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Arsenic Removal from Contaminated Water by Various Physicochemical Processes

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***Abstract*—Efficiency of ion exchange, electro membrane, and electrochemical ion-exchange (EIX) processes on arsenic removal were evaluated in laboratory. Batch studies were performed with chloride (IRA410) as well as hydroxyl (modified IRA410) exchangeable forms of anion exchange resins (AER), whereas, column study was done with only hydroxyl exchangeable AER to evaluate its performance on arsenic removal. A plate and frame type electrolytic cell with ruthenium dioxide coated titanium plates (RuO_2/Ti) as anode, and stainless steel plates as cathode, was fabricated to do experiment to evaluate the performance on arsenic removal by electro membrane as well as EIX processes. Though, As(V) removal was significant during batch kinetic study, As(III) removal was poor by both the AER. Breakthrough curves were developed by passing As(V) contaminated water at a flow rate of 5 ml/min through 3 different bed depths of 5 cm, 7.5 cm, and 10 cm of modified IRA410 columns having 1 cm internal diameter. The columns could efficiently remove from 500 µg/l of As(V) contaminated water to below 10 µg/l. In electro membrane process, effects of electrolyte concentration, effects of applied voltage, and initial concentration of As(V) were evaluated. EIX process was found to be inefficient in removing As(V) from contaminated water.**

***Index Terms*—Arsenic, ion-exchange, EIX, BDST.**

I. INTRODUCTION

In nature, arsenic appears in ground water mainly as arsenite [As (III)] and arsenate [As(V)]. An acceptable norm in many countries, including India, for arsenic (expressed as total arsenic) in drinking water is 10 µg/L [1]. Various technologies practiced for arsenic removal from ground water based on various principles are namely, chemical coagulation and precipitation [2]; oxidation [3]; biological process [4]; electrocoagulation [5]; adsorption on various materials such as alumina [6], Fe or Mn oxi-hydroxides [7] or zerovalent iron corrosion products [8] etc.; reverse osmosis [9]; membrane filtration/ nanofiltration [10]; and ion exchange [11]. Most importantly, none of these technologies has been universally accepted in terms of both cost effectiveness as well as efficiency in removal of arsenic below permissible limit. Coagulation/precipitation with various chemical salts is usually encumbered by problems associated with the treatment and disposal of the resulting waste sludge. Bioconversion and photochemical oxidation of As(III) need another units to remove As(V). Adsorption process remains ineffective in low concentration and needs pre oxidation of As(III) to As(V) for effective removal. Furthermore, frequent regeneration of adsorbent and disposal of spent adsorbent are the other disadvantages with adsorption process. Disposal of arsenic containing sludge produced in electrocoagulation process generates a new problem. In addition, it requires air injection, high voltage (40 V) and high current (4A) for effective performance of electrocoagulation process [12]. Reverse osmosis, membrane filtration and ion exchange processes have high arsenic removal efficiency that can lower down arsenic concentration in treated water as low as 2-5 µg/L [13]. In electrochemical ion exchange (EIX) process an electric potential in place of chemical reagents is used to elute ion exchange media [14]. In this paper, comparisons on the efficiency of ion exchange, electro membrane and EIX methods on arsenic removal have been made.

II. MATERIALS AND METHODS

All the chemicals used were either of analytical reagent (AR) grade or laboratory reagent (LR) grades. Sodium arsenite ($NaAsO_2$) and sodium arsenate ($Na_2HAsO_47H_2O$) salts of 98.5% purity were procured from Loba Chemie (India) and used to prepare synthetic As(III) and As(V) contaminated water, respectively. Anion exchange resin (AER) IRA410 was procured from CDH, India. IRA410 was treated with 1M NaOH solution to replace chloride form of the resin to hydroxyl form [15]. IRA410 and modified IRA410 (i.e., hydroxyl exchangeable form of IRA410) were used in this project for different experiments (Table I). Anion permeable membrane (APM) (Table II) was procured from Membrane International Inc., USA. Unless otherwise specified, standard techniques as described in Standard method [16] was followed throughout the experiment. Arsenic concentration in water sample was measured using.

TABLE I: CHARACTERISTICS OF ANION EXCHANGE RESIN IRA-410

Parameter	**Characteristics**
Name	IRA410
Type	Strongly basic anion exchanger resin
Particle size	20-50 mesh
Ionic form	Cl^-
Ion exchange capacity	3.0-3.5 meq/g
pH range	0-14
Moisture	38%

Atomic Absorption Spectrophotometer (AAS) (Varian, equipped with vapor generation assembly (VGA), at 193.7

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nm wavelength and 0.5 mm slit width in oxyacetylene flame. An acrylic glass tube of 1 cm internal diameter and 25 cm long was used as ion exchange column. Distilled water spiked with arsenic was passed through a bed of AER in the column, at controlled rate with the help of a peristaltic pump (Model: pp10, Miclins India). The experiments were carried out at laboratory room temperature.

TABLE II: PROPERTIES OF ANION PERMEABLE MEMBRANE (APM), AMI-7001S

Technical Specification of AMI-7001S	
Parameter	**Specification/type**
Functionality	Strong Base AEM
Polymer Structure	Gel polystyrene cross linked with divinylbenzene
Functional Group	Quaternary Ammonium
Ionic Form as Shipped	Chloride
Electrical Resistance (Ohm.cm2) 0.5 mol/L NaCl	<40
Permselectivity (%) 0.1 mol KCl/kg / 0.5 mol KCl/kg	90
Total Exchange Capacity (meq/g)	1.0 ±0.1
Water Permeability (ml/hr/ft2) @5psi	<10
Thermal Stability (C °)	90
Chemical Stability Range (pH)	1-10

A plate and frame type cell, as described by [17], was fabricated with acrylic sheet of thickness 10 mm. Stainless steel plate with size of 5 cm × 2.5 cm with 1 mm thick was used as cathode and ruthenium dioxide coated on titanium (RuO_2/Ti) of the same dimension was used as anode (Titanium Tantalum Product Ltd., Chennai, India). The geometric dimensions of cathode and anode compartments were 3 cm × 3 cm × 6 cm and middle compartment was 2 cm × 3 cm × 6 cm (Fig. 1). The middle compartment thus formed in between the anode and cathode compartments, was separated with APMs (AMI7001). The treated water (effluents) from the middle chamber was collected into the same reservoir and re-circulated for a specified period of time or desired degree of treatment was achieved. Similarly, anolyte and catholyte solutions were introduced and re-circulated at controlled flow rates. A direct current (DC) power supply was used as the source of constant applied voltage for the experiments. The electrodes were connected to the DC power source through platinum weir. Schematic diagram of the experimental set up of the cell is shown in Fig. 2.

Kinetic study was performed at 180 rpm, 28 ± 2^0C, in a series of 250 ml conical flasks containing 0.2 g of modified IRA-410 (i.e., OH^- exchangeable form) in 100 ml of 500 ppb As(V) solutions. A sample containing no resin was also run as a "Blank". Equilibrium study was performed for As(V) removal from 100 ml of 500 µg/1 of As(V) by either IRA410 or modified IRA-410 through bottle point isotherm technique as suggested by [18]. Column studies were conducted in a glass column of 1 cm internal diameter using modified IRA 410 resin at three different depths of 5 cm, 7.5 cm, and 10 cm. The columns were charged with 500 ppb As(V) spiked distilled water and were operated in the up-flow mode with a volumetric flow rate of 5 ml/min, thus the empty bed contact time (EBCT) were 0.8, 1.2, and 1.6 min, respectively.

As described in a previous section, the electro membrane cell used in this experiment consists of 3 compartments, where middle compartment was separated from anode and cathode compartments using APMs (Fig. 2). Effects of electrolyte solution concentrations, applied voltages, and initial arsenic concentrations on performance of the cell were evaluated in batch re-circulation mode of operation. Two liters of catholyte, anolyte, and arsenic contaminated water were taken in three reservoirs to feed into respective chambers and re-circulated at the rates of 9.0 ml/min through middle chamber and 13.5 ml/min through cathode and anode chambers. Thus the HRT in all the chambers of the cell was maintained at 4 min. Evaluations of effects of electrolyte concentrations were performed with 0.01 M, 0.1 M, and 0.2M NaCl solutions; applied voltages were performed at 5V, 7.5V, and 10V; and initial concentrations of arsenic were performed at 100, 500, 1000 and 5000 µg/l in distilled waters. While performing experiments to evaluate the performance of one operating parameter, the other parameters were kept constant or varied. The details of related experiments performed are given in Table III.

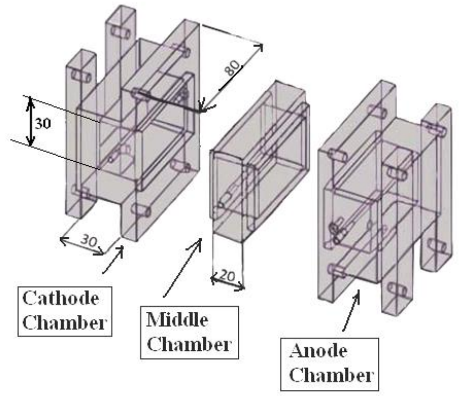

Fig. 1. Three separate chambers of electro membrane cell. (All dimensions are in mm. Dimension of cathode chamber is same to that of anode chamber. Wall thickness = 10 mm).

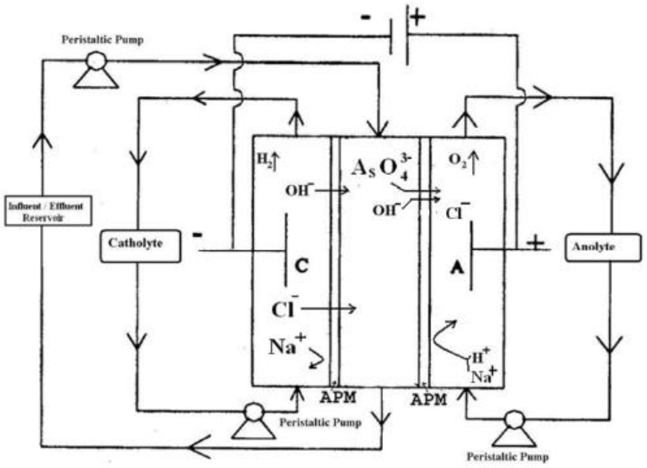

Fig. 2. Schematic diagram of the electro membrane cell. APM = Anion permeable membrane; AER = Anion exchange resin; A = Anode; C = Cathode; M = Middle Chamber.

TABLE III: LIST OF EXPERIMENTS DONE TO EVALUATE THE EFFECTS OF PARAMETERS IN ELECTRO MEMBRANE PROCESS

To evaluate the effects of	Variables	Other conditions
Electrolyte	0.01 M, 0.1 M, 0.2M NaCl	As(V) = 500 µg/l; 5V
Voltages	5V, 7.5V, and 10V	As(V),500 µg/l; 0.1M NaCl
Initial arsenic	100, 500, 1000 and 5000 µg/l	5V; 0.01M, 0.1M and 0.2M of NaCl

Performance of EIX process on arsenic removal was performed in the electrochemical cell by addition of modified IRA410 in middle chamber in re-circulating mode of operations. The experiments performed in the EIX cells are given in Table III.

III. RESULTS AND DISCUSSIONS

A. Batch Kinetic Study on Arsenic Removal by Ion Exchange Resin

Kinetic study on As (III), and As (V) removal by IRA410 (Cl^- exchangeable form) and modified IRA410 (OH- exchangeable form) of AER. About 94% of As(V) removal by modified IRA410 was noticed within first 60 minutes of reaction, whereas, the maximum removal was 97% after 270 minutes of reaction (Fig. 3). Performance of IRA410 was noticed to be inferior as only 81% removal took place after 60 minutes. Therefore, 60 min was considered as the equilibrium time for further studies. Although, As(V) removal was good, As(III) removal was less than 21% by either of the resins even after 270 minutes of reaction.

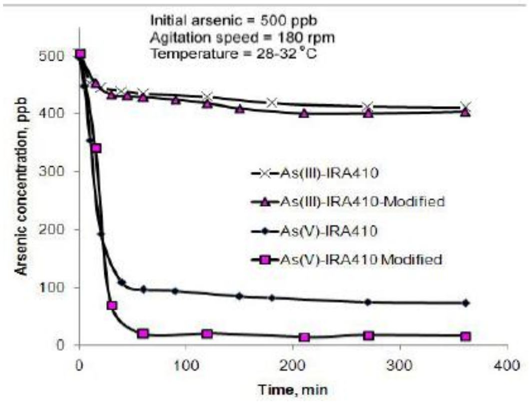

Fig. 3. Batch kinetic study of As(III), and As(V) removal by modified anion exchange resin (IRA410).

B. Equilibrium Isotherms Studies

On the basis of kinetic study, equilibrium isotherm studies (equilibrium time = 60 min) were performed with both the resins on As(V) (initial = 500 µg/l) removal. The equilibrium data fitted well to both the Langmuir (Fig. 4), and Freundlich (Fig. 5) isotherms. Maximum capacity (q_m) of the resins IRA410 and modified IRA410 estimated from Langmuir isotherm were 28.57 and 30.3 mgg^{-1} respectively.

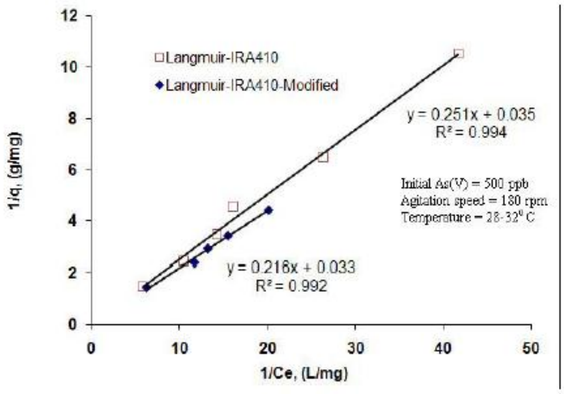

Fig. 4. Langmuir isotherm plot on Arsenic removal by ion exchange resins.

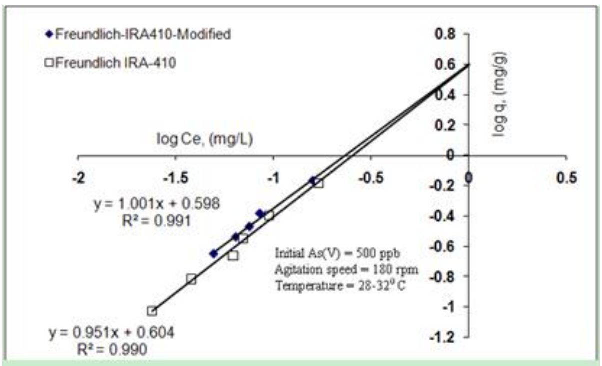

Fig. 5. Freundlich isotherm plot on As(V) removal by IER.

C. Column Study

Column study was performed with modified IRA410. The breakthrough curves generated for different bed depths are shown in Fig. 6. The points where the effluent solute concentrations reached more than 95% of their maximum (i.e. initial) concentration of 500 µg/l was considered as point of exhaustion. The columns reached to the point of exhaustion (effluent As(V) ~ 475 µg/l) after an operating period of 420, 528, and 612 hours for the columns having ion-exchange resin depths 5, 7.5 and 10 cm, respectively. The capacities of the resin with reference to the exhaust point, calculated from the breakthrough curve were 14.10, 14.73, and 14.85 mg/g of resin, respectively. Throughput volumes and service time at break point (effluent As(V) = 10 µg/l) were 43.2, 72, 97.2 l and 144, 240, 324 h, respectively, for the respective columns with bed depths 5, 7.5 and 10 cm. It was observed that service time linearly varied with bed depth (R^2 =0.998) and the constants *a* =36, and *b* =34, where '*a*' is slope and '*b*' is the intercept of the BDST curve (inset of Fig. 6).

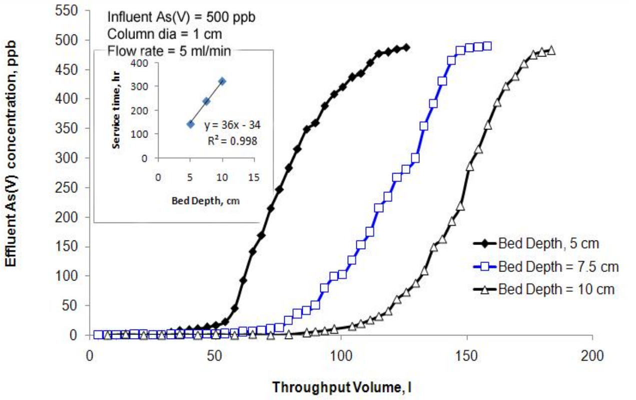

Fig. 6. The breakthrough curves of As(V) removal by IRA 410 Resin packed columns of different bed depths (initial As(V) = 0.5 mg/l, flow rate = 5 ml/min).

D. Electro Membrane Process of Arsenic Removal

Efficiency of electro membrane process is largely influenced by the electrolyte concentration, applied voltage, and initial concentration of the pollutant. Experiments performed to evaluate the performance of electro membrane process are summarized in Table III.

1) Effect of electrolyte solution concentration

In electro membrane process, the electrical circuit must be complete before any electrochemical migration to take place. For this to happen it is important to select a suitable electrolyte solution as catholyte and anolyte. Solutions of sodium chloride (NaCl) of 0.01, 0.1 and 0.2 M were used as electrolyte in cathode chamber (catholyte) and anode chamber (anolyte) to evaluate the performance of the electrochemical cell on removal of arsenic from the middle chamber, which was fed with 500 µg/l of As (V) water in 0.1M NaCl solution. The experiment was carried out at an applied voltage of 5V. pH was measured and samples were taken from all the three reservoirs at regular intervals of time to analyze for arsenic concentration. The results are shown in Fig. 7. Reduction in arsenic concentration in the middle chamber when 0.01, 0.1 and 0.2 M of NaCl was used as electrolytes were 3.2 % , 13.9% and 14.7% respectively, suggesting better removal at higher NaCl containing electrolyte. However, enhancement in arsenic removal (13.9% to 14.7%) in last two cases was only marginal. There was no arsenic found in the catholyte suggesting that there was no leakage between middle chamber and cathode chamber. Hence, its removal was mainly by migration through membrane as AsO_4^{3-} to anode.

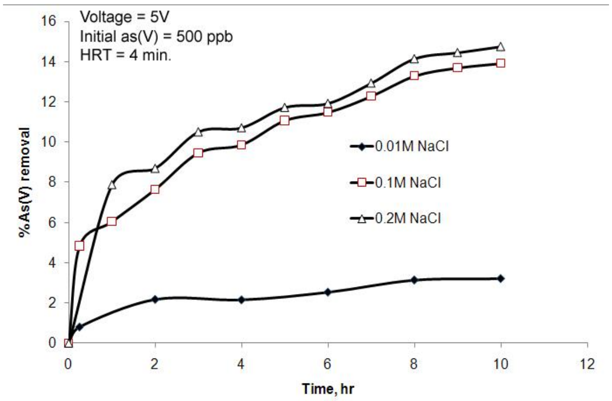

Fig. 7. Arsenic removal efficiency of electromembrane process at different electrolyte concentrations.

2) *Effect of applied voltage*

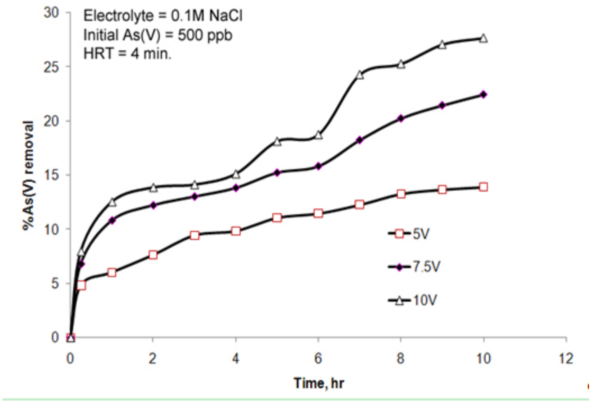

Fig. 8. Effects of applied voltage on As(V) removal in electromembrane process.

As in electro membrane process, voltage is the driving force, it is important to evaluate the performance of EIX cell on arsenic removal, through migration from middle chamber to anode chamber, under different applied voltages. The EIX cell was operated at different applied voltages of 5 V, 7.5V, and 10V to evaluate its performance on As(V) removal. Here, 0.1 M NaCl solution was used as electrolyte solution. With the increase in applied voltage, arsenic removal rate was increased. The removal efficiency (Fig. 8) was 13.9%, 22.5%, and 27.7% after 10 h at applied voltages of 5, 7.5, and 10 V, respectively. It was clear that arsenic anion migration was accelerated by increasing voltage as shown in figure 8.

3) *Effect of initial concentration of As(V)*

Electro membrane process efficiency on arsenic removal is greatly depends upon the concentration gradient between two adjacent chambers viz, anode chamber and middle chamber. To know the effects of initial concentration of arsenic on the efficiency of the cell, experiment was carried out by feeding the middle chamber with 0.1N NCl water spiked with different arsenic concentrations of 100, 500, 1000, and 5000 µg/l. Here, the cell was operated at 5V using 0.1M NaCl solution as electrolyte. The removal efficiency of arsenic from middle chamber was found to be the minimum of 4.18% and maximum of 31.3% when the reactor was subjected to 100 and 5000 µg/l of As(V) respectively (Fig. 9a and Fig. 9b).

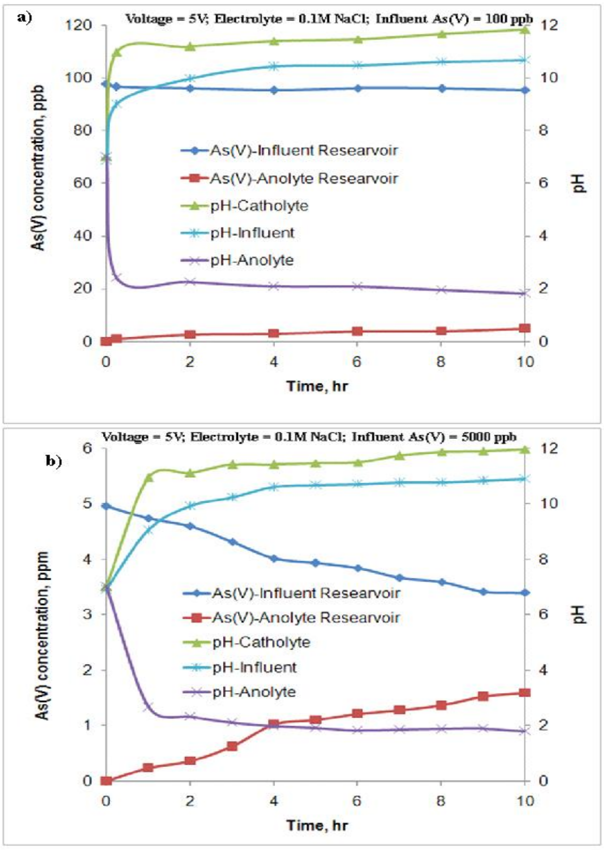

Fig. 9. Effects of initial As(V) concentration on electromembrane process.

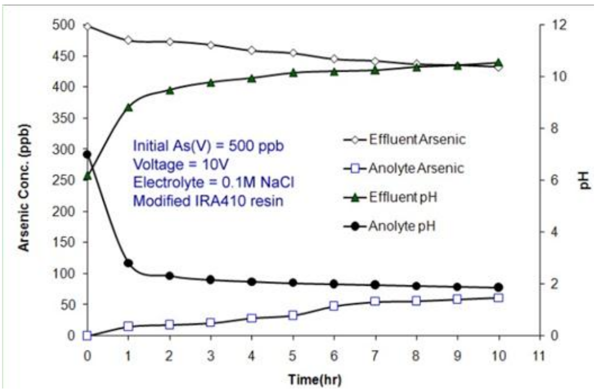

Fig. 10. Performance of EIX process on As(V) removal.

E. Electrochemical Ion Exchange (EIX) Process on Arsenic Removal

To evaluate the performance of electrochemical ion exchange (EIX) process on arsenic removal efficiency an experiment was conducted with 5.00 g resin filled in middle chamber and 500 ppb As(V) solution was re-circulated through the same. The anolyte and catholyte were also recirculated through anode and cathode chambers respectively. The experiment was performed at 10V with 0.1N of NaCl as electrolytic solution. Arsenic removal was only 13.3% at the above experimental conditions (Fig. 10).

F. Change in pH during Electromembrane and EIX Processes

Initial pH of electrolyte solutions as well as arsenic contaminated water was near neutral in all the reservoirs. However, with time the pH of the contents in the three reservoirs were changed due to chemical reactions in cathode as well as anode surfaces. pH of the anolyte was decreased whereas catholyte was increased might be due to oxidation and reduction of water in anode and cathode surfaces respectively.

$$2H_2O_{(aq)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$$
(Oxidation of water at anode surface)

$$2H_2O_{(aq)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$$
(Reduction of water at cathode surface)

Being separated by APM, hydroxyl ions formed in the cathode chamber might have passed it to reach to the middle chamber under the driving force of electric voltage, to increase the pH of water in the middle chamber. Though, hydrogen ions were formed in the anode chamber, those could not reach to the middle chamber due to its separation by APM.

IV. CONCLUSION

Anion exchange resins (IRA410 and modified IRA410) were found inefficient on As(III) removal. Hydroxide exchangeable forms (modified IRA410) was found to be better than chloride exchangeable form (IRA410) of AER on arsenic removal from contaminated water. Maximum capacity (q_m) calculated from Langmuir isotherm was 32.3 mg of As(V)/g of modified resin. Modified IRA410 column of 5 cm, 7.5 cm, and 10 cm with 1cm diameter could effectively reduce from 43L, 72L, and 97L of 500 µg/l of As(V) contaminated water, respectively, to below 10 µg/l when charged at a flow rate of 5 ml/min. percentage As(V) removal efficiency was increased with the increase in NaCl concentration in electrolytes, applied voltage, and initial As(V) concentration in electromembrane process. Under various operating conditions tried, best removal efficiency was 31.3% from 5 mg/l of initial arsenic concentration by electromembrane process performed at an applied voltage of 5V and 0.1M NaCl was used as electrolyte. Thus performance wise ion exchange process was found to be the best followed by electromembrane processes. EIX process was found to be inefficient where only 13.3% arsenic was removed after 10 hrs of experiment at 10V.

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