

Heavy metal removal from copper smelting effluent using electrochemical cylindrical flow reactor

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Abstract

The purpose of this study is mainly to evaluate the performance of the continuous recirculation flow cell at low current density and pH (the pH at which the effluents are available) in removing heavy metals from copper smelting effluent by cathodic reduction. During the electrolysis at different pH, % removal of heavy metals removal, energy consumption and heterogeneous reaction rate constants were investigated at given flow rate and current density on the selected industrial effluent. The overall specific energy consumption at the pH 0.64 was observed to be lowest, which is 10.99 kWh/kg of heavy metal removal.

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1. Introduction

The global significance and human health impact of heavy metal pollution are major public concern. Industrialization, urbanization and use of fertilizers and pesticides in agriculture have resulted in increased contamination of our environment by heavy metals. The adverse effects of chemical pollutants in the environment are not limited to ourselves, but may be passed on to future generations by way of genetic mutations, birth-defects, inherited diseases and so on [1–3]. Various techniques have been employed for the treatment of heavy metals, including precipitation, adsorption [4–5], biosorption [6], ion-exchange [7–9], electrochemical [10,11], electrodialysis [12,13] and ion-exchange-assisted membrane separation [14–17]. Precipitation is most applicable among these techniques and considered to be the most economical. However, this technique produces a large amount of precipitate sludge that requires further treatment. Reverse osmosis and ion-exchange can effectively reduce metal ions, but their uses were limited due to a number of disad-

vantages such as high material and operational cost, in addition to the limited pH range for the ion-exchange resin. There has been a serious environmental challenge for the metallurgical industry, especially for copper smelters, due to pressures from public opinion and the numerous environmental regulations imposed. The typical characteristics of the effluent are shown in the Table 1. The copper smelting effluent bearing arsenic may contain varying amounts of oxyanion, arsenite, and arsenate. The presence of heavy metal ions such as Cu, Pb, Cd, Ni, and Zn limit the solubility of arsenic because of the formation of sparingly soluble metal arsenates. Due to its toxicity, it should be recovered or removed from the effluent prior to disposal. When arsenic is not recovered it should be removed from the arsenic-bearing residue and stabilized in the form of a solid compound before disposal [18].

The disposal of arsenic has been accomplished in practice by the formation of calcium arsenates and arsenites, sulphides and ferric arsenate because of their low solubility. Adding lime to the solution, obtaining a calcium arsenate compound has precipitated arsenic. However, the stability of this compound has been questioned because under the influence of atmospheric carbon dioxide, calcium arsenates decomposes to calcium carbonate and liberates arsenic oxide in the solution [19]. Because of this, it has been noted that there has not been significant and inno-

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Table 1
Characteristics of a typical effluent

Properties	Before treatment
pH	0.64
Total suspended solids (TSS)	8,760 mg/L
Total dissolved solids (TDS)	83,672 mg/L
SO ₄ ²⁻	49,136 mg/L
Arsenic	1,979 mg/L
Bismuth	85 mg/L
Cadmium	76.05 mg/L
Cobalt	0.04 mg/L
Chromium	2.3 mg/L
Copper	164.48 mg/L
Iron	88 mg/L
Nickel	12 mg/L
Lead	4.6 mg/L
Antimony	1.5 mg/L
Zinc	455.67 mg/L
pH	0.64
Total suspended solids (TSS)	8,760 mg/L
Total dissolved solids (TDS)	83,672 mg/L
SO ₄ ²⁻	49,136 mg/L

vative improvements. For a long-term stability, the formation of more stable forms has been under study, but at present the industries are adopting the ferric arsenate precipitation [20]. But in this method the problems aroused 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 we are in need to raise the pH by the addition of an alkali. Also the sulfate concentration is more in the effluent. Due this reason the alkali consumptions are more. The addition of chemicals may elevate the total dissolved solids (TDS) level and thus TDS is not reduced in the treated effluent. The treatment produces a large amount of sulfate. An electrochemical method of treatment has been investigated for the removal of arsenic (incoming contamination levels are around 2000 mg/L) and other heavy metal cations (in different range of levels of 500 mg/L) from the metallurgical effluent with the objective of this investigation is to minimize all of the above drawbacks by adopting cathodic removal of heavy metal from copper smelting effluent using electrochemical reduction [21] in a cylindrical flow reactor. In the next operation of sequence is to decide whether to follow either electrochemical reduction or electrocoagulation [22–24] for further treatment. In this paper, the effluent was collected from copper smelting industry containing heavy metals such as As, Cu, Cd and Zn as given in Table 1. An attempt has been made electrochemically to remove As, Cu, Cd and Zn as sulphides by electroreduction. During the electrolysis at different pH, % removal of heavy metals removal, energy consumption and mass transfer coefficient were investigated at given flow rate and current density on selected industrial effluent.

2. Materials and methods

All the reagents used were of AR grade. The effluent was collected from the industry. The ion-selective membrane used

was NEOSEPTA anion-exchange membrane in case of divided cell. The pH of the effluent was adjusted with the addition of 10N sodium hydroxide solution.

2.1. Electrochemical batch reactor

The batch reactor consisted of a divided PVC cell, in which the two compartments separated by anion-exchange membrane as shown in Fig. 1a. The cell was fitted with stainless steel plate as cathode in one of the compartment and titanium expanded mesh coated with TiO₂ and IrO₂ as anode in another compartment. Each compartment has a capacity of 300 mL. All experiments were carried out by taking 250 mL of effluent in the cathodic compartment and equal volume of 5000 mg/L of H₂SO₄ in the anodic compartment. Electrolysis was carried at constant current for 6 h at two different current densities 2 A/dm² and 4 A/dm². A magnetic stirrer was used to ensure uniform concentration. One millilitre sample was collected for every hour from both the compartment for analysis.

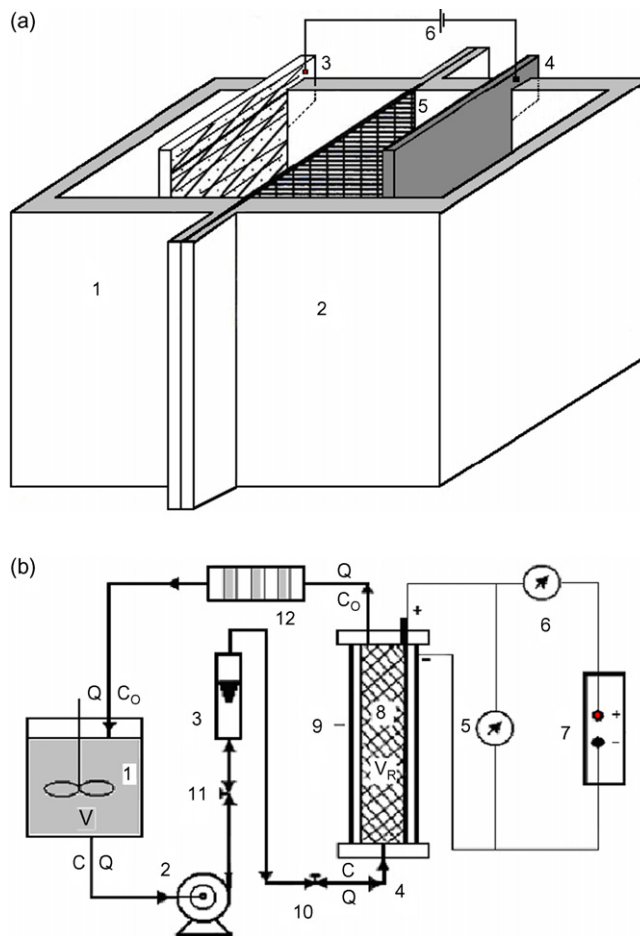


Fig. 1. (a) Experimental setup of electrochemical batch reactor: (1) anodic compartment, (2) cathodic compartment, (3) titanium expanded mesh (coated with TiO₂ and IrO₂) anode, (4) stainless steel cathode, (5) NEOSEPTA anion-exchange membrane, (6) DC regulated power supply. (b) Experimental setup of flow cell: (1) reservoir, (2) pump, (3) rotameter meter, (4) electrolytic cell, (5) voltmeter, (6) ammeter, (7) 5 A, 30 V DC regulated power supply, (8) Ti/TiO₂ IrO₂ coated expanded mesh cylinder anode, (9) stainless steel cathode, (10 and 11) valves and (12) filter press (Lab-model).

2.2. Electrolytic batch recirculation system

A schematic view of the experimental setup of this system is shown in Fig. 1b. The setup consists of a filter press, a reservoir, a magnetic driven self-priming centrifugal pump, a flow meter and the electrolytic cell connected to an electrical circuit consists of 5 A, 30 V DC regulated power supply, an ammeter and a voltmeter. The electrolytic cylindrical flow reactor consists of the cathode, which was a stainless steel pipe of 15.4 cm height and 8 cm diameter, and the catalytic anode, made of Ti/TiO₂, IrO₂ coated expanded mesh cylindrical shape, measuring 15.4 cm long and 5 cm diameter which was held axially inside the cathode such that 1.5 cm as inter-electrode distance. Provisions are made for electrical connections so as to constitute an electrolytic cell. The holdup of the cell is 750 mL where as the reservoir capacity is 2 L. Additionally, the cell had one inlet at the bottom cover and one outlet at the top cover. The area of cathode is 3.87 dm².

Electrolysis was carried out under batch continuous recirculation mode. The effluent was taken in the reservoir, which was allowed to flow from it and was recirculated through the reactor using a pump. The flow rate was measured and adjusted by rotameter. The required current was passed using regulated power supply and cell voltage was noted. The experiments were conducted at a constant current density of 0.75 A/dm² and flow rate of 20 L/h for different pH viz. 0.64, 1, 1.5, 2, 3, 5. The samples were drawn periodically from the reservoir and analyzed.

All the collected samples were diluted to appropriate volume and analyzed for As, Cu, Cd and Zn ions using atomic absorption spectrometer (AAS). Arsenic was also analyzed using Gutzeit Generator [25] and the results were verified. Sulphate ions present in the sample solution were estimated by Turbidity method using UV–vis spectrophotometer. After electrolysis the effluent was filtered and the weight of the sludge was obtained and analyzed.

3. Theoretical approach

3.1. Reaction mechanisms

The dilute effluent containing heavy metals such as copper, cadmium, zinc and arsenic, etc., and sulfate in the reactor initially gets ionized and the anions specifically sulphate, arsenate (AsO₄³⁻) and arsenite (AsO₃³⁻) due to their affinity move towards anode. That is in the anode compartment, the anions reach from the cathode compartment, reacts with H⁺ ions in the bulk of anode compartment to perform the following reactions.



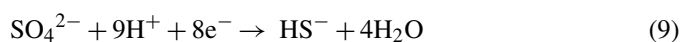
At anode as the pH is low, the following reaction takes place at the anode, which results in the liberation of oxygen equation



Along with this, at the cathode compartment, the arsenic present in the solution undergoes the following reaction and may even arsenic get reduced into arsine (AsH₃). Also the reduction of heavy metals (including arsenic(V) to arsenic(III)) may take place.



The sulphate present in the effluent will get reduced to HS⁻ at the cathode which is one of the key reactions. This reaction is represented as



At pH < 7, along with the above reactions, the general cathodic side reactions take place at the cathode and results in the liberation of hydrogen. This is represented as



The HS⁻ is produced from the above reaction reacts readily with heavy metals, arsenic(III) and arsenic(V) and will precipitates out as metal sulphides arsenic sulphide from the solution. This is given as



The OH⁻ produced from the Eq. (11) neutralizes H⁺ produced the pH of the effluent increases and further it reacts with heavy metals as per the reaction (15).



3.2. Process modeling

Depending on possible mode of operation, there is a gradual depletion of the concentration of the heavy metals and sulphate (M_n, AsO₄³⁻, AsO₃³⁻, SO₄²⁻) in the batch reactor or reservoir of batch recirculation system. In order to design and control the plant process, the development of a model is essential which permits the prediction of the variation of concentration of heavy metals (M_n: As, Cu, Cd and Zn) or sulphate with time in the reactor or reservoir of batch recirculation system. The basic assumptions involved in the ensuing derivation may be outlined as followed. Table 2 gives the relevant list of symbols used.

Back mix flow exists in the present in case of batch reactor or flow reactor. It was arrived based on residence time distribution

Table 2
List of symbols

Parameter	Symbol
Specific electrode area (A_e/V_R)	a
Membrane area (in divided cell)	A_m
Electrode area	A_e
Concentration heavy metals (including arsenic) in cathode compartment (divided cell).	C''
Concentration of anions in the cathode compartment.	C'
Concentration anions (arsenic or sulphate ion) build up in the anodic compartment	C_a
Reservoir entry concentration or reactor exit concentration	C_o
Reservoir exit concentration or reactor entry concentration	C
Faraday's constant 96,500 C/mol or As/mol	F
Current	I
Current density	i
Potential dependent electrochemical heterogeneous reactions rate constant for reduction of heavy metals and sulphate to metals/sulphides/hydroxide	k_e
Transfer coefficient	k_m
Heterogeneous reaction rate constant	k
Electrons exchanged	n, z
Specific energy consumption	E
Volumetric flow rate	Q
Coefficient of correlation	r
Time	t
Volume of the cathode compartment (divided cell)	V_c
Volume of the anode compartment (divided cell)	V_a
Reservoir volume	V
Reactor volume	V_R
Percentage of conversion ($100 \times (1 - C(t)/C(0))$)	$X(t)$
Migration overall parameter	α
Reactor residence time (V_R/Q)	τ_R
Reservoir residence time(V/Q)	τ

(RTD) tracer experiment. Hence the concentration of reactive species is same throughout the flow reactor and equal to the exit concentration. An approximate model may be described by a continuous stirred tank reactor (CSTR) in which the reactions take place. A dynamic material balances to each of component or species can be written as

$$\begin{aligned}
 &[\text{rate of change mass in the system}] \\
 &= [\text{rate of mass input}] - [\text{rate of mass output}] \\
 &\mp \sum [\text{rate of mass disappeared or generated due to} \\
 &\text{physico chemical phenomena}]
 \end{aligned}$$

3.2.1. Model for heavy metals or sulphate ions variation in divided cell

The mass balance of heavy metals (M_n , AsO_4^{3-} , AsO_3^{3-}) in the cathode compartment can be written as

$$V_c \left(\frac{dC''}{dt} \right) = -k_e A_e C'' + k_m A_m (C'' - C_a) - \alpha I A_m C'' \quad (16)$$

Left-hand side (LHS) represents the rate of change of mass of heavy metals (including arsenic) in the V_c volume of the cathode compartment, where C'' is the concentration of heavy metals/arsenic anions (M_n , AsO_4^{3-} , AsO_3^{3-}) in the cathode compartment. The next three terms of the right-hand side (RHS)

represent the rate of mass of disappearance/appearance of M_n , AsO_4^{3-} , and AsO_3^{3-} in the solution in which the first term is due to indirect reduction of heavy metals on cathode (that is the term k_e is potential dependent electrochemical reactions rate constant for heavy metals to form precipitates of sulphides or hydroxides through Eqs. (6)–(9) and (12)–(15). Second term represents for diffusion and last terms account migrations through the membranes. That is the third term is the migrational fluxes from cathode compartment to anode compartment. Migrational flux of arsenic anions through membrane is defined as $(zFD/RT)C'' \text{ grad } \Phi$, assuming Nernst–Einstein relation on the basis of local arsenic anions concentration, C'' , 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 $\alpha I C''$ in which migrational flux was assumed to vary linearly with the current, I . Therefore the migrational rate of arsenics to anode compartment is $\alpha I A_m C''$, where A_m is membrane area. The mass balance of anions in the anode compartment can be written as

$$V_a \left(\frac{dC_a}{dt} \right) = k_m A_m (C' - C_a) + \alpha I A_m C' \quad (17)$$

LHS represents rate of change of mass arsenic anions or sulphate ion in the anodic compartment, where V_a is the volume of the anode compartment, C_a is the concentration arsenic anions or sulphate ion build up in the anodic compartment whereas C' represents the concentration of arsenic anions or sulphate in the cathode compartment. First term represents for diffusion and last term accounts for migration through the membrane from cathode compartment to anode compartment.

3.2.2. Model for heavy metals or sulphate ions variation in batch recirculation reactor

One possible mode of operation is that which involves the continuous recirculation of the effluent. To this effect, there is a gradual depletion of the concentration of the heavy metals (M_n , AsO_4^{3-} , AsO_3^{3-}) in the reservoir takes place. The mode of operation is depicted in Fig. 1b. In order to design and control the plant process, the development of the model is essential which permits the prediction the variation of concentration of heavy metals (M_n : As, Cu, Cd and Zn) with time in the reservoir. The basic assumptions involved in the ensuing derivation may be outlined as followed.

Back mix flow exists in the present in case of batch recirculation reactor system. It was arrived based on RTD tracer experiment. Hence the concentration of reactive species is same throughout the reactor and equal to the exit concentration. An approximate model may be described by a CSTR in which the reactions take place. The mass balance of heavy metals or sulphate in the reactor can be written as

$$V_R \left(\frac{dC_o}{dt} \right) = QC - QC_o - [k A_e C_o] \quad (18)$$

Left hand side (LHS) represents the rate of change of heavy metals in the reactor, V_R and C_o is the concentration heavy

metals leaving the reactor. The first two terms of the RHS represents rate mass of heavy metals ions entering and leaving the reactor, Q is the volumetric flow rate and C is the concentration of heavy metals entering the reactor. The next terms of the right-hand side inside the square bracket represent the rate of mass of disappearance/appearance of heavy metals due to chemical/electrochemical reactions of heavy metals to form precipitates of sulphides or hydroxide. The mass balance for the effluent reservoir tank is

$$V \left(\frac{dC}{dt} \right) = QC_o - QC \quad (19)$$

The concentration species (bulk of the solution) varies due to the various reactions. Since there is no accumulation of heavy metals or sulphate ion in liquid phase of reactor, the concept of the pseudo-steady state theory can be assumed to apply to all the components of the reactor. Hence at steady state conditions, a mass balance for of heavy metals can be written as

$$QC - QC_o - [kA_e C_o] = 0 \quad (20)$$

We can rewrite the Eq. (20) as

$$\tau_R = \frac{V_R}{Q} = \frac{C - C_o}{kaC_o} \quad (21)$$

Or rewriting Eq. (20) as

$$\frac{C_o}{C} = \frac{1}{1 + ka\tau_R} = \frac{1}{1 + (kA_e/Q)} \quad (22)$$

The mass balance Eq. (19) can be solved after substitution of expression for C_o from the Eq. (23), knowing the initial concentration $C = C_o^o$ at $t=0$, the resultant equation can be written as

$$\frac{C}{C_o^o} = \exp \left[-\frac{t}{\tau} \frac{kA_e/Q}{1 + kA_e/Q} \right] \quad (23)$$

where C_o^o is the initial concentration of heavy metals in the reservoir.

It should be noted that the percentage of extent of conversion is defined as $X(t) = [(C_o^o - C)/C_o^o] \times 100$. According to the Eq. (23), the unconverted heavy metal, which is C/C_o^o , decreases exponentially with time. From the linearized plot of $\ln C/C_o^o$ versus t , the slope gives the value $[(kA_e/Q)/\tau(1 + kA_e/Q)]$ from which the value of k , the heterogeneous reaction rate constant can be computed.

4. Results and discussion

As stated earlier, experiments have been carried out in a batch recirculation flow reactor and as well few experiments in batch divided cell. The results are presented in Figs. 2–5 and in the Table 3 by varying operating conditions such current density in case of the divided cell and pH in a batch continuous recirculation undivided cylindrical flow cell.

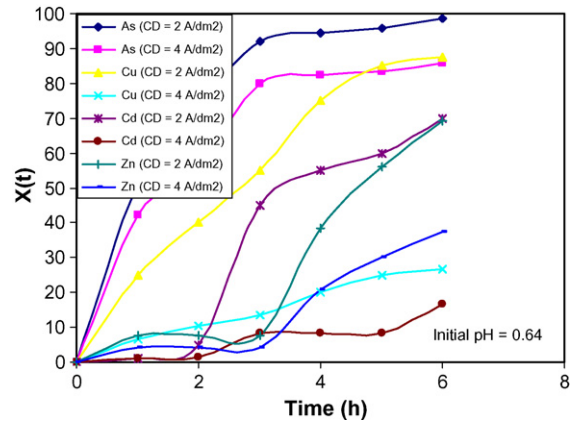


Fig. 2. Effect of simultaneous removal of As, Cu, Cd and Zn with electrolysis time in a divided cell when operated at different current density.

4.1. Performance of electrochemical divided cell for removal of heavy metals and sulphates

From Fig. 2, it was observed that the removal of arsenic was above 99.5% at lower current density. Hence its removal was mainly by migration through membrane as AsO_4^{3-} and AsO_3^{3-} to anode chamber as well as to a small extent may be by evolution of arsine gas through cathode surface. This was confirmed by analysis of sludge which contains mere CuS which was black in colour. In general arsenic sulphides precipitation will takes place only at around pH of 2–3. The pH of effluent was very low and the build up of sulphate in the anode compartment was from the initial value of 5030 to 31,545 mg/L at 2 A/dm² where as the sulphate concentration of increases to 53,716 mg/L at 4 A/dm². On the other hand the weight of precipitate obtained in the cathode compartment also decreases with increase of current density this may due to deposition of heavy metals such as copper, cadmium, etc. It was also further observed that the pores of the membrane would have been closed due to the adherence of precipitates of hydroxides and sulphides on membrane. One more information is to be noted from Fig. 2 that only after maximum removal of arsenic after 2 h of electrolysis other heavy metal reduces pH.

4.2. Performance of electrochemical flow cell for removal of heavy metals

The study is primarily conducted to evaluate the performance of the continuous recirculation flow cell at low current density and at low pH (the pH at which the effluent is available) to adopt cathodic removal of the heavy metals so that the next operation of sequence is to decide whether to follow either the same electroreduction with different conditions of operation or electrocoagulation for the arsenic that can separately be stabilized by electrocoagulation as ferric arsenate ($FeAsO_4$) such that the reduction of addition of alkali may be considerably reduced TDS in the treated effluent.

While the effluent is circulated through the reactor the colour of the effluent visibly turned to black colour as the effluent comes out of the reactor. It is due to the fact that the arsenate, arsenite, sulphate and other heavy metals electrochemically reduced at the

Table 3
Results obtained during the electrolysis in (i) batch recirculation cell and (ii) batch divided cell in heavy metal removal (HMR)

Mode of operation	Batch recirculation reactor					Batch reactor divided cell	
	$i = 0.75 \text{ A/dm}^2$					$i = 2.0 \text{ A/dm}^2$	$i = 4.0 \text{ A/dm}^2$
	0.64–0.88 ^a 2.24 V ^b	1.5–2.96 ^a 2.51 V ^b	2–3.25 ^a 2.83 V ^b	3–4.13 ^a 2.82 V ^b	5–6.25 ^a 3.29 V ^b	4.13 V ^b	0.64–0.88 ^a 8.18 V ^b
[As] _o (mg/L)	1979	1789	1968	1789	1979	1979	1979
[As] _f (mg/L)	103	744	414	275	671	26.91	279.43
<i>E</i> (kWh/kg As)	13.85	27.86	21.12	21.61	29.18	25.39	115.51
$k \times 10^4$ (cm/s)	6.17	1.85	3.08	3.83	2.21	0.197	0.106
Correlation coefficient (<i>r</i>)	−0.9400	−0.9681	−0.9914	−0.9891	−0.9350	−0.990	−0.950
[Cu ⁺⁺] _o (mg/L)	164.48	166.24	161.76	148.89	113.26	164.48	164.48
[Cu ⁺⁺] _f (mg/L)	1.96	16.51	5.27	3.91	3.91	20.56	120.62
<i>E</i> (kWh/kg Cu)	159.88	194.46	209.78	225.63	349.01	344.36	4,476.06
$k \times 10^4$ (cm/s)	10.14	5.98	6.83	6.93	5.27	0.095	0.015
Correlation coefficient (<i>r</i>)	−0.9396	−0.9237	−0.9838	−0.9886	−0.9506	−0.988	−0.993
[Cd ⁺⁺] _o (mg/L)	76.05	76.55	74.19	71.24	66.99	76.05	76.05
[Cd ⁺⁺] _f (mg/L)	39.33	32.67	29.32	18.62	54	22.81	63.38
<i>E</i> (kWh/kg Cd)	707.63	663.54	731.63	621.67	2937.95	930.88	15,494.9
$k \times 10^4$ (cm/s)	1.26	1.67	1.78	2.75	0.379	0.052	0.066
Correlation coefficient (<i>r</i>)	−0.986	−0.9416	−0.9891	−0.9756	−0.9975	−0.9659	−0.9251
[Zn ⁺⁺] _o (mg/L)	455.67	578.79	591.52	538.62	621.53	455.67	455.67
[Zn ⁺⁺] _f (mg/L)	166.04	220.46	360.94	273.88	147.48	140.20	284.79
<i>E</i> (kWh/kg Zn)	89.71	81.25	142.37	123.56	80.51	157.099	1,148.88
$k \times 10^4$ (cm/s)	1.48	1.93	1.06	1.55	3.11	0.042	0.018
Correlation coefficient (<i>r</i>)	−0.9225	−0.8239	−0.8153	−0.8706	−0.8597	−0.9142	−0.927
Sludge weight (g)	–	–	–	–	–	0.938	0.593
% Removal of sulphate	–	–	–	–	–	47.5	95.64
<i>E</i> _o (kWh/kg HMR)	10.99	18.23	16.53	16.55	20.04	20.11	101.88

*E*_o, overall specific energy consumption, kWh/kg of total heavy metal removal.

^a pH value.

^b Cell voltage.

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. 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 gets reduced and simultaneously the pH is increased.

Fig. 3a shows the experimental results of arsenic removal in the cylindrical reactor when the pH is varied. At pH 0.64 the removal rate was very fast during initial half-an-hour of electrolysis. But in general the removal rate of arsenic was constant up to one hour of electrolysis in all pH values and varies afterwards. As the set pH value changes, the profile of percentage of arsenic removal vs. time for each pH changes which was not in regular order of pH. This may due to liberation of arsine gas. That is 94.8% at pH 0.64, 84.6% at pH 3 and less than 80% at all other pH values.

Fig. 3b shows the kinetics of the experimental results of copper removal in the cylindrical reactor when the pH is varied. At pH 0.64, 1.5 and 2 the removal rate was very fast during initial 1 h of electrolysis and afterwards the rate of removal of Cu is practically zero. But in general at higher pH removal rate is constant may be following zero order kinetics. The percentage of removal of copper follows somewhat regular order. At lower pH behaviour due to is precipitation. That is 98.81% at pH 0.64, 97.37% at pH 3 and around 96% at all other pH values.

Fig. 3c represents the experimental results of cadmium removal in the cylindrical reactor when the pH is varied. At pH 0.64 the Cd removal was practically zero in first 1 h, next 4 h the concentration is linear and next 3 h also linear but the rate is slower. At pH 2 and 3 curve looks to be first order where as at pH 5 trends is linear since it may follows zero order precipitation kinetics. The percentage of removal of cadmium follows somewhat irregular order due to mixed kinetics. At lower pH, the behaviour is due to precipitation and metal deposition. That is 48.3% at pH 0.64, 73.8% at pH 3 and 19.4% at pH 5.

Fig. 3d represents the experimental results of zinc removal in the cylindrical reactor when the pH is varied. At pH 0.64 the zinc removal was may be due to zinc metal deposition which amounts to 63.6% where as at pH 5 the zinc removal may be entirely due to precipitation of zinc which amounts to 76.3%. The zinc and cadmium follow more or less similar behaviour.

4.3. Power consumption

The results, which are presented in the Fig. 4 and Table 3, 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 (or stirring in case of divided cell) of the electrolyte around electrolyte cycle and a small fraction of the energy is necessary to maintain a sufficiently fast flow through electrodes.

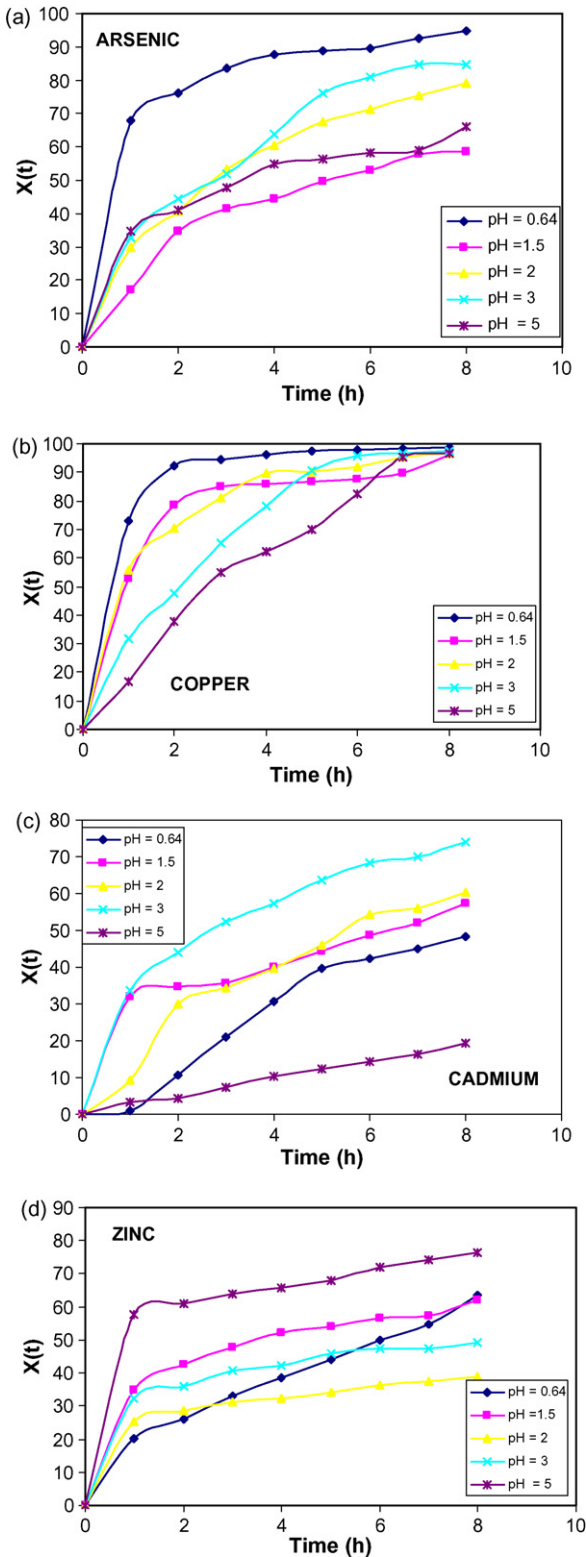


Fig. 3. Comparison of the % removal of As, Cu, Cd and Zn with electrolysis time in a batch recirculation setup at different pH. (a) pH 0.64, (b) pH 1.5, (c) pH 2.0, (d) pH 3.0 and (e) pH 5.0.

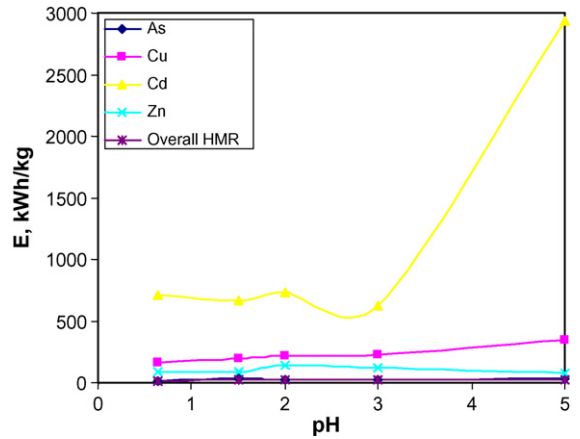


Fig. 4. Effect of pH on specific energy consumption in heavy metals removal (HMR).

The specific energy consumption for electrolysis, E (kWh/kg), is computed using the following expression

$$E = \frac{V_{\text{cell}}It/10^3}{(C_o - C_t)V/10^3} \quad (24)$$

where the numerator represents the power input in kWh, V_{cell} is the cell voltage in volts, I is the current applied in amperes in the circuit and t is duration of electrolysis in hours for bringing the initial concentration, C_o (mg/L), of effluent to final concentration, C_t (mg/L), in the volume of the reservoir, V (liters).

At the pH 0.64 with the flow rate of 20 L/h, it was observed that the power consumption was 13.85 kWh/kg of arsenic removal (from 1979 mg/L to 103 mg/L) and if the computation was done based on Cd removal, the power consumption observed was 707.6 kWh/kg Cd removal (from 76.05 mg/L to 39.33 mg/L) which found to be the highest value. However the overall specific energy consumption at the pH 0.64 with the flow rate of 20 L/h it was observed to be lowest which is 10.99 kWh/kg of heavy metal removal (i.e. As from 1979 to 103 mg/L, Cu from 164.48 to 1.96 mg/L, Cd from 76.05 to 39.33 mg/L and Zn from 455.67 to 166.04 mg/L) and overall specific energy consumption also increases as pH increases. Further it was also noticed that at the same flow rate the power consumption per kilogram of arsenic removal increases as the pH increases up to 5 except for the pH 1.5.

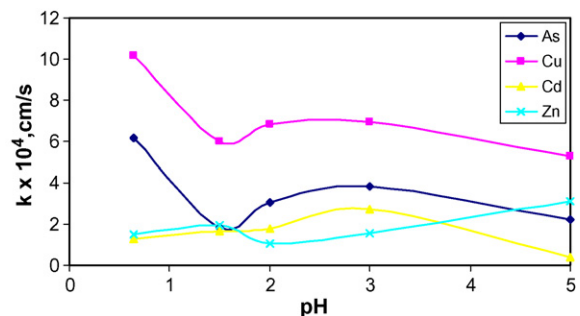


Fig. 5. Effect of pH on transfer rate coefficient in heavy metals removal (HMR).

4.4. Heterogeneous reaction rate constant

It should be noted that the percentage of HMR or percentage of conversion is defined as $X(t) = 100[C_0^o - C(t)]/C_0^o$. According to the Eq. (23), C/C_0^o decreases exponentially with time. From the linearized plot of $\ln C/C_0^o$ versus t , the slope gives the value $[(kA_e/Q)/\tau(1 + kA_e/Q)]$ from which the value of k , the heterogeneous reaction rate constant was computed.

The results obtained are presented in Fig. 5 and Table 3 with correlation r in respect of removal heavy metals by electrolytic reduction. The increase in pH rate of effluent into the reactor significantly decreased the value of the reaction rate constant (except in case of zinc ion removal) for the heavy metal studied and this resulted in lower extent of fractional conversions. The increase in initial value of pH of effluent into the reactor significantly decreases the value of reaction rate constant for removal of the heavy metal and this intern resulted in lower extent of fractional conversions. It is to be noted that reaction rate constant, as regards to As and Cu ions, varies in like manner in entire range of pH where as Cd ion also follow the same trends only in the range of the pH 2–5 and as far as the removal of zinc ion considered the reaction rate constant increases in the range of pH 2–5.

5. Conclusions

This study evaluates the performance of the continuous recirculation flow cell at low current density and pH (the pH at which the effluents are available) for removing heavy metals by cathodic reduction. During the electrolysis at different pH, % removal of heavy metals removal, energy consumption and mass transfer coefficient were investigated at given flow rate and current density on the selected industrial effluent. The maximum % removal of arsenic was 94.8% (power consumption was 13.85 kWh/kg As) and of copper was 98.81% at pH of 0.64 (power consumption was 159.88 kWh/kg Cu) where as percentage of removal of Cd^{++} (power consumption was 621.67 kWh/kg Cd) was 73.8% at pH 3 and Zn^{++} 76.3% (power consumption was 80.51 kWh/kg Zn) were at pH 5, respectively. However the overall specific energy consumption at the pH 0.64 it was observed to be lowest which is 10.99 kWh/kg of heavy metal removal (i.e. As from 1979 to 103 mg/L, Cu from 164.48 to 1.96 mg/L, Cd from 76.05 to 39.33 mg/L and Zn from 455.67 to 166.04 mg/L).

Thus, it can be concluded that electrolytic reduction of heavy metals in a flow cell can be effectively applied for the removal of heavy metals containing sulphate effluent at low pH either by prolonging the time of electrolysis or by performing next sequencing of electrolysis at appropriate operating conditions.

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