <sup>#</sup> (M) | -dc/dt (×10 <sup>6</sup> M min <sup>-1</sup> ) |       |
|--|--|-------|------------------------|--|-------|
|  | A  | B     |                        | A  | B     |
| 0.50   | 33.33  | 30.00 | 0.04                   | 17.14  | 23.33 |
| 0.55   | 32.00  | 27.50 | 0.09                   | 24.00  | 35.00 |
| 0.70   | 30.00  | 30.00 | 0.14                   | 27.50  | 40.00 |
| 0.90   | 30.00  | 27.50 | 0.19                   | 40.00  | 70.00 |
| 1.00   | 30.00  | 26.66 | 0.24                   | 43.30  | 100.0 |
|  |  |       | 0.29                   | 55.00  | 110.0 |

[K<sub>3</sub>Fe(CN)<sub>6</sub>] = 0.55 × 10<sup>-3</sup> M; [NaAsO<sub>2</sub>] = 1.0 × 10<sup>-2</sup> M; [IrCl<sub>3</sub>] = 6.68 × 10<sup>-5</sup> M (for B only); [NaOH] = 10.0 × 10<sup>-2</sup> M (for # only), [NaOH] = 20.0 × 10<sup>-2</sup> M (for \* only).

and the iridium(III) species and in the presence of iridium(III), AsO<sub>2</sub>(OH)<sup>2-</sup> species of As<sup>III</sup> preferably forms the complex with Ir<sup>III</sup>.

Reactive species of catalyst and the inorganic substrate are obtained in steps I and II of Scheme 1, which combine to form the activated complex in step III. Reaction of complex with a molecule of hexacyanoferrate(III) in the slow and rate determining step results in the reduced form of oxidant along with the formation of HAsO<sub>3</sub> and IrCl<sub>6</sub><sup>4-</sup>. In the subsequent fast steps another molecule of oxidant regenerates the reactive form of catalyst and hydration of HAsO<sub>3</sub> by a water molecule converts it into arsenic acid H<sub>3</sub>AsO<sub>4</sub> [22]. Proposed Scheme 1 gets support from the positive effect of ionic strength of the medium on the rate of oxidation of arsenic(III) by hexacyanoferrate(III) which indicates that the reaction is taking place between the similarly charged ions.

**3.3.1.1. Derivation of rate law for the reaction in presence of iridium(III) chloride.** At any moment total concentration of As<sup>III</sup> ([As<sup>III</sup>]<sub>T</sub>) may be given as

$$[\text{As}^{\text{III}}]_{\text{Total}} = [\text{H}_3\text{AsO}_3] + [\text{AsO}_2(\text{OH})^{2-}] + \text{Complex} \quad (6)$$

Concentration of IrCl<sub>6</sub><sup>3-</sup>, and H<sub>3</sub>AsO<sub>3</sub> and AsO<sub>2</sub>(OH)<sup>2-</sup> may be calculated from steps I, II and III of Scheme 1, respectively

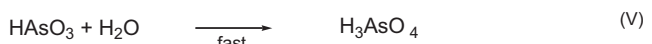
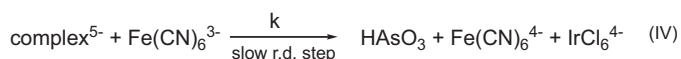
$$[\text{IrCl}_6^{3-}] = \frac{K_1 [\text{IrCl}_5(\text{H}_2\text{O})^{2-}] [\text{Cl}^-]}{[\text{H}_2\text{O}]} \quad (7)$$

$$[\text{H}_3\text{AsO}_3] = \frac{[\text{AsO}_2(\text{OH})^{2-}] [\text{H}_2\text{O}]^2}{K_2 [\text{OH}^-]^2} \quad (8)$$

$$[\text{AsO}_2(\text{OH})^{2-}] = \frac{[\text{C}^{5-}]}{K_3 [\text{IrCl}_6]^{3-}} \quad (9)$$

Concentration of AsO<sub>2</sub>(OH)<sup>2-</sup> after substituting the value of IrCl<sub>6</sub><sup>3-</sup> from Eq. (7) may be written as

$$[\text{AsO}_2(\text{OH})^{2-}] = \frac{[\text{C}^{5-}] [\text{H}_2\text{O}]}{K_1 K_3 [\text{IrCl}_5(\text{H}_2\text{O})^{2-}] [\text{Cl}^-]} \quad (10)$$



**Scheme 1.** Mechanism for the reaction in the presence of catalyst.

Substituting the value of AsO<sub>2</sub>(OH)<sup>2-</sup> in Eq. (8) we get

$$[\text{H}_3\text{AsO}_3] = \frac{[\text{C}^{5-}] [\text{H}_2\text{O}]^3}{K_1 K_2 K_3 [\text{OH}^-]^2 [\text{IrCl}_5(\text{H}_2\text{O})^{2-}] [\text{Cl}^-]} \quad (11)$$

Now putting the values of H<sub>3</sub>AsO<sub>3</sub> and AsO<sub>2</sub>(OH)<sup>2-</sup> from Eqs. (11) and (10) into the Eq. (6), total concentration of As<sup>III</sup> may be given as

$$[\text{As}]_{\text{T}} = \frac{[\text{C}^{5-}] [\text{H}_2\text{O}]^3}{K_1 K_2 K_3 [\text{OH}^-]^2 [\text{IrCl}_5(\text{H}_2\text{O})^{2-}] [\text{Cl}^-]} + \frac{[\text{C}^{5-}] [\text{H}_2\text{O}]}{K_1 K_3 [\text{IrCl}_5(\text{H}_2\text{O})^{2-}] [\text{Cl}^-]} + [\text{C}^{5-}] \quad (12)$$

From this the concentration of the complex C comes out to be

$$[\text{C}^{5-}] = \frac{K_1 K_2 K_3 [\text{OH}^-]^2 [\text{IrCl}_5(\text{H}_2\text{O})^{2-}] [\text{Cl}^-] [\text{As}]_{\text{T}}}{[\text{H}_2\text{O}]^3 + K_2 [\text{OH}^-]^2 [\text{H}_2\text{O}] + K_1 K_2 K_3 [\text{OH}^-]^2 [\text{IrCl}_5(\text{H}_2\text{O})^{2-}] [\text{Cl}^-]} \quad (13)$$

Rate of reaction in terms of decreasing concentrations of hexacyanoferrate(III) is given by

$$-\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = k [\text{C}^{5-}] [\text{Fe}(\text{CN})_6^{3-}] \quad (14)$$

Substituting the value of the concentration of complex [C<sup>5-</sup>] from Eq. (13) into Eq. (14) and multiplying the equation by 2 because two molecules of oxidant are used for regenerating the original active form of catalyst i.e. IrCl<sub>6</sub><sup>3-</sup>, we get the rate law in terms of decreasing concentrations of hexacyanoferrate(III) as

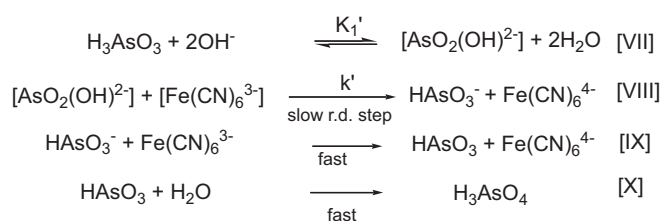
$$-\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{2k K_1 K_2 K_3 [\text{Fe}(\text{CN})_6^{3-}] [\text{OH}^-]^2 [\text{IrCl}_5(\text{H}_2\text{O})^{2-}] [\text{Cl}^-] [\text{As}]_{\text{T}}}{[\text{H}_2\text{O}]^3 + K_1 [\text{OH}^-]^2 [\text{H}_2\text{O}] + K_1 K_2 K_3 [\text{OH}^-]^2 [\text{IrCl}_5(\text{H}_2\text{O})^{2-}] [\text{Cl}^-]} \quad (15)$$

As the oxidation was studied in aqueous medium thus the inequality [H<sub>2</sub>O]<sup>3</sup> ≫ K<sub>1</sub>[OH<sup>-</sup>]<sup>2</sup>[H<sub>2</sub>O] + K<sub>1</sub>K<sub>2</sub>K<sub>3</sub>[IrCl<sub>5</sub>(H<sub>2</sub>O)<sup>2-</sup>][OH<sup>-</sup>]<sup>2</sup>[Cl<sup>-</sup>] may be consider valid and the final rate law reduces to

$$\text{Rate} = -\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = k_c [\text{Fe}(\text{CN})_6^{3-}] [\text{IrCl}_5(\text{H}_2\text{O})^{2-}] [\text{OH}^-]^2 [\text{Cl}^-] [\text{As}^{\text{III}}]_{\text{T}} \quad (16)$$

In this equation k<sub>c</sub> is another constant and equals to 2kK<sub>1</sub>K<sub>2</sub>K<sub>3</sub>. k<sub>c</sub> represents the overall rate constant for the reaction taking place in the presence of iridium(III) chloride. With the help of Eq. (16) the values of k<sub>c</sub> were calculated from the slopes of the graphs of rate versus the concentrations of [Fe(CN)<sub>6</sub><sup>3-</sup>], [As<sup>III</sup>], [OH<sup>-</sup>]<sup>2</sup> and [Ir<sup>III</sup>] which were found to be 1.40, 1.51, 1.81 and 1.11 (×10<sup>6</sup> M<sup>-5</sup> min<sup>-1</sup>). Fair constancy in the rate constant values obtained from four different variations of the catalyzed reaction indicates the validity of the proposed mechanism and the final rate law (16).





**Scheme 2.** Mechanism for the reaction in the absence of catalyst.

### 3.3.2. Mechanism of reaction in the absence of iridium(III) chloride

According to Scheme 2 sodium arsenite in alkaline medium gives rise to  $\text{AsO}_2(\text{OH})_2^{2-}$  which in turn combines with hexacyanoferrate(III) in the slow and rate determine step to give  $\text{HAsO}_3^{1-}$ .  $\text{HAsO}_3^{1-}$  is quickly oxidized by hexacyanoferrate(III) in the subsequent fast step giving rise to  $\text{HAsO}_3$ . Conversion of  $\text{HAsO}_3$  into  $\text{H}_3\text{AsO}_4$  in aqueous medium is well established [22]. In the present work it was observed that increase in ionic strength of the medium with the help of a standard solution of potassium chloride also increases the reaction velocity indicating that the reaction is taking place between similarly charged species. The proposed mechanism is consistent with the experimental findings.

The path by which  $\text{As}^{\text{III}}$  is oxidized by one and two equivalent oxidants has been discussed by previous workers [12–14]. Evidence of formation of  $\text{As}^{\text{IV}}$  as an unstable intermediate is found in a number of publications ([22] and the references cited therein). It appears that a competition for complex formation takes place between hexacyanoferrate(III) and the iridium(III) species. Under the conditions when reaction takes place in the presence of catalyst,  $\text{AsO}_2(\text{OH})_2^{2-}$  species of  $\text{As}^{\text{III}}$  preferably forms the complex with  $\text{Ir}^{\text{III}}$ . In the absence of iridium(III) chloride, which is the case when reaction takes place in the absence of catalyst, hexacyanoferrate(III) being one electron transfer oxidant abstracts one electron from  $\text{AsO}_2(\text{OH})_2^{2-}$  giving rise to  $\text{AsO}_2(\text{OH})_2^{1-}$  which in turn is further oxidized by a second molecule of hexacyanoferrate(III) giving rise to  $\text{HAsO}_3$ .

**3.3.2.1. Derivation of rate law for the reaction in absence of iridium(III) chloride.** Concentration of  $\text{AsO}_2(\text{OH})_2^{2-}$ , calculated from equilibrium step (VII) of Scheme 2 is given as

$$[\text{AsO}_2(\text{OH})_2^{2-}] = \frac{K_1' [\text{H}_3\text{AsO}_3] [\text{OH}^-]^2}{[\text{H}_2\text{O}]^2} \quad (17)$$

Rate in terms of decreasing concentrations of hexacyanoferrate(III) is given by step (VIII) as

$$\text{Rate} = -\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = k' [\text{AsO}_2(\text{OH})_2^{2-}] [\text{Fe}(\text{CN})_6^{3-}] \quad (18)$$

Now putting the value of  $\text{AsO}_2(\text{OH})_2^{2-}$  from Eq. (17) into Eq. (18) and multiplying the equation by 2 because two molecules of oxidant are involved in the reaction, the rate is given as

$$\text{Rate} = -\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{2k'K_1' [\text{Fe}(\text{CN})_6^{3-}] [\text{OH}^-]^2 [\text{H}_3\text{AsO}_3]}{[\text{H}_2\text{O}]^2} \quad (19)$$

In this case also as the reaction was studied in aqueous medium the final rate law (19) takes the form as-

$$\text{Rate} = \frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = k_u [\text{Fe}(\text{CN})_6^{3-}] [\text{OH}^-]^2 [\text{H}_3\text{AsO}_3] \quad (20)$$

$k_u$  is the overall rate constant for the reaction which takes place in the absence of catalyst. Values of  $k_u$  were calculated with the help of the slopes of the graphs plotted between the rate and

**Table 5**  
Effect of various parameters on the removal of arsenic(V) (In each case 1.0g adsorbent was taken).

| Experimental details                                  | Total arsenic concentration (ppb) |         |         |         |         | Total dissolved substances (ppt) |         |         |         |         | Conductivity (mS) |         |         |         |         | pH** |
|---|-----------------------------------|---------|---------|---------|---------|----------------------------------|---------|---------|---------|---------|-------------------|---------|---------|---------|---------|------|
|   | Set (1)                           | Set (2) | Set (3) | Set (4) | Set (5) | Set (1)                          | Set (2) | Set (3) | Set (4) | Set (5) | Set (1)           | Set (2) | Set (3) | Set (4) | Set (5) |      |
| Sample water (from reaction mixture)                  | 1000                              | 1000    | 1000    | 1000    | 1000    | 8.6                              | 8.4     | 8.5     | 8.6     | 8.6     | 17.3              | 17.7    | 17.2    | 17.2    | 17.2    | 6.0  |
| Sample water (after precipitation with Prussian blue) | 1000                              | 1000    | 1000    | 1000    | 1000    | 16.9                             | 16.3    | 16.9    | 16.8    | 17.0    | 33.9              | 32.7    | 33.8    | 33.9    | 34.0    | 2.1  |
| Sample water (after treating with various adsorbents) | 500                               | 500     | 10*     | 300     | 500     | 13.7                             | 13.2    | 8.5     | 12.2    | 9.6     | 27.4              | 26.5    | 17.1    | 24.5    | 19.2    | 2.2  |

\* Obtained minimum concentration of arsenic.

\*\* Initial pH 9.20.

$[\text{As}^{\text{III}}]$ ,  $[\text{OH}^-]^2$  and  $[\text{Fe}(\text{CN})_6^{3-}]$  and these values were found to be 1.14, 1.14,  $1.10 (\times 10^2 \text{ M}^{-3} \text{ min}^{-1})$ . Fair constancy in the rate values obtained from three different variations confirms the validity of the proposed Scheme 2 and the rate law (20).

Interesting part of study is that a straight line with positive intercept at y-axis was obtained on plotting rate values against the concentration of catalyst. Slope of this graph gives the rate and extent of the reaction taking place in the presence of catalyst, while the intercept at y-axis gives the rate and extent of the reaction which takes place in the absence of catalyst. It may be pointed out that the reaction which takes place in the presence of catalyst includes the reaction which proceeds in its absence. This results in the intercept at y-axis. Rate and extent of the reaction taking place in the absence of catalyst was calculated from the intercept of the catalyst graph and was found to be  $0.63 \times 10^2 \text{ M}^{-3} \text{ min}^{-1}$ , which closely resembles with the value of the rate constant calculated with the help of Eq. (20). Close resemblance between the values finally confirms the validity of the rate laws (16) and (20) and the proposed mechanisms.

## 4. Arsenic removal studies

### 4.1. Method

The arsenic removal experiments were performed in the solution obtained after completion of the reaction. The present study involves three steps; (i) Study of the kinetics of oxidation of As(III) to As(V) by hexacyanoferrate(III) (ii) precipitation of hexacyanoferrate(II) with the help of iron(III) nitrate as Prussian blue and (iii) the subsequent removal of the As(V) by its adsorption on ash of endocarp of coconut (adsorbent-I), ash of Bagasse (adsorbent II), ash of dead Unio shell (collected from shores of rivers and ponds) (adsorbent-III), activated charcoal (adsorbent-IV) and coal (adsorbent-V). Hexacyanoferrate(III) reduces to hexacyanoferrate(II) during the oxidation of arsenic(III) to arsenic(V). After completion of the reaction the spent reaction mixture was acidified and ferric nitrate was added to the reaction mixture which precipitates hexacyanoferrate(II) as Prussian blue in the reaction mixture. Removal of hexacyanoferrate(II) is necessary to improve the quality of water from the drinking point of view and also due to its interference in the identification of arsenic(V) with the arsenic test kit (Orlab Pvt. Ltd.). The resultant solution was filtered and was mixed with 1.0 g each of different adsorbents with constant stirring for 10 min. Solid contents of the mixture were allowed to settle. With the help of arsenic test kit, supernatant liquid was analyzed after 30 min to check the total arsenic contents (as arsenic(V)). Mechanism of adsorption of arsenic(V) was studied by Fourier transform infrared analysis (FTIR).

### 4.2. Results and discussion

Decrease in pH, conductivity and total dissolved substances (TDS) along with the decrease in total arsenic concentration in the spent reaction mixture obtained from the kinetic study support the arsenic removal (Table 5). As shown in Fig. 6; 1.0 g of ash of dead Unio shell (Adsorbant III) effectively removes arsenic(V) species by lowering the arsenic(V) concentration from an initial  $1000 \mu\text{g l}^{-1}$  to below  $10 \mu\text{g l}^{-1}$  (10 ppb). According to EPA, USA, level of 10 ppb of arsenic(V) satisfies the regulation level for drinking water. Chitin, a natural polysaccharide, is found in diatoms, nematodes, mollusks etc. consisting of (1,4)2-acetamide-2-deoxy-D-glucose units some of which are deacetylated and are known as chitosan [23]. Chitin and chitosan are highly basic polysaccharides with unique properties like the ability to form films [24] to react with polyan-

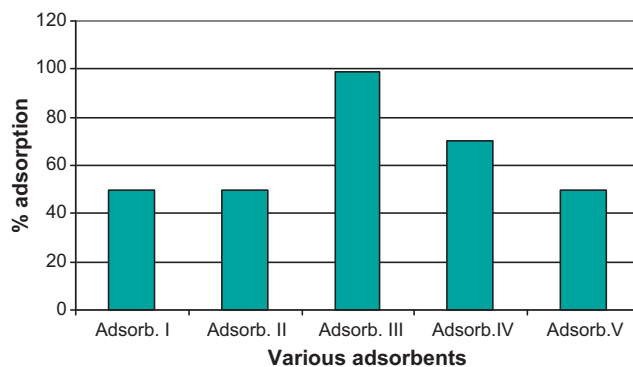


Fig. 6. Efficiency of various natural adsorbent for arsenic(V) removal. Adsorb. I = ash of endocarp of coconut, Adsorb. II = ash of Bagasse, Adsorb. III = ash of dead Unio shell, Adsorb. IV = activated charcoal and Adsorb. V = coal.

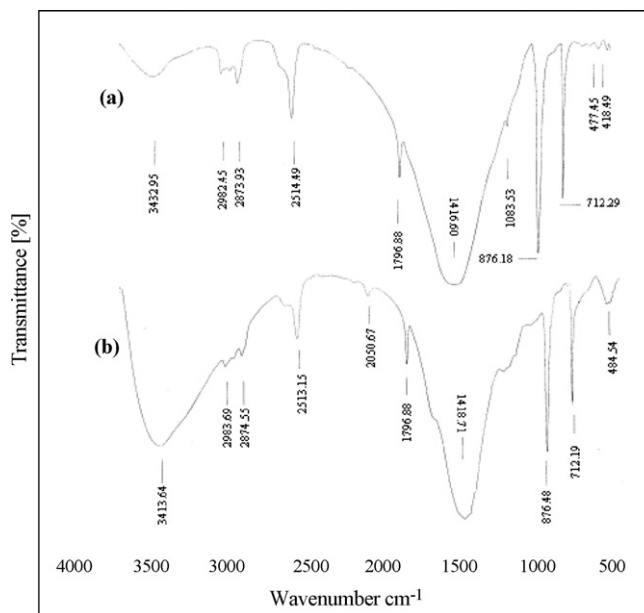
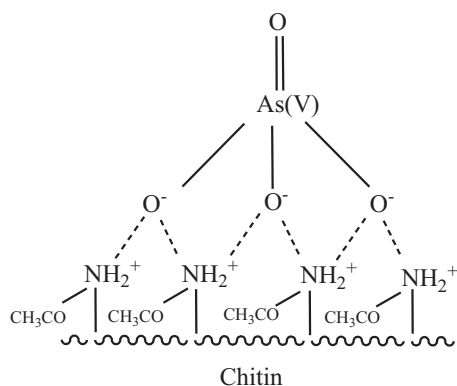


Fig. 7. IR spectra of ash of Unio (a) pure ash (b) ash after adsorption of arsenic(V).

ions [25–26] as well as to chelate and to remove metal ions [27]. Amide group ( $-\text{NH}-$ ) of chitin in acidic medium is protonated and bears a positive charge ( $-\text{NH}^+-$ ) which facilitates the adsorption of negatively charged  $\text{AsO}_4^{3-}$  at the surface of the ash of Unio. Presence of electrostatic forces between the oppositely charged ions ( $\text{AsO}_4^{3-}$  and  $\text{CH}_3\text{CO-NH}_2^+$ ) gets support from the IR spectral studies which were performed on the important suggestions given by the referees. In IR spectra of Unio ash before and after adsorption of arsenic(V) species (Fig. 7) major change are found only in the increase in intensity and the shifting of peak of amide group stretching frequency from  $3432.9 \text{ cm}^{-1}$  to  $3413.6 \text{ cm}^{-1}$ . This shift indicates that the amide group attached to the ash of Unio is affected by the arsenic(V) molecule. This result further confirms that arsenic(V) is bound to the ash and the functional group mainly responsible for arsenic(V) binding is the amide group of chitin which is present in the ash. As calcium carbonate is the major component of ash, the possibility of precipitation of arsenate in the form of  $\text{CaHAsO}_4$  can be ruled out on the basis of spectra in which no change in the characteristic peaks [28] of calcium carbonate ( $1796.8 \text{ cm}^{-1}$ ,  $1416.6 \text{ cm}^{-1}$ ,  $1083.5 \text{ cm}^{-1}$ ,  $876.1 \text{ cm}^{-1}$ ,  $712.2 \text{ cm}^{-1}$ ) are obtained. Schematic arsenate anion-sorption mechanism may be given as



## 5. Conclusion

Homogeneous catalysis by iridium(III) chloride in the oxidation of arsenic(III) in alkaline medium may be extended to other reactions also involving the inorganic substrates which are very important from the industrial point of view. Further, the removal of arsenic(V) from aqueous solutions is extremely important from the environmental point of view. The present study may lead to find out a cost effective and safe method to purify drinking water contaminated with arsenic. Generally arsenic containing reaction mixtures are thrown away in the laboratories and industries, which causes arsenic contamination of the soil and environment. The present study gives an economical solution to check this type of arsenic contamination.

## Acknowledgment

Financial assistance from the Council of Scientific and Industrial Research, New Delhi, India (No. 01(2150)/07/EMR-II) is gratefully acknowledged.

## References

- [1] M. Pettine, F. Millero, Effect of metals on the oxidation of As(III) with  $\text{H}_2\text{O}_2$ , *Mar. Chem.* 70 (2000) 223–234.
- [2] M.C. Dodd, N.D. Vu, A. Ammann, V.C. Le, R. Kissner, H.V. Pham, T.H. Cao, M. Berg, U.V. Gunten, Kinetics, mechanistic aspects of As(III) oxidation by aqueous chlorine, chloramines, and ozone: Relevance to drinking water treatment, *Environ. Sci. Technol.* 40 (2006) 3285–3292.
- [3] V.K. Sharma, W. Rivera, V.N. Joshi, F.J. Millero, D. O'Connor, Ferrate(VI) oxidation of thiourea, *Environ. Sci. Technol.* 33 (1999) 2645–2650.
- [4] P.K. Tandon, M. Dhusia, S. Sahgal, Oxidation of cyclic ketones by alkaline hexacyanoferrate(III) catalyzed by rhodium(III), *J. Mol. Catal. A: Chem.* 301 (2009) 146–151.
- [5] P.K. Tandon, Co-catalysis by transition metal ions in the hydrogen ion catalysed oxidation of iodide ions: A kinetic study, *Transition Met. Chem.* 28 (2003) 494–499.
- [6] P.K. Tandon, A. Mehrotra, A.K. Singh, R. Baboo, P.B. Dwivedi, Co-catalysis by ruthenium(III) in hydrogen ions catalyzed oxidation of iodide ions: A kinetic study, *Int. J. Chem. Kinet.* 36 (2004) 545–553.
- [7] P.K. Tandon, A. Mehrotra, M. Srivastava, S.B. Singh, Iridium(III) catalyzed oxidation of iodide ions in aqueous acidic medium, *Transition Met. Chem.* 32 (2007) 541–547.
- [8] P.K. Tandon, A.K. Singh, R. Baboo, P.B. Dwivedi, Iridium(III) catalyzed oxidation of cyclic ketones by cerium(IV), *Transition Met. Chem.* 29 (2004) 663–670.
- [9] P.K. Tandon, S. Sahgal, A.K. Singh, Gayatri, M. Purwar, Oxidation of ketones by ceric perchlorate catalysed by iridium(III), *J. Mol. Catal. A: Chem.* 232 (2005) 83–88.
- [10] P.K. Tandon, S. Sahgal, M. Gayatri, M. Purwar, Dhusia, Oxidation of ketones by cerium(IV) in presence of iridium(III) chloride, *J. Mol. Catal. A: Chem.* 250 (2006) 203–209.
- [11] P.K. Tandon, S. Sahgal, A.K. Singh, S. Kumar, M. Dhusia, Oxidation of cyclic ketones by cerium(IV) in presence of iridium(III) chloride, *J. Mol. Catal. A: Chem.* 258 (2006) 320–326.
- [12] B. Krishna, H.S. Singh, Kinetics and mechanism of oxidation of As(III) by ferricyanide ion in alkaline media, *J. Inorg. Nucl. Chem.* 31 (1969) 2964–2966.
- [13] M.C. Agarwal, V.K. Jindal, S.P. Mushran, Kinetics of arsenite–ferricyanide reaction in an alkaline medium, *J. Inorg. Nucl. Chem.* 32 (1970) 1257–1262.
- [14] D. Mohan, D. Gupta, Y.K. Gupta, Kinetics and mechanism of the oxidation of arsenic(III) by hexacyanoferrate(III) in alkaline medium, *Inorg. Chem.* 16 (1977) 1026–1029.
- [15] J.C. Change, C.S. Garner, Kinetics of aquation of aquopentachloroiridate(III) and chloride anation of diaquotetrachloroiridate(III) anions, *Inorg. Chem.* 4 (1965) 209–215.
- [16] F.A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley Eastern Ltd., New Delhi, 1976, pp. 434.
- [17] I.A. Poulson, G.S. Garner, A. Thermodynamic, Kinetic study of hexachloro and aquopentachloro complexes of iridium(III) in aqueous solutions, *J. Am. Chem. Soc.* 84 (1962) 2032–2037.
- [18] T.M. Loefer, R.O. Plane, Raman spectra and structures of arsenious acid and arsenites in aqueous solution, *Inorg. Chem.* 7 (1968) 1708–1714.
- [19] G. Jander, H. Hofman, Der Molekularzustand der arsenigen Säure in wäßrigen Lösungen, *Z. Anorg. Allg. Chem.* 296 (1958) 134–153.
- [20] A. Simon, R. Pactzold, Untersuchungen an Selen – Sauerstoff-Verbindungen. I. Die Struktur der selenigen Säure, *Z. Anorg. Allg. Chem.* 301 (1959) 246–260.
- [21] E. Perfitti, G.S. Pokrovski, K.B. Busserolles, V. Majer, F. Gibert, Densities and heat capacities of aqueous arsenious and arsenic acid solutions to 350°C and 300 bar, and revised thermodynamic properties of  $\text{As}(\text{OH})_3$  (aq)  $\text{AsO}(\text{OH})_2$  (aq) and iron sulfarsenide minerals, *Geochim. Cosmochim. Acta* 72 (2008) 713–731.
- [22] S. Dholya, A. Prakash, R.N. Mehrotra, Kinetics and mechanism of oxidation of arsenous acid by 12-tungstocobaltate(III) ion, *J. Chem. Soc. Dalton Trans.* (1992) 819–822.
- [23] G.A.F. Roberts, *Chitin Chemistry*, Macmillan, London, UK, 1992, p. 1.
- [24] N.L. Yusof, L.Y. Lim, E. Khor, Flexible chitin films: structural studies, *Cabohydr. Res.* 339 (2004) 2701–2711.
- [25] N. Acosta, I. Aranaz, C. Peniche, A. Heras, Tramadol release from a delivery system based on alginate-chitosan microcapsules, *Macromol. Biosci.* 3 (2003) 546–551.
- [26] C. Peniche, W. Argüelles-Monal, H. Peniche, N. Acosta, Chitosan: An attractive biocompatible polymer for microencapsulation, *Macromol. Biosci.* 3 (2003) 511–520.
- [27] A. Bhatnagar, M. Sillanpää, Applications of chitin- and chitosan-derivatives for the detoxification of water and wastewater- a short review, *Adv. Colloid Interface Sci.* 152 (2009) 26–38.
- [28] K.V. Narasimhulu, J.L. Rao, EPR. IR spectral studies of the sea water mussel *Mytilus coradinus* shells, *Spectrochim. Acta Part A* 56 (2000) 1345–1353.