



CONFERENCE PAPER

Detection of effective parameters in arsenic removal with capacitive deionization process and arsenic removal from wastewater

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ABSTRACT

Access to water is a problem the magnitude of which increases day by day. In addition to water scarcity, water contamination also plays an important part in the exacerbation of this problem. Underground and surface waters can be polluted as a result of human activities as well as natural sources. One of the most commonly found natural pollutants is arsenic. Risks and effects of arsenic on health make it necessary to be treated from water. Conventional methods of arsenic removal make it necessary for new studies to be conducted because of problems such economical and special equipment needs. The MCDI process stands out with its advantages such as being economic, flexibly and installation a package process. In this study, using the optimum conditions which are operating times, flow rate, current, voltage, number of cycles, previously determined for Voltea brand MCDI, the removal of arsenic from the wastewater produced by Emet Bor Operation Directorate Espey Open Quarry and Concentrator Facility, Hisarcik Open Quarry and Concentrator Facility and Boric Acid Production Facility during their activities has been studied. The removal efficiency of the MCDI process for arsenic was 94%.

Keywords: Arsenic, membrane capacitive deionization, groundwater

1. INTRODUCTION

The scarcity of drinking water sources in the world and pollution in the existing drinking waters threaten living beings, particularly human beings. The source of this pollution can either be human activities or through natural ways in the environment [1].

In addition to surface waters, groundwater is also widely used for drinking water. The sources of groundwater are generally surface waters, and they are formed by the accumulation of surface waters and rainfall in cracks rocks, and gaps. As well as being a source of drinking water, groundwater is of great importance for agriculture, livestock, mining and industry [2]. The waters can carry various impurities according to the soil and rock properties of the environment they are in. Common pollutants are arsenic, boron, iron, fluoride, lead and manganese [1].

Arsenic is a metalloid which is among common elements. It has an atomic number of 33, atomic mass

of 74.92 amu and a density of 5.72 g cm⁻³. 0.00015% of the earth's crust consists of this element, and its main species are arsenate, arsenite and arsenic sulfur [3]. Arsenic has been classified by the World Health Organization as a carcinogenic and toxic element found in water used for human consumption purposes. The maximum safe arsenic concentration that may be found in these waters as set by WHO is 10 µg L⁻¹ [4]. Studies show that the concentration of arsenic in natural waters may reach 5000 µg L⁻¹ [5]. However, arsenic concentrations in water may reach as high as 48,000 µg L⁻¹ with anthropogenic arsenic pollution in various parts of the world [6].

Arsenic is known to cause problems associated with its accumulation in the body. Arsenic doses above 10 µg L⁻¹ are considered toxic. There are clinical studies showing that concentrations above 100 µg L⁻¹ may cause increased risk of bladder cancer, 150 µg L⁻¹ and above an increase in the frequency of skin cancers, 200 µg L⁻¹ and above chronic influence arsenicosis, and 300 - 400 µg L⁻¹ may cause increased risk of lung

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and skin cancer and other skin diseases. At higher concentrations, various disorders such as vascular system damage (black foot) and diabetes can be seen [7].

Arsenic should be removed water before discharge to the environment to prevent its negative effects on health. Conventional methods such as coagulation and electrocoagulation, active alumina, ion exchange, zeolite adsorption and reverse osmosis have been previously used in this removal process [8–10]. The methods of arsenic removal are generally very successful. The development of new technologies are needed due to issues such as the formation of arsenic rich sludge, the need for expensive special equipment, and not being economical at low concentrations.

Capacitive deionization is a successful technology that has recently been used in desalination and purification processes. It was also reported to be effective in removal of heavy metals such as copper, iron and cadmium from aqueous solutions [11–14]. In addition to these ions, efforts have been made using CDI technology to remove ions and boric acid which cause hardness [15, 16]. There are also studies on removal of ions such as fluoride and nitrate chromium, including the removal of salt from underground waters, which are defined as hard water [17–19]. Studies have also been carried out on CDI for removal of arsenic which has low concentrations from water [20].

Arsenic species commonly found in natural waters are As (III) and As (V) predominantly, as negatively charged compounds of $H_2AsO_4^-$ ve $HAsO_4^{2-}$ [20].

Capacitive deionization process is the process of displacing ions in water by applying low voltages (1-2 V) to two parallel electrodes with water passing in between [21]. Compared with conventional systems,

CDI results in energy efficiency, has a low energy potential, and directly uses electricity [21]. The simplicity of the CDI process, and its ability to be installed as a package can be seen as other advantages. The CDI process is made more efficient by using ion exchange membranes.

In this study, effective parameters were determined in arsenic removal by using membrane capacitive deionization process (MCDI). In addition, the efficiency of the MCDI process in arsenic removal was determined at different concentrations. Finally, arsenic removal process was performed on Eti Mining Operation wastewater using the MCDI process. of other languages in figures and tables is avoided. Papers should be checked by a native English speaker with expertise in the field prior to submission.

2. MATERIALS & METHODS

2.1. MCDI Process and Operation Conditions

The Voltea Brand MCDI system that was used in the study is schematically shown in Fig 1. The MCDI system consisted of 24 consecutive cells. Each cell contained a graphite current distributor (thickness $\delta = 250 \mu\text{m}$), chemically identical porous carbon electrodes to work as cathode and anode (PACMM 203, Irvine, CA, USA, $\delta_e = 362 \mu\text{m}$), anion- and cation-selective membranes to control ion flow (Neosepta AM-1 and Neosepta CM-1, Tokuyama Co., Japan, $\delta \approx 130 \mu\text{m}$) and textile separator ($\delta = 115 \mu\text{m}$) that allowed water flow and separated the electrodes from each other. The resistance of the carbon electrodes was $1 (\pm 0.2) \Omega \cdot \text{cm}^2$, and the total electrode area was 1.18 m^2 . The anion- and cation-selective membranes had resistance values of approximately $2 \Omega \cdot \text{cm}^2$ [23].

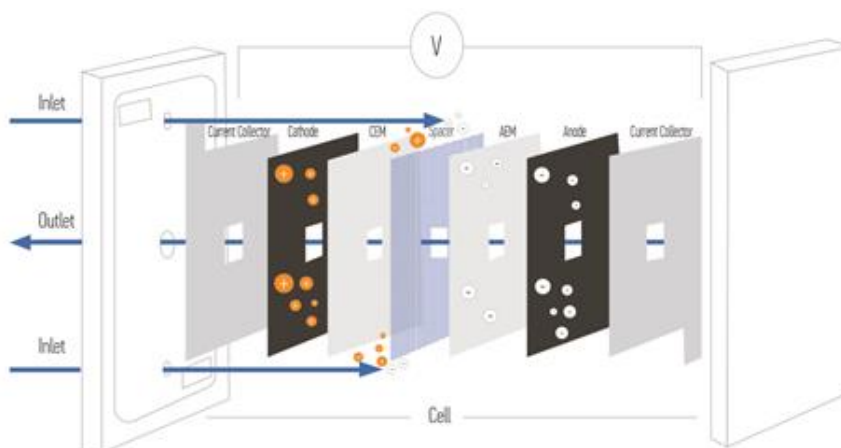


Fig 1. Schematic Representation of MCDI Process [22]

2.2. CDI Experiment

The CDI device could be operated automatically or manually at three stages. These stages were desorption (purification), preliminary (pre-purification) and desorption (wasting) stages. A single reactor was used for these stages, and the purified water and concentrated flow could be guided

automatically from different channels. Additionally, in the CDI device, there was a preliminary treatment cell with a volume of 1L and a filter of $0.1 \mu\text{m}$ porosity to prevent particulate matter from entering the reactor. There were conductivity probes in the inlet and purified water outlet channels of the reactor, and the conductivity values were automatically measured and transmitted to the computer via software. Values such as electrical potential difference (V), current (A) and pressure could be measured automatically.

The device could be operated manually, but it could also be operated automatically based on the principle of a model generating flow at a constant voltage, depending on values such as required efficiency, flow rate and input conductivity.

The potential and flow rate were kept constant in the MCDI system. The electrical potential difference was kept constant at 1.5V depending on the resistance to avoid hydrolysis conditions. Since the device reactor had a volume of 0.3L, it was kept at a flow rate of 0.3 L min⁻¹ by adopting a fully mixed reactor. Energy consumption increased above this value, and it took a long time to fully discharge the reactor at the preliminary stage below this value. Depending on this, the volume of the concentrate flow increased. In the optimization experiments conducted with the MCDI system, the operating times were determined to be 1440 seconds for adsorption and 60 seconds for system preparation (complete removal of the concentrate present in the reactor and charging of the electrodes for adsorption/desorption). The duration of desorption varies depending on input conductivity [24].

2.3. Chemical Analysis

ICP MS was used for Arsenic and Boron measurements. Turbidimetric method was used for sulfate analysis, allowing analysis at a concentration of 1-40 mg L⁻¹ SO₄²⁻. The EDTA titrimetric method was used for the calcium analysis. Based on the results of calcium analysis, magnesium was found by calculation method based on EDTA titrimetric method. Ultraviolet spectrophotometric method used for NO₃⁻ analysis and argentometric method used for chloride analysis [Standart Methods].

2.4. Preparation of Synthetic Waters

Synthetic water ion contents used in laboratory studies were prepared with standard arsenic solution (H₂AsO₄ in HNO₃ 0.5 mol L⁻¹), NaNO₃ and MgSO₄·7H₂O.

3. RESULTS & DISCUSSION

3.1. The Effect of Influent Concentration of Arsenic on Removal

Synthetic waters containing arsenic at different concentrations between 50 and 2000 µg L⁻¹ were treated with the CDI system. As shown in Table 1, an increase in arsenic concentration led to an increase in removal efficiency. Ion intensity is a driving force in migration of ions to electrodes. The increase in removal efficiency was related to this.

Considering that the limit value determined by WHO is 10 µg L⁻¹, this limit value could only be reached at a 100 µg L⁻¹ arsenic concentration with 93.69% treatment efficiency.

Table 1. Removal efficiency of different arsenic concentrations

Influent Concentration µg L ⁻¹	Removal Efficiency %
50	91
100	93,69
200	93,87
300	94,91
400	95,62
500	96,23
750	97,59
1000	97,85
1500	98,34
2000	98,81

3.2. The Effect of Different Types and Amounts of Ionic Content on Arsenic Removal

The experiments on different ions continued with the value of 100 µg L⁻¹ in which the limit value of arsenic concentration could be reached.

As: Cl⁻, As: SO₄²⁻ and As: NO₃⁻ contents were prepared at 100 µg/L: 100 mg/L, and the effects of monovalent and divalent ions on removal efficiency were determined. As: Cl⁻: NO₃⁻: SO₄²⁻ was prepared at 100 µg L⁻¹: 100 mg L⁻¹: 100 mg L⁻¹: 100 mg L⁻¹ to study the removal of As from synthetic groundwaters using CDI.

In the experiment conducted on As: Cl⁻ (100 µg L⁻¹ : 100 mg L⁻¹ and 100 µg L⁻¹ : 200 mg L⁻¹) aqueous solution, arsenic removal efficiency was 98% and 98.7%, and Cl⁻ removal efficiency was 95% and 95.5%, respectively, as shown in the Fig 2. It was found that arsenic ions at a concentration of 100 µg L⁻¹ were purified by CDI with a removal rate of 93.69%. However, as mentioned above, the ionic strength of the solution is the driving force when ions move to the electrodes. As the ionic strength of the solution increases, the removal efficiency of arsenic and Cl⁻ ions also increases.

In the experiments conducted with different As:NO₃⁻ concentrations (100 µg L⁻¹ : 100 mg L⁻¹ and 100 µg L⁻¹ : 200 mg L⁻¹), Arsenic removal efficiency was found to be as 98.54% and 98.62%, and NO₃⁻ removal efficiency was found as 96.5% and 97.75%, respectively.

In the experiments conducted with different As: SO₄²⁻ concentrations (100 µg L⁻¹: 100 mg L⁻¹ and 100 µg L⁻¹ : 200 mg L⁻¹), Arsenic removal efficiency was found as 99.06% and 99.36%, and SO₄²⁻ removal efficiency was found as 95% and 96.9%, respectively.

Comparison of the ion removal efficiencies is given in Fig 2. Increased ion concentrations have also increased recovery efficiencies.

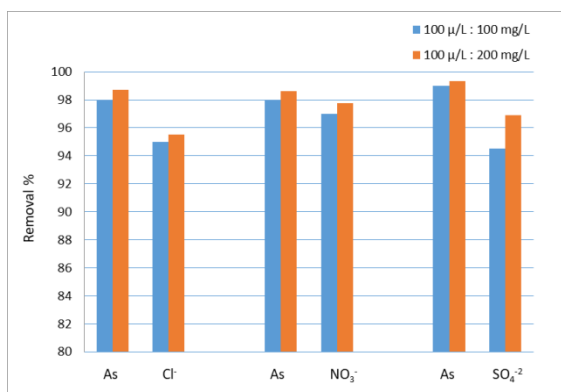


Fig 2. Ion removal efficiencies at different concentrations (100 µg L⁻¹ : 100 mg L⁻¹ and 100 µg L⁻¹ : 200 mg L⁻¹)

In the experiment conducted on As : Cl⁻ : NO₃⁻ : SO₄²⁻ solution (100 µg L⁻¹ : 100 mg L⁻¹ : 100 µg L⁻¹ : 100 mg L⁻¹), removal efficiencies were 98.72%, 94.76%, 98%, and 95%, respectively and is shown in Fig 3.

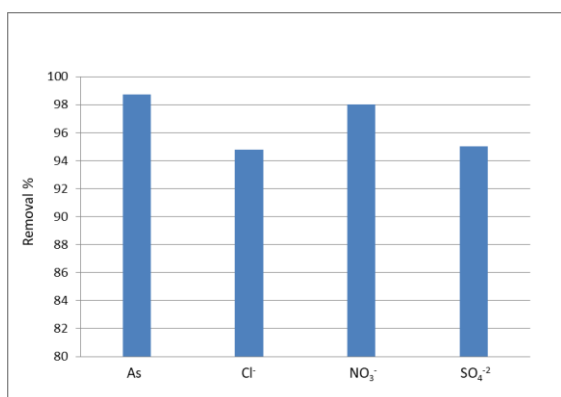


Fig 3. Ion removal efficiencies from synthetic groundwater (As : Cl⁻ : NO₃⁻ : SO₄²⁻, 100 µg L⁻¹ : 100 mg L⁻¹ : 100 µg L⁻¹ : 100 mg L⁻¹)

It is known that there are many different effects in the adsorption of ions from solution to the electrode surface. Most important ones are pore size of the electrodes and ions hydrated radii. Also the high ionic valence is important for the effective removal of ions. The sequence of the hydrated radii of the ions was SO₄²⁻ (3.79 Å) > NO₃⁻ (3.35 Å) > Cl⁻ (3.31 Å), respectively. Former studies with CDI have presented diversing consequences related to the preferential

selection of ions. Studies have shown that the pore size of the electrodes, including micropores (<2 nm) and mesopores (2-50 nm), and the distributions of these sizes cause the ions to show very variable tendencies in their preferential migration to the electrodes. As a consequence, the reason for more efficient removal of monovalent ions than divalent ions is the outcome of the fact that divalent ions (6-7Å⁰ in diameter) cannot be adsorbed into the pores in the electrode surface area because of the reduction of the small-sized pores by monovalent ions (4Å⁰ in diameter) [22].

Considering the studies done with different concentration, arsenic removal efficiencies are close to each other. Cl⁻ and SO₄²⁻ removal efficiencies are also close to each other when evaluated together with experimental errors. Accordingly, a sequence of As ≡ NO₃⁻ > SO₄²⁻ ≡ Cl⁻ can be mentioned.

3.3. Treatment of Mine Wastewaters having Arsenic with CDI

In this study, wastewaters produced as a result of the activities of Espey Open Pit Mining and Concentrator Facility, Hisarcık Open Pit Mining and Concentrator Facility and Boric Acid Production Facility of Emet Boron Processing Directorate located in Kütahya province of Turkey were treated. The characteristics of the wastewater are presented in Table 2. The CDI process is generally quite successful up to 5000 µS cm⁻¹. Due to high water conductivity, the experiments were conducted on 70% diluted samples.

Based on the results of the study, it was observed that the arsenic could be removed with a maximum efficiency of 94%. As shown in Table 2, removal efficiencies for SO₄²⁻, Cl⁻, and B anions were 99%, 90% and 81%, respectively; and removal efficiencies for Mg²⁺, Ca²⁺, and Na⁺ cations were 99%, 98% and 88%, respectively.

As a result of these studies, it can be seen that the standard for arsenic has been met as <10 µg L⁻¹. It has been demonstrated that MCDI process can be successfully used in arsenic removal from groundwater, surface water, and wastewater.

Table 2. Wastewater characteristic of boron mining facility

Component	Unit	Feed groundwater	Sample diluted %70	Purified groundwater mg L ⁻¹	Removal Efficiency %
pH	-	4,5	6,8	7,2	-
Cl ⁻	ppm	33,5	10	1	90
SO ₄ ²⁻	ppm	7352	2206	20	99
As	ppm	7	2.1	0.0087	99
B	ppm	4976	1493	54.84	81
Ca ²⁺	ppm	545	164	2.5	98
Mg ²⁺	ppm	952	286	3	99
Na ⁺	ppm	150	45	5	88
İletkenlik	µS	6040	2000	62	97

As shown in Table 3, in the first and second cycles, the potentials are 1.2 and 1.3 V, respectively, and the current values are 25 A and 15 A, respectively. The conductivity retention is finally 97.6%.

All deionization processes can be used for arsenic removal. In a study conducted by electro dialysis, wastewater containing arsenic was treated in the range of 2.1 - 15 mg L⁻¹ arsenic and potential was used in the range of 10 - 20 V and current in the range of 4.5 - 11.3 A was used. At the end of 400 minutes, the arsenic concentration could be lowered to less than 10 µg L⁻¹ [25]. In another study, ferric chloride and ferric sulfate coagulant materials were used to treat water containing 30 µg L⁻¹ arsenic and purified 99% [26]. In a study with reverse osmosis, water containing between 100 and 382 µg L⁻¹ arsenic was tried to be treated and 93% - 99% removal efficiencies were obtained [27].

Table 3. Energy Expenditures and Recoveries within treatment

Process Information	Unit	Cycle 1	Cycle 2
Initial Conductivity	µS cm ⁻¹	6050	2844
Average Removal Rate (for conductivity)	%	53	95
Average Current Density	A	25.3	15
Average Voltage	V	1.2	1.3
Water Recovery	%	65	68

As a result, comparing MCDI with other deionization methods, it can be seen that MCDI is quite successful in arsenic removal. MCDI is an energy efficient process when compared to electrochemical methods.

4. CONCLUSIONS

Underground and surface waters are exposed to arsenic pollution due to both human and natural causes. Arsenic is a pollutant that must be treated since it has a serious hazard endangering living organisms. MCDI process is a new technology that is very successful in ion removal. In this study, the mechanism of arsenic removal was tried to be determined by using optimum conditions (operation time, flow, current, voltage, number of cycles) previously determined for Voltea brand MCDI system. Arsenic was lowered below the 10 µg L⁻¹ limit in studies conducted on synthetic solutions. Moreover, arsenic was tried to be removed from wastewaters produced as a result of the activities of Espey Open Pit Mining and Concentrator Facility, Hisarcık Open Pit Mining and Concentrator Facility and Boric Acid Production Facility of Emet Boron Processing Directorate located in Kütahya, province of Turkey. Arsenic removal efficiency in these wastewaters containing 2100 µg L⁻¹ arsenic was 99.5%. When the effect of other ions and electron selectivity in the removal of arsenic ions from wastewaters by MCDI process was examined, it was found that the order for anions was $As \equiv SO_4^{2-} > Cl^- > B$, and the order for cations was $Mg^{2+} \equiv Ca^{2+} > Na^+$.

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