

Removal of arsenic and sulphate from the copper smelting industrial effluent

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Abstract

Effluent from the processing of arsenic-bearing ores may contain varying amounts of As(III) and As(V), oxyanion, arsenite and arsenate. The industries are adopting the ferric arsenate precipitation; the problems aroused in this method are the formation of large amount of sludge. The effective pH range for the precipitation of ferric arsenate is 4–8. But pH of the effluent is about 0.6 only and the sulphate concentration is more in the effluent. Therefore it is required to raise the pH for precipitation of ferric arsenate by the addition of an alkali. Due this reason the alkali consumption is more. The addition of chemicals may elevate the total dissolved solids (TDS) level.

This investigation aims at the removal of arsenic (incoming contaminants levels are in the range of 1000–2000 mg/L containing other heavy metals) from the metallurgical effluent either by electrodialysis (ED) or electrochemical ion-exchange (EIX) technique, followed by electrocoagulation (EC). Using ED, at the current density of 2 A/dm², arsenic can be removed up to 91.4% and sulphate up to 37.1%. Using EIX, at the current density of 3 A/dm², arsenic can be removed up to 58.2% and sulphate up to 72.7%. Using EC, at the current density of 1.5 A/dm², arsenic can be removed up to below detectable limit by atomic absorption spectrometer. By combining both the EIX and EC processes the consumption of alkali needed to raise the pH can be effectively minimized.

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1. Introduction

While smelting of ores that are mined for their metals such as lead, copper, zinc, gold and silver [1], arsenic and arsenical compounds enter the effluent in the dissolved form through industrial discharges from metallurgical industries.

As arsenic is a cause for skin, liver, lung and kidney or bladder cancer, it is a big headache to the nation [2,3]. Due to carcinogenic nature of arsenic compounds, the purpose should now be to reduce the exposure of arsenic-contaminated water to a level as close to zero as possible. According to the World Health Organization (WHO), the maximum contamination level of arsenic in drinking water is 50 and 10 µg/L as a provisional guideline value [4]. This standard has been retained by the U.S. Environmen-

tal Protection Agency (USEPA) and is currently the maximum contaminant level. The range of values under consideration by USEPA is from 2 to 20 µg/L for total arsenic.

Wastewater from the processing of arsenic-bearing ores may contain varying amounts of As(III) and As(V), oxyanion, arsenite, and arsenate. The presence of metal ions such as Cu, Pb, Ni and Zn limit the solubility of arsenic because of the formation of sparingly soluble metal arsenates. When arsenic is not recovered, it should be removed from the arsenic-bearing residue and contained in the form of solid compound before disposal. The removal of arsenic is hindered by the fact that arsenic has a variety of valence states. Inorganic arsenic presents dominantly in contaminated water as arsenite and arsenate. At the pH range of most natural and wastewater sources arsenite is more toxic, mobile and less efficiently removed than arsenate [5]. Arsenic is most effectively removed or stabilized when it is present in the pentavalent arsenate form. For the removal of arsenic from wastewater by coagulation using iron is the preferred option.

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The solidification/stabilization of arsenic is yet to be a clear-cut process [1].

A common method for removing arsenic from aqueous waste streams is through precipitation [6]. Typical precipitates are arsenic sulphides, calcium arsenates or ferric arsenates. Each of these precipitates has limited pH ranges within which they exhibit solubility minima. For example, those calcium arsenates that exhibit the lowest equilibrium concentrations of arsenate ion are stable at high pH, whereas ferric arsenates are stable only at low pH. However, the stability of calcium arsenates has been questioned because under the influence of atmospheric CO₂, calcium arsenates reacts to form calcium carbonate and liberates arsenic oxide in the solution [6]. The removal of arsenic from hydrometallurgical process wastewaters was by precipitation and co precipitation with iron(III). At relatively high concentrations of iron(III) and arsenic(V) and at low pH, the precipitation results in the formation of ferric arsenate, socordite [7], FeAsO₄·2H₂O. At low concentrations of arsenic(V) and high iron(III) concentrations the coprecipitation of arsenic with ferrioxihydroxide (ferrihydrite) occurs. The solid coprecipitate has been referred to basic ferric arsenate, FeAsO₄·Fe(OH)₃ [8].

Bench-scale studies indicate that arsenic removal can be enhanced by coagulation [9,10] or membrane processes [11] that would be sufficiently effective to meet a standard for arsenic in the range now under consideration (2–20 µg/L). At present, the industries are adopting the ferric arsenate precipitation, but the problems encountered in this method are the formation of large amount of sludge, the effective pH range for the precipitation of ferric arsenate is 4–8. But pH of the effluent is about 0.6 only. Therefore the pH has to be raised with the addition of an alkali for effective precipitation. Due this reason the alkali consumption is more and consequently the sulphate concentration will be more in the effluent. The addition of chemicals may elevate level the TDS and thus TDS is not reduced in the treated effluent.

The principal objective of the present investigation is to develop effective treatment procedure for the metallurgical effluent generally for removal of arsenics and sulphates. The incoming effluent contains contaminants levels in the range of 1000–2000 mg/L together with other heavy metal cations. A combination techniques are to be considered is a special electrodialysis, ED [12,13] or an electrochemical ion exchange, EIX [14–22] technique followed by electrocoagulation, EC [1,9,23,24] so that the generation of large amount of sulphate in the effluent can be minimized.

2. Materials and methods

2.1. Materials

All the chemicals used were of analytical grade. Actual effluent from industry was used for investigations whose characteristics are given in Table 1. The ion-selective membranes were NEOSEPTA anion-exchange membranes and a strong base Amberlite IRA-400 anion-exchange resin was used for the EIX experiments.

Table 1
Characteristics of the effluent (pH 0.6 and temperature, $T=30^{\circ}\text{C}$)

Properties	Value (mg/L)
pH	0.6
Colour of effluent	Light sky blue
Total suspended solids (TSS)	8760
Total dissolved solids (TDS)	83,672
Acidity	74,871
Alkalinity	BDL
SO ₄ ²⁻	49,136
Oil and grease	BDL
Arsenic	1628
Bismuth	85
Cadmium	24
Cobalt	0.04
Chromium	2.3
Copper	93
Iron	188
Lead	4.6
Nickel	12
Antimony	1.5
Zinc	142

2.2. Experimental setup and procedure

2.2.1. Electrodialytic separation process

The schematic diagram of the experimental setup for membrane process is shown in Fig. 1, which consists of a specially designed ED unit that has an effective membrane area of 7 cm × 7 cm. The ED device is a filter press type cell provided with three compartments viz., an anodic, middle and a

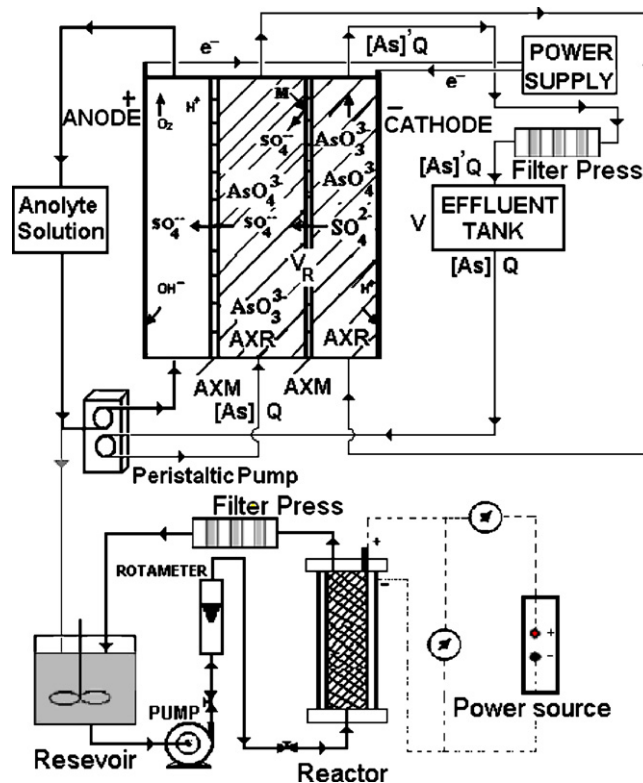


Fig. 1. Schematic diagram of the experimental setup.

cathodic. The geometric dimensions of each of the compartments were 7 cm × 7 cm × 1.5 cm. Stainless steel plate area of 7 cm × 7 cm was used as a cathode and noble metal oxides (TiO₂ and RuO₂) coated on expanded Ti mesh of area 40 cm² embedded in PVC frame was used as an anode. The middle or effluent compartment is formed in between the anodic and cathodic compartments with the help of two anionic exchange membranes (AXM). Since membranes divide the cell, separate liquids are taken as catholyte and anolyte. The effluent which is to be treated is taken as catholyte and mild sulphuric acid (0.05N) is to be taken as anolyte for the provision of electrolytic conductivity.

As per the plan for the first stage, a peristaltic pump passes the effluent from reservoir into the middle compartment and from there it is again circulated through the cathode compartment. The outlet from the cathode compartment is taken to the filter press where the effluent gets filtered off from the precipitate and again allowed to enter into the effluent reservoir (of capacity of 500 ml) for continuous recirculation.

Similarly 0.05N H₂SO₄ from the anolyte reservoir of capacity of 500 ml is pumped through another head of peristaltic pump into the anodic compartment. The outlet from this compartment is allowed to pass into the anolyte reservoir for continuous recirculation. The effluent is pumped at the rate of 18 ml/min and the acid is pumped at the rate of 14 ml/min. The difference in the flow rate between the catholyte and the anolyte is followed in order to maintain the level of the liquids in the reservoir. Since the effluent has to pass the two compartments, it is pumped faster than the acid, which in turn prevents the pressure development in the cathode compartment. If pressure develops in the cathode compartment the catholyte (effluent) will enter into the anode compartment, which results in increase in acid level and decrease in effluent level, which leads to an inefficient process.

After the steady flow has been reached, current corresponding to the current density was allowed to pass through the cell stack by means of the dc-regulated power supply. Experiments were conducted at various current densities specifically at 1.0, 1.5, 2.0, 2.5, 3.0 A/dm². Like this each run of electrolysis is carried out for 6 h.

At every hour sample of the acid and the effluent are collected, analyzed for sulphate in UV–vis spectrophotometer and arsenic in atomic absorption spectrometer (AAS). The pH of the samples is measured in pH meter and TDS is measured by means of conductivity meter.

2.2.2. Electrodialytic separation process in combination with ion-exchange resin

It is again a three-compartment cell and anion-exchange membranes separate the cell into three compartments. The electrodes used were as that of previous one. The experimental setup is shown in Fig. 1. To enhance the removal of sulphate, the middle and cathodic compartments were packed with anion-exchange resin (AXR). The purpose of the resin is twofold. It enhances electrical conductivity and increases residence time of the arsenic and sulphate ions in the reactor. Arsenic and sulphate ions are removed from the effluent by AXR when it is flowing in the middle compartment. The adsorbed anions then

migrate under the influence of an electric field through an anion membrane into the anode compartment.

The experimental procedure is same as that of the membrane process. After the steady flow has been reached, experiments are conducted at various current densities specifically at 1, 2, and 3 A/dm².

At every hour sample of the acid and the effluent are collected and analyzed for various parameters such as sulphate, total arsenic content, pH and TDS.

2.2.3. Electrocoagulation process

Electrocoagulation consists of an in situ generation of coagulants by an anodic dissolution of iron electrodes. That is generation of metallic cations takes place at the anode, whereas at the cathode, typically a H₂ production occurs. The generated gas helps the flotation of flocculated particles, and therefore the process sometimes is named as electro flocculation [23]. The process generates iron hydroxides, which would coprecipitate with arsenic anions.

Electrocoagulation was carried out using an undivided electrochemical cell in a galvanostatic condition. The anode was mild steel (sacrificial) available in commercial market. The cathode was stainless plate. The effective surface area of anode and cathode were 7 cm × 7 cm. The electrodes were positioned vertically and parallel to each other with an inter-electrode gap of 10 mm in a 0.5 L of effluent from the reservoir of the ED/EIX reactor is taken as the electrolyte for each electrocoagulation experiments. A dc power supply was used as the source of constant electric current for the experiments. To enhance the mass transport and to maintain a uniform concentration of the electrolyte, the reactor solution was constantly stirred using a magnetic stirrer. The temperature of the reactor was maintained constant. The current corresponding to optimized current density of 1.5 A/dm² is passed. If the solution is highly acidic as such or alkaline, both will passivate the anode from the liberation of ferrous ions into the solution. The effective pH for Fe²⁺ liberation is 2–3. Therefore alkali should be added to raise the pH to 2. After the effluent has been raised for the required pH, current corresponding to the current density is passed for 30 min. Every 10 min samples are collected and analyzed for arsenic and Fe content. Within these 30 min the stoichiometric requirement of Fe is produced from the anode. Then pH is adjusted to the range 4–8, which is the effective pH range for precipitation of ferric arsenate. Any oxidizing agent (e.g. H₂O₂) is added drop by drop with constant stirring, to ensure the conversion of As(III) to As(V).

2.3. Theoretical approach

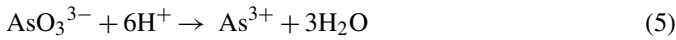
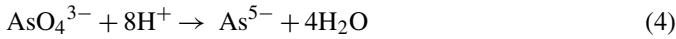
2.3.1. Reaction mechanisms

The dilute effluent containing arsenic and sulphate enters the middle compartment, which initially gets ionized. The reactions taking place in the bulk can be represented as





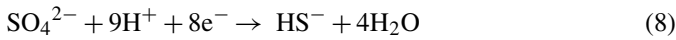
The anions specifically sulphate, arsenate (AsO_4^{3-}), arsenite (AsO_3^{3-}), due to their affinity towards anode, passes through the anion-exchange membrane separating the compartments and the acid in the anode compartment thus gets enriched. Since the effluent is highly acidic, in the bulk of the middle compartment the following reactions can also eventually take place:



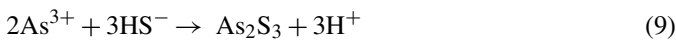
The effluent from the middle compartment is recirculated to the cathode compartment, where the arsenic present in the solution may get reduced into arsine (AsH_3) depending upon the conditions of electrolysis. That is a series reactions of arsenic(V) to arsenic(III) may take place:



As the concentration of sulphate is much higher than the arsenics, the sulphate present in the effluent predominantly gets reduced to HS^- at the cathode. This reaction is represented as



Here again the above bulk reactions will take place along with the above electrode reaction. The HS^- produced from the above reaction reacts readily with arsenic(III) and arsenic(V) and produce arsenic sulphides which precipitate out from the solution as shown below:



As the $pH < 7$, the following cathodic side reactions always take place at the cathode and results in the liberation of hydrogen. This is represented as



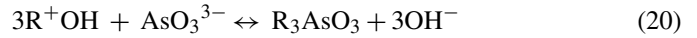
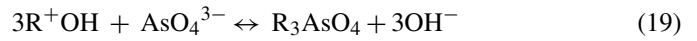
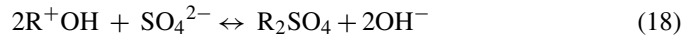
In the anode compartment, the anions reach from the middle compartment, reacts with H^+ ions in the bulk of anode compartment to yield the following reactions:



As the pH solution is low, the following reaction takes place at the anode with the liberation of oxygen:



The anionic resin adsorbs so formed anions (AsO_4^{3-} , AsO_3^{3-} , SO_4^{2-}). These equilibrium reactions are represented as



2.3.2. Development of model for removal of arsenic

In electrochemical treatment of effluent containing arsenic together with heavy metals like Cu, Cd, Zn and several possible reactions can occur at the electrodes; however the scope of this paper is limited to discussions with respect to arsenics and sulphates removal only. In this process, arsenics are reduced indirectly in bulk precipitating sulphides via HS^- (Eqs. (8) to (10)) or directly at the cathode to yield arsine through series reaction (Eqs. (6) and (7)). Since the concentrations of arsenic ions are so low, the electrochemical direct reduction of these ions by Eqs. (6) and (7) are not so active hence the primary reaction which occurs at the cathode is reduction of sulphate ion (Eq. (8)) with the liberation of HS^- , which is a robust reducing agent. As the effluent is generally acidic, in such case, the side reactions (Eqs. (11) and (12)) are take place generating hydrogen which is not useful in present context of effluent treatment and this leads to reduction of current efficiency. As regards to the reactions in the bulk, the HS^- produced from the above reaction (Eq. (8)) reacts readily with arsenic(III) and arsenic(V) and produce arsenic sulphides which precipitates out from the solution (Eqs. (9) and (10)). The indirect electroreduction rate of arsenic depends on the pH, flow rate, temperature and the diffusion of the reducing agent into the effluent. Denoting r_{HS^-} and r_{As} are the rates of the disappearance of HS^- and arsenic, respectively, from bulk of reactions which can be expressed as

$$\begin{aligned} -r_{HS^-} &= k_1[As^{3+}][HS^-] + k_2[As^{5+}][HS^-] \\ &= k_3[As][HS^-] \end{aligned} \quad (21)$$

As there may be migrations of arsenite and arsenate ions into anodic compartment, an account has to be taken while the rate of the disappearance of arsenic is considered. Migrational flux of arsenics through membrane is defined as $(zFD/RT) \text{ grad } \Phi$ [As], assuming Nernst–Einstein relation on the basis of local concentration, [As], potential gradients, $\text{grad } \Phi$ and the diffusion coefficient of arsenic anions (arsenate and arsenite) in the medium, D . For the sake of simplicity overall parameter α can be used to express the migration flux as αI [As] in which migrational flux was assumed to vary linearly with the current, I . Therefore the migrational rate of arsenics to anode compartment is $\alpha I a$ [As] where a is the specific area ((A_e/V_R)) of membrane, A_e is membrane area and V_R volume of the reactor. Hence the expression for the rate of depletion of arsenic in the reactor is given by

$$-r_{As} = k_4[As][HS^-] + \alpha I a [As] \quad (22)$$

As the above expressions are only applicable for bulk, a relationship between concentrations of reacting species in the

bulk of the effluent and on the electrode surface has to be developed.

The basic relationship applicable to all electrochemical reactions is Faraday's law that relates the amount of substance reacted at the surface to the charge (It) passed is $M_A It/nF$ (assuming 100% current efficiency) and the characteristic measurable parameter is current density, i , which is I/A_e . Thus the electrochemical reaction rate, $-r'_A$ (for the disappearance of reactant A) can be expressed as

$$-r'_A = - \left(\frac{V_R}{A_e} \right) \frac{d[A]}{dt} = \frac{i}{nF} \quad (23)$$

where I is the current passed in time t , M_A is the molecular weight, n is the number of electrons transferred per mole of reaction, A_e electrode area, V_R reactor volume and F is the Faraday (96,500 C or As/mol). It has to be noted $-r'_A = -d[A]/dt = i a/nF$ where a is specific electrode area (A_e/V_R). Assuming that the main electrode reaction is governed by a simple Tafel type expression, then

$$-r'_A = - \left(\frac{V_R}{A_e} \right) \frac{d[A]}{dt} = \frac{i}{nF} = k'[A]_s \exp(bE) \quad (24)$$

Considering the reduction reaction (8) in which the reaction may also be assumed to be governed by a simple Tafel type expression, then

$$\begin{aligned} -r'_{\text{SO}_4^{2-}} &= r'_{\text{HS}^-} = k'_1[\text{SO}_4^{2-}]_s \exp(bE) \\ &= k'_1[\text{HS}^-]_s \exp(bE) = \frac{i}{nF} \end{aligned} \quad (25)$$

The reactant SO_4^{2-} is transported from the bulk to electrode surface where it under goes electrochemical reduction to HS^- and it may be transported back to bulk by diffusion to proceed for reaction with arsenics in the bulk. The reaction may be assumed to be under diffusion control. Then

$$r'_{\text{HS}^-} = \frac{i}{nF} = k'_L([\text{HS}^-] - [\text{HS}^-]_s) \quad (26)$$

Elimination of $[\text{HS}^-]_s$ using Eqs. (25) and (26) results as

$$\frac{i}{zF} = k'[\text{HS}^-] \quad (27)$$

$$\text{where } \frac{1}{k'} = \frac{1}{k'_L} + \frac{1}{k'_1 \exp(bE)} \quad (28)$$

Rewriting Eq. (22) after substituting the expression for $[\text{HS}^-]$ from (27) as

$$-r_{\text{As}} = \left(\frac{k_4}{k'} \left(\frac{I}{zFA} \right) + \alpha I a \right) [\text{As}] \quad (29)$$

During electrolysis, since constant potential or current is applied, the rate of generation of $[\text{HS}^-]$ will remain constant under a given set of experimental conditions, but it varies as the applied potential or current is altered. However the concentration of sulphates is much larger than arsenic which results in net

variation of $[\text{HS}^-]$ is negligible. Then

$$-r_{\text{As}} = k_L a [\text{As}] \quad (30)$$

The mode of operation of ED/EIX system is depicted in Fig. 1 involves the continuous recirculation of the effluent. There is a gradual depletion of the concentration of the arsenic in the reservoir. In order to design the plant for treatment processes, the development of the model is essential which permits the computation of the variation of concentration of the arsenic with time in the reservoir. The basic assumptions involved in the ensuing derivation may be outlined as follows:

Back mix flow exists in the present reactor system. It was arrived based on residence time distribution (RTD) tracer experiment. An approximate model which represents the given ED/EIX system in which the reactions take place is described by a continuous stirred tank flow reactor (CSTR). A dynamic material balances to each of the component or species at reactor can be written as

$$\begin{aligned} &\left[\begin{array}{l} \text{rate of change mass of} \\ \text{species in the reactor} \end{array} \right] \\ &= \left[\begin{array}{l} \text{rate of mass} \\ \text{input} \end{array} \right] - \left[\begin{array}{l} \text{rate of mass} \\ \text{out put} \end{array} \right] \\ &\mp \sum \left[\begin{array}{l} \text{rate of mass of species disappeared} \\ \text{or generated physico chemical phenomena} \end{array} \right] \end{aligned}$$

The concentration variation of arsenic in the ED/EIX can be written as

$$V_R \left(\frac{d[\text{As}]'}{dt} \right) = Q[\text{As}] - Q[\text{As}]' - k_L A_e [\text{As}]' \quad (31)$$

LHS represents the rate of change of arsenic in the free volume of reactor, V_R is and $[\text{As}]'$ is the concentration of arsenic in the stream leaving the ED/EIX system. The first two terms of the RHS are rate mass of arsenic entering and leaving the ED/EIX system where Q is the volumetric flow rate and $[\text{As}]$ is the concentration of arsenic. The last term in the right-hand side represents the rate of disappearance of mass in the solution due to reaction and migration. The reservoir is always a perfectly back-mix system. The mass balance for the effluent reservoir is

$$V \left(\frac{d[\text{As}]}{dt} \right) = Q[\text{As}]' - Q[\text{As}] \quad (32)$$

Further it can also be assumed that the reactor is under steady state condition as $d[\text{As}]'/dt=0$, and rewrite Eq. (31) as

$$\frac{[\text{As}]'}{[\text{As}]} = \frac{1}{1 + k_L a \tau_R} \quad (33)$$

The mass balance Eq. (32) can be solved after substitution of the expression for $[\text{As}]'$ from Eq. (33), knowing the initial concentration of arsenic, $[\text{As}] = [\text{As}]_0$ at $t=0$ in reservoir, then the resultant equation can be written as

$$\frac{[\text{As}]}{[\text{As}]_0} = \exp \left[-\frac{t}{\tau} \left(\frac{k_L a \tau_R}{1 + k_L a \tau_R} \right) \right] \quad (34)$$

Table 2
Effect of current densities on pH, % removal of arsenic, power consumption and rate constant in an electrodiolytic separation process

Current density (A/dm ²)	Cell voltage (V)	pH		Arsenic (mg/L)		Removal (%)	Power consumption (kWh/kg)	Rate coefficient (s ⁻¹ × 10 ⁺⁵)
		Acid/anolyte reservoir	Effluent/catholyte reservoir	Acid/anolyte reservoir	Effluent/catholyte reservoir			
1.0	4.15	1.52–1.34	0.57–1.05	0–15.1	1268.8–507.5	60	32.05	5.6
1.5	4.45	1.54–1.05	0.64–0.78	0–37.8	1282.0–193.6	84.89	35.90	8.3
2.0	5.60	1.53–0.94	0.66–0.83	0 11.1	1295.3–111.7	91.38	55.64	13.9
2.5	5.80	1.47–0.86	0.59–0.82	0–23.3	1266.2–113.8	91.01	73.65	12.8
3.0	6.25	1.74–1.04	0.81–1.10	0–33.4	1275.5–101.4	92.05	91.80	10.3

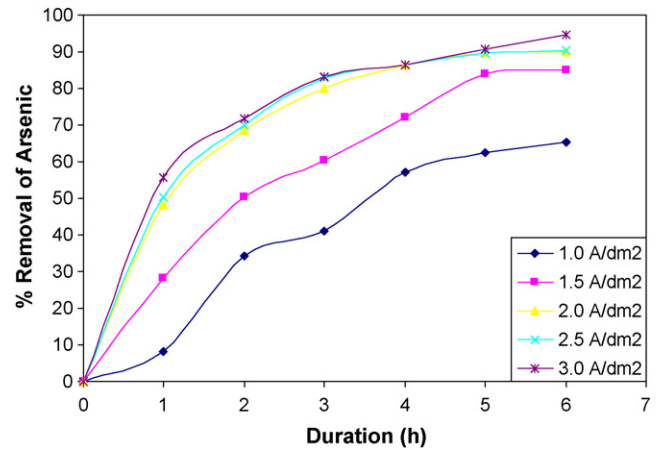


Fig. 2. Effect of current densities on concentration histories of % arsenic removal.

where $[As]_0$ is the initial concentration of arsenic in the reservoir. It should be noted that the extent of conversion is defined as $X = ([As]_0 - [As])/[As]_0$. The unconverted species $(1 - X)$, which is $[As]/[As]_0$, decreases exponentially with time. According to Eq. (34), the slope of the plot $\ln([As]/[As]_0)$ versus t or $\ln(1 - X)$ versus t , gives the value $[(k_L a \tau_R)/\tau(1 + k_L a \tau_R)]$ from which the value of $k_L a$, the overall rate transfer coefficient, may be computed. The results obtained are presented in Table 2 in respect of removal of arsenic in the effluent reservoir.

3. Results and discussion

3.1. Electrodiolytic separation process

As the effluent enters into the middle compartment, when current is passed, the anions especially sulphate, arsenate, arsenite move into the anode compartment through AXM and the acids in the anode compartment gets enriched. While the effluent is circulated into the cathode compartment, however anions present move through the membrane from cathode compartment to middle compartment, further the colour of the effluent visibly turned to black as the effluent enters into cathode compartment. It is due to the fact that the arsenate, arsenite, sulphate and other heavy metals electrochemically reduced at the cathode surface to yield precipitates of heavy metals (including arsenics) as sulphide. This was confirmed by analysis of sludge which contains mere sulphides of arsenic and other heavy metals at low pH. Now this precipitate is filtered off in a filter press and the effluent is recirculated for better treatment. Thus the TDS of the effluent in the reservoir of catholyte gets reduced and simultaneously the pH is increased while those of acids in the reservoir of anolyte get enriched.

The results of the experiments at various current densities between 1 and 3 A/dm² were presented in Tables 2 and 3 as well in Figs. 2 and 3. As the current density increases, arsenic and sulphate removal in the effluent increases, which can be noted from the tables and figures.

Regarding arsenic removal, the optimized current density is 2 A/dm², as seen from the overall rate transfer coefficient, $k_L a$.

Table 3
Effect of current densities on % removal of sulphate and power consumption in an electrolysytic separation process

Current density (A/dm ²)	Cell voltage (V)	Sulphate (mg/L)		Removal (%)	Power consumption (kWh/kg)
		Acid/anolyte reservoir	Effluent/catholyte reservoir		
1.0	4.15	3265–11,251	60,665–48,973	19.27	2.087
1.5	4.45	4,169–19,303	60,224–48,370	19.70	3.330
2.0	5.60	4037–28,513	70,813–44,521	37.10	4.000
2.5	5.80	3574–29,230	64,195–46,326	27.84	4.790
3.0	6.25	3838–35,928	64,526–43,458	32.65	5.230

It is computed from Eq. (34), in which the slope of the plot $\ln([As]/[As]_0)$ versus t , gives the value $[(k_L a \tau_R)/\tau(1 + k_L a \tau_R)]$ from which the value of $k_L a$ is obtained. The computed values from data of Fig. 2 assuming batch recirculation system using Eq. (34) are given in Table 2. Sulphates removal also does the same as shown in Table 3. It was observed that the removal of arsenic as well as sulphate from the effluent was low at lower current density. It is due to their removal may be mainly by migration as AsO_4^{3-} , AsO_3^{3-} and SO_4^{2-} through membrane to anode chamber and to a small extent through cathode surface at lower current densities. This was confirmed by analysis of acid build up in the anode chamber. As shown in Fig. 2, the removal of arsenic remains constant between 2 and 3 A/dm² at low pH, further it was also noted that at 4 A/dm² and higher current densities (not shown in figures and tables) the weight of precipitate obtained also decreases with increase of current densities which may be due to deposition of heavy metals such as copper, cadmium, etc., and evolution of arsine gas in the cathode compartment. It is to be noted from Fig. 2 that maximum removal rate of arsenic is high in beginning of the process which may be due to concentration polarization initially comparatively larger concentration difference of HS^- between bulk and electrode surface exists consequently faster depletion of the arsenic in the bulk, after 2 h of electrolysis removal rate is zero. It is to be noted that maximum of only 4% of arsenic removal in the effluent is achieved by migration through the membrane to anodic compartment where as a minimum of 80% of arsenic in effluent is removed by reaction in cathodic compartment. As regard to

removal of sulphate in effluent is considered, it is primarily by migration through the membrane to anodic compartment.

At this optimized condition at 2 A/dm² the removal for arsenic and sulphate is 91.4% and 37.1%, respectively. Hence, the experiments were carried by a new technique called EIX (that is by coupling anion exchange and electro dialysis) in order to enhance the removal of sulphate in the effluent.

3.2. Electrolysytic separation process coupling with ion exchange

As the effluent enters into the middle compartment the anions, especially sulphate, arsenate, arsenite move into the anode compartment through AXM when current is passed. They also as well get adsorbed on AXR in the middle compartment and the adsorbed ions then migrate under the influence of an electric field through AXM into the anode compartment where the anions get concentrated. When the effluent is circulated into the cathode compartment, arsenic gets reduced as sulphide precipitate and to some extent as arsine gas at the cathode and further anions present gets adsorbed on AXR in the cathode compartment and the adsorbed ions then migrate under the influence of an electric field through AXM into middle compartment. And other heavy metals (Zn, Fe, Cu, Cd and Ni) are removed as their precipitates (sulphides, hydroxides) or as the metal itself depending on the conditions of electrolysis. The precipitate is filtered off in the filter press from the effluent and is recirculated into for better treatment. Thus the TDS of the effluent in the reservoir catholyte gets reduced and the pH is increased while that of acids in the reservoir of anolyte gets increased. The AXM excludes H^+ produced at the anode from entering the middle compartment that serve to balance the charge with incoming anions to produce acid. The initial H^+ ion strength of the effluent is 1.042N whereas the final H^+ ion strength is 0.4N.

The results of the experiments were carried out at various current densities between 1 and 3 A/dm² presented in Tables 4 and 5 as well in Figs. 4–6. Here again from the calculations and tabulations, it is obvious that as the current density increases, the removal of sulphate also increases. As the current density increases, the mobility and adsorption by resin of sulphate is more than that for arsenic. Hence the sulphate has been removed more than the arsenic in this resin coupling process. Fig. 6 shows a typical variation of concentration–time profile of sulphate in the effluent reservoir at the current density of 1 A/dm².

It is to be noted that maximum of 3% of arsenic removal in the effluent is achieved by migration through the membrane to

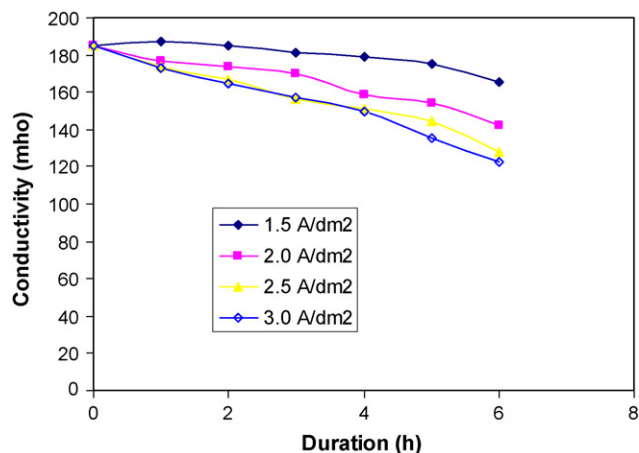


Fig. 3. Effect of current densities on conductivity profile in an electrolysytic separation process.

Table 4
Effect of current densities on pH, % removal of arsenic, power consumption and rate constant in an electrodialytic separation process in coupling with ion exchange

Current density (A/dm ²)	Cell voltage (V)	pH		Arsenic (mg/L)		Removal (%)	Power consumption (kWh/kg)	Rate coefficient (s ⁻¹ × 10 ⁻⁵)
		Acid/anolyte reservoir	Effluent/catholyte reservoir	Acid/anolyte reservoir	Effluent/catholyte reservoir			
1.0	3.40	0.93–0.80	0.53–0.66	0–19	1336.75–355.75	73.4	20.38	4.17
2.0	6.30	0.84–0.73	0.53–0.77	0–10	1321.75–691	47.7	124.99	2.22
3.0	8.05	0.94–0.83	0.66–0.91	0–29	1255.50–525	58.2	294.60	3.47

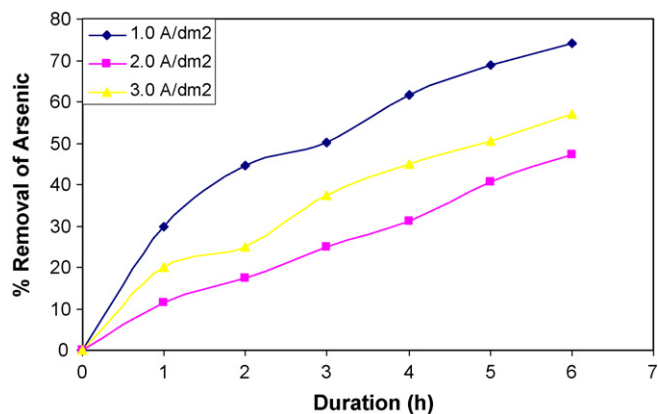


Fig. 4. Effect of current densities on concentration histories of % arsenic removal in an electrodialytic separation process in coupling with ion exchange.

anodic compartment where as a minimum of 50% of arsenic in effluent is removed by reaction in cathodic compartment. As regard to removal of sulphate in effluent is considered, it is primarily by migration through the membrane to anodic compartment, which is nearly around 76% in 6 h.

When sufficient concentration of arsenic is build up in the anolyte reservoir it can be separately treated cathodically in a reactor system as shown in Fig. 1 for which details are discussed elsewhere [25].

The results, which are presented in Fig. 4 and Table 2, show that the pH of the effluent significantly influences the power consumption. Only a few percent of total energy requirement of the electrochemical step is needed for pumping of the electrolyte around electrolyte cycle and a small fraction of the energy is necessary to maintain a sufficiently fast flow through electrodes.

The specific energy consumption or power consumption for electrolysis, E , kWh/kg is computed using the expression $[V_{\text{cell}}It/10^3]/[(C_0 - C_t)V/10^6]$ where the numerator represents the power input in kWh, V_{cell} is the cell voltage, V; I is the current applied in amperes in the circuit and t is duration of electrolysis in hours for bringing the initial concentration, C_0 , mg/L, of effluent to final concentration C_t , mg/L, in the volume of the reservoir, V liters.

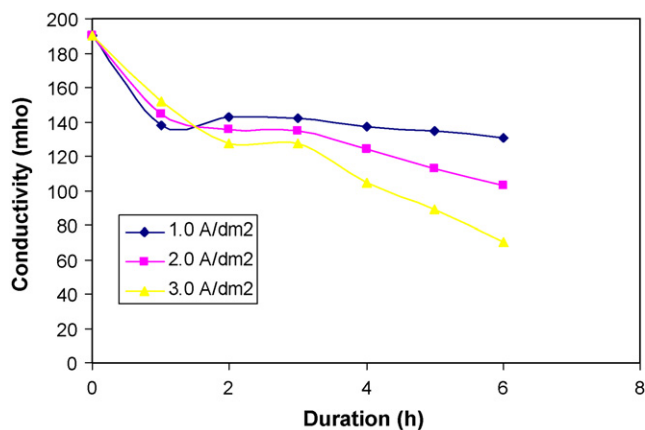


Fig. 5. Effect of current densities on conductivity profile in an electrodialytic separation process in coupling with ion exchange.

Table 5

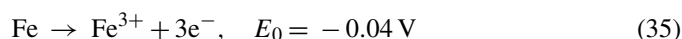
Effect of current densities on % removal of sulphate and power consumption in an electrodiolytic separation process in coupling with ion exchange

Current density (A/dm ²)	Cell voltage (V)	Sulphate (mg/L)		Removal (%)	Power consumption (kWh/kg)
		Acid/anolyte reservoir	Effluent/catholyte reservoir		
1.0	3.40	13,788–24,487	57,356–33,090	42.31	0.82
2.0	6.30	12,486–33,090	58,349–19,744	66.16	1.92
3.0	8.05	12,045–38,605	62,430–17,042	72.70	3.13

Power consumption for sulphate removal is also reasonable Tables 3–5. Because of the sulphate minimization, the conductivity also decreases (see Figs. 3–5). When sufficient concentration of arsenic is build up in the anolyte reservoir either it can be separately treated cathodically in a reactor system as shown in Fig. 1 for which details are discussed elsewhere [25] or a treatment is carried out in a separate cycle for the removal of arsenic, with the same experimental arrangement, with replacement of effluent by this acid. Along with arsenic, other hazardous metals, which was present in the effluent also gets reduced. The arsine gas, which is the most toxic form of arsenic, insignificant quantity may be generated, however can be scrubbed. The acid used in this process may be reused for the next cycle.

3.3. Electrocoagulation

In the case of the application of iron electrodes, the process generates iron hydroxides, which would coprecipitate with arsenic anions. The main electrode reactions are as shown in the following [24] where Fe is oxidized into ferric ion in a single step:



In two-step process where iron is firstly oxidized to ferrous ion which, depending on anode potential, then oxidizes to ferric ion:

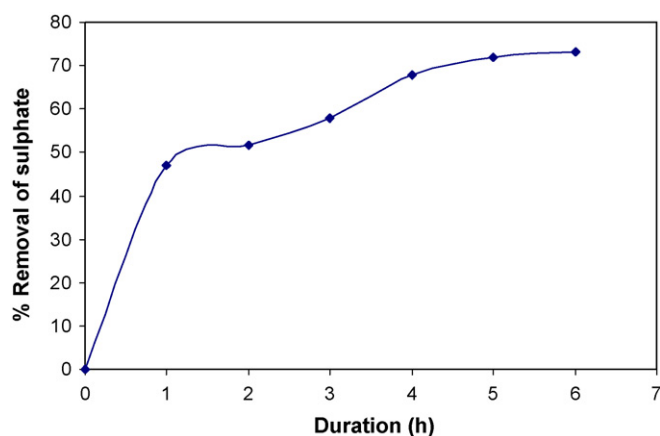
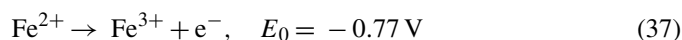
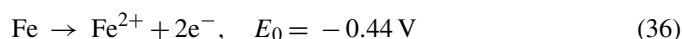
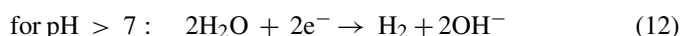
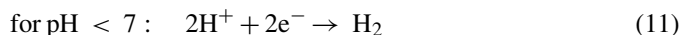


Fig. 6. Typical concentration histories of % sulphate removal in an electrodiolytic separation process in coupling with ion exchange at 1 A/dm².

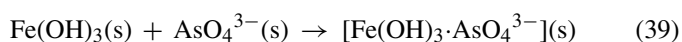
The second step would take place at the anode. The general cathode reaction takes place at the cathode and results in the liberation of hydrogen. This is represented as



Typically at the cathode the solution becomes alkaline with time. The applied current forces OH⁻ ion migration to the anode, so the pH near the anode is higher than in the bulk solution, thus favouring ferric hydroxide formation:



The oxidation states of As in water are As(III), arsenite, and As(V), arsenate. In the pH range of 4–8 the predominant species of As(V) present a net negative charge. On the other hand, the species of As(III) generally has no net charge. Based on this, it is expected that the As(V) removal efficiency would be higher than As(III), since the As(V) anions (AsO₄³⁻, HAsO₄²⁻ or H₂AsO₄⁻) are coprecipitate with or adsorbed by the Fe(OH)₃ colloids:



The arsenate anion is negatively charged at low pH values because it is the anion of a strong acid. In contrast arsenite removal by adsorption and coagulation is less effective because its main form, arsenious acid (H₃AsO₃), is a weak acid and is partially ionized at pH values where removal by adsorption on Fe(OH)₃ gel occurs most effectively at pH 4–8 (see Fig. 7). To insure that the arsenic is in the +5 oxidation state, the effluent may be treated with oxidants (H₂O₂). The arsenate

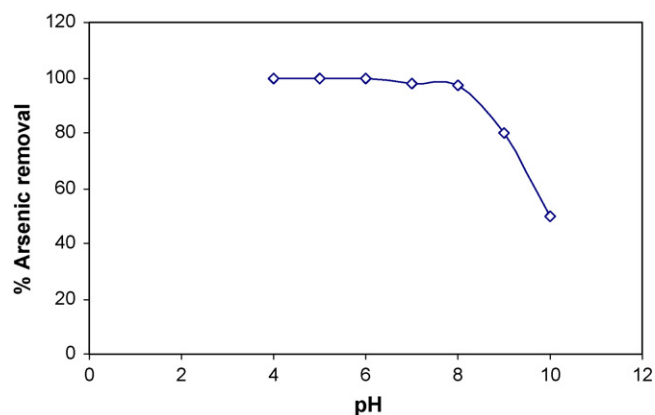


Fig. 7. Typical pH-dependent data on precipitation of ferric arsenate in EC process.

anion remains negatively charged at low pH values, and is thus effectively adsorbed and removed by ferric hydroxide gels. Since sulphate has been minimized in the EIX process, the alkali consumption required for pH raise of effective coagulation is also minimized.

4. Conclusions

In this study, an attempt has been made to remove the arsenic by ion-exchange method followed by electrocoagulation. It was a successful attempt to remove all arsenic from the effluent. Experiments were conducted at various current densities ranging between 1.0 and 3.0 A/dm² as three stages.

As first stage, experiments were carried out in a three compartment plate and frame type cell, the compartments being separated by anion-exchange membranes with stainless steel as cathode and TiO₂ and RuO₂ coated titanium electrode as anode. In this stage arsenic has been removed up to 92% but the sulphate removal is very low. Hence in the second stage, cathode and the middle compartments of the same cell is packed with anion-exchange resin. In this stage the reversal takes place. Sulphate is removed up to 73.4% but the removal of arsenic is very low. And to remove the remaining arsenic content, the effluent after getting reduced in sulphate concentration in the ion-exchange process, was treated by electro coagulation method with stainless steel as cathode and mild steel as anode (sacrificial anode). After the treatment, the treated effluent was analyzed using atomic absorption spectrometer, which showed that the arsenic has been removed below the tolerance limit along with sulphate and other heavy metals. It is also observed that since the sulphate has been minimized during ion-exchange process itself, the alkali consumption needed in electro coagulation to raise the pH for effective coagulation is minimized.

Acknowledgement

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References

- [1] M. Leist, R.J. Casey, D. Caridi, J. Hazard. Mater. B 76 (2000) 125–138.
- [2] C. Ravault, B. Fabres, M. Ledrans, Institut de veille sanitaire (2003) 108.
- [3] K.H. Morales, L. Ryan, T.L. Kuo, M.M. Wu, C.J. Chen, Water Environ. Health Perspect. 108 (7) (2000) 655–661.
- [4] World Health Organization (WHO), Guidelines for Drinking Water Quality, WHO, 1993, p. 41.
- [5] K.N. Ghimire, K. Inoue, H. Yamaguchi, K. Makino, T. Miyajima, Water Res. 37 (2003) 4945–4953.
- [6] T. Nishimura, R.G. Robins, Miner. Proc. Extr. Met. Rev. 18 (1998) 283–308.
- [7] R.G. Robins, Discussion, Am. Mineral. 72 (1987) 842–844.
- [8] R.G. Robins, in: D.R. Gaskell (Ed.), EPD Congress '90, TMS, Warrendale, PA, 1990, pp. 93–104.
- [9] H.K. Hansen, P. Nunez, R. Grandon, Miner. Eng. 19 (5) (2006) 21–524.
- [10] N. Adhoum, L. Monsier, N. Bellakhal, J.E. Belgaied, J. Hazard. Mater. B 12 (2004) 207–213.
- [11] L.G. Twidwell, J. McCloskey, P. Miranda, M. Gale, I. Gaballah, in: J.P. Hager, R. Solozabal (Eds.), Proceedings of the Rewas '99, Global Symposium on Recycling, Waste Treatment and Clean Technology, The Minerals, Metals and Materials Society, Warrendale, PA, USA, 1999, pp. 1715–1726.
- [12] A. Tor, T. Buyukerkek, Y. Cengeloglu, M. Ersoz, Desalination 171 (2004) 233–241.
- [13] A. Tor, Y. Cengeloglu, M. Ersoz, G. Arslan, Desalination 170 (2004) 151–159.
- [14] M. Greiter, S. Novalin, M. Wendland, K.D. Kulbe, J. Fischer, J. Membr. Sci. 210 (2000) 91–102.
- [15] A. Mahmoud, L. Muhr, S. Vasiluk, A. Aleynikoff, F. Lopicque, J. Appl. Electrochem. 33 (10) (2003) 875–884.
- [16] N. Meyer, W.J. Parker, P.J. Van Geel, M. Adiga, Desalination 175 (2005) 153–165.
- [17] V. Roquebert, S. Booth, R.S. Cushing, G. Crozes, E. Hansen, Desalination 131 (2000) 285–291.
- [18] A. Smara, R. Delimi, C. Poinsignon, J. Sandeaux, Sep. Purif. Technol. 44 (2005) 271–277.
- [19] O. Souilah, D.E. Akretche, M. Amara, Desalination 167 (2004) 49–55.
- [20] J. Wang, S. Wang, M. Jin, Desalination 132 (2000) 349–352.
- [21] K.H. Yeon, J.H. Song, S.H. Moon, Water Res. 38 (2004) 1911–1921.
- [22] I. Monzie, L. Muhr, F. Lopicque, G. Grévilot, Chem. Eng. Sci. 60 (2005) 1389–1399.
- [23] K. Niclson, D.W. Smith, J. Environ. Eng. Sci. 4 (2005) 65.
- [24] K.H. Henrik, N. Patricio, R. Deborah, S. Italo, G. Rodrigo, Electrochim. Acta 52 (2007) 3464–3470.
- [25] S. Raghu, C. Ahmed Basha, J. Hazard. Mater. 139 (2) (2007) 381–390.