

Application of Electrochemical Process for Removal of Chromium and Copper from Kahrizak Leachate

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Abstract: Sanitary landfills are considered as environmentally method to disposal of solid wastes. However, the production of leachate is usually a major problem related to such method. Leachates contain large amounts of organic pollutants, ammonia nitrogen, heavy metals and etc. although their chemical composition is affected by several factors including seasonal precipitation, waste origin and the age of the landfill. In this research, the performance of an electrochemical system with iron electrodes for removing heavy metal ions (chromium and copper) was studied. This study was conducted in a batch setup. The effect of current density, reaction time and initial pH=7 were investigated. Equipment related to Electrochemical unit include power supply and 8 iron plate electrodes connected into a beaker with the effective Volume of 1.5 L. leachate sample experimented was taken from solid waste landfill of kahrizak of located at south of Tehran. The Results showed when current density and time reaction increased, removal efficiency of chromium and copper, increased. at initial pH=7, density 1A and reaction time 60 minutes, Cu, Cr, respectively up to 95% and 84% were removed. The study gave indications on the removal mechanisms of the investigated metals. Copper ions are hydrolyzed and co-precipitated as hydroxides. Cr (VI) was proposed to be reduced first to Cr (III) at the cathode before precipitating as hydroxide.

Key words: Electrochemical process % Heavy metal % Kahrizak leachate % Current density % Iron electrode

INTRODUCTION

Tehran with approximate population of 10 million people is producing daily amount of 6000 tons of solid waste. After being collected from the collection stationeries they were transferred by semi-trailers to the Kahrizak waste disposal site in South part of Tehran. This site can and do produce leachates, it has been estimated up to 500 m³ can be produced per day [1].

Leachate from municipal solid waste landfill sites are often defined as hazardous and heavily polluted wastewaters [2].

The leachates may contain a large amount of organic matter (both biodegradable and biorefractory carbon), ammonia-nitrogen, heavy metals, chlorinated organic and inorganic salts [3]. Landfill leachate has been identified as one of the major threats to groundwater resources, So leachate must be treated with proper technology to reduce

pollutants before disposal or reuse. Heavy metal has become one of the most serious leachate problems [4-6]. These inorganic micro-pollutants are considerable concern because they are non biodegradable, highly toxic and probably carcinogen [7]. They are non biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain [8].

Among the heavy metals, chromium and copper are most important. they widely used in many of the industrial processes such as metal cleaning and plating baths, refineries, paper and pulp, fertilizer and wood preservatives [9,10].

The excessive intake of copper by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation and possible necrotic changes in the liver and kidney [11].

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Most of the chromium is discharged into aqueous waste as Cr (III) and Cr (VI). Cr (VI), which is the more toxic of the two, is present as either dichromate ($\text{Cr}_2\text{O}_7^{2-}$) or as chromate (CrO_4^{2-}) [12].

At short-term exposure levels above the maximum contaminant level, Cr (VI) causes skin and stomach irritation or ulceration. Long-term exposure at levels above maximum contaminant can cause dermatitis, damage to liver, kidney circulation, nerve tissue damage and death in large doses [13].

The main techniques, which have been utilized to reduce the heavy metal ion content of effluents, include adsorption; biosorption, reduction and filtration reverse osmosis, ion-exchange, foam flotation and surface adsorption. These methods generate lot of sludge and high cost [14-16].

An effective technology that meets the requirements of process cleanliness, ease of manipulation and low operational and investment costs is electrochemical [17]. This technology was first employed in the 19th century to treat wastewater on ships and has recently been utilized as an alternative to more conventional treatment processes [18].

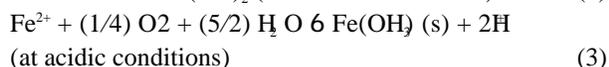
Removal mechanisms reported in the electrolysis process generally include oxidation, reduction, decomposition, whereas the mechanisms in the electro coagulation process include coagulation, adsorption, precipitation and flotation. Electrocoagulation utilizes aluminum or iron anodes to produce aluminum or iron hydroxide flocs by reaction at the anodes followed by hydrolysis [19-21].

Theory of EC: The electrochemical process using iron electrodes generate low concentration non-toxic iron oxides and/or hydroxide species in the aqueous media by the electrochemical dissolution of electrode material [22]. With iron as electrode materials the reactions are

C On the anodic electrode surface:



C At the vicinity of the electrode:



C On the cathodic electrode surface:



The iron hydroxide flocs act as absorbents for heavy metal ions. Furthermore, heavy metal ions combine with the electro generated OH ions at the cathode and precipitate in form of their insoluble hydroxides.

Both phenomena act synergistically leading to a rapid removal of heavy metal pollutants from leachate. The most common complex is the hydrated ion $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ [23]

MATERIALS AND METHODS

The experiments were carried out by batch process. Leachate was obtained from kahrizak landfill in south of Tehran. The total dissolved solids (TDS), pH and chemical oxygen demand (COD) etc, for leachate sample were determined consider Standard Methods (APHA, 1998) and characteristics of leachate sample are given in Table 1.

The leachate was first filtered using screen filter to remove large suspended solids before it was used for the subsequent studies. The experimental setup is shown in Fig. 1.

Batch experiments were carried out in a conventional 2000mL beaker. There are eight electrodes, four anodes and four cathodes of the same dimensions. Iron cathodes and anodes were made from plates with dimensions of 2cm × 15cm × 0.5 cm (width × length × depth). The active area of each electrode was 2 × 10 cm .and the spacing between electrodes was 15 mm. The electrodes were placed vertically parallel to each Other and they were connected to a digital dc power supply. All the runs were performed at constant temperature of 25°C.

The pH and conductivity were adjusted to a desirable value using NaOH or H₂SO₄ and NaCl (Merck), respectively [23-25]. The chloride salt added to the solution can also prevent the formation of the oxide layer on the anode and therefore reduce the passivation problem of the electrodes.

In each run, 1.5 liter of the leachate was placed into the electrolytic cell. The current density was adjusted to a desired value and the coagulation was started. Samples were extracted every 10 min and then filtered through a mixed cellulose acetate membrane (0.42 μm).

The residual concentration of chromium and copper were determined using inductivity coupled plasma (ICP) according to the standard method (APHA,1992).The amount of chromium and copper removal were measured at pH 7 and in current density of 0.5, 0.75 and 1A [23-25].

Table 1: Characteristics of leachate used

Characteristic	Value
COD(mg/l)	66680
TDS (mg/l)	9540
BOD5 (mg/l)	2450
Conductivity (mS/cm)	16.89
Temperature (C°)	21.4
pH	7.82

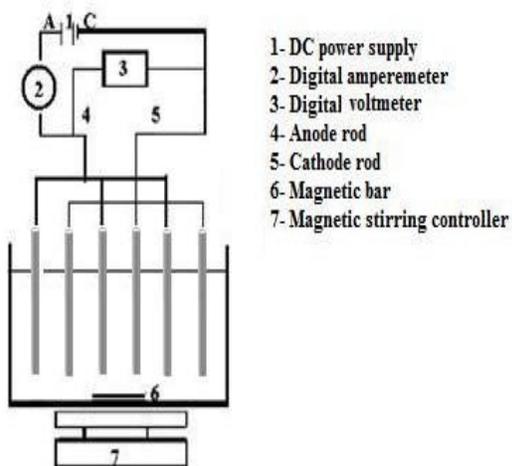


Fig. 1: A schematic diagram of the experimental setup

RESULTS AND DISCUSSION

The electrochemical process is affected by several operating parameters, such as initial pH, pollutants concentrations, current density, COD and contact time. Chromium and copper removal efficiency at different condition (electrical current) in various times was evaluated [26]. Preliminary laboratory testing of the electrolysis cell involved determining the effect of applied electrical current on the efficiency of Cr²⁺ and Cu²⁺ removal.

It is well-known that electrical current not only determines the coagulant dosage rate but also the bubble production rate and size and the flocs growth which can influence the treatment efficiency of the electrochemical. Therefore, the effect of current density on the pollutants removal was investigated [27,28].

As expected, it appears that for a given time, the removal efficiency increased significantly with increase of current density [29,30]. The highest current density (1A) produced the quickest treatment with > 85% copper reduction and >55% chromium reduction occurring after only 20 min and the lowest heavy metals removal efficiency occurred in the lowest current density (0.5 A). This might be attributed to the difference in removal mechanisms of each heavy metal in the treatment process.

Table 2: Concentration of Chromium removal during electrochemical process using iron electrodes (Initial pH = 7).

Concentration (mg/l)			
1 amp.	0.75 amp.	0.5 amp.	Time (min)
1.39 ± 0.42	1.39 ± 0.42	1.39 ± 0.42	0
1.08 ± 0.28	1.13 ± 0.41	1.13 ± 0.31	10
0.58 ± 0.11	0.9 ± 0.2	0.99 ± 0.27	20
0.3 ± 0.23	0.65 ± 0.23	0.87 ± 0.26	30
0.39 ± 0.18	0.5 ± 0.24	0.67 ± 0.23	40
0.3 ± 0.23	0.31 ± 0.14	0.52 ± 0.23	50
0.21 ± 0.13	0.24 ± 0.21	0.39 ± 0.09	60

Table 3: Percent of copper removal during electrochemical process using iron electrodes (Initial pH = 7).

Current density (Amp.)			
1	0.75	0.5	Time (min)
2.28 ± 0.24	2.28 ± 0.25	2.28 ± 0.24	0
1.3 ± 0.83	1.68 ± 0.53	1.7 ± 0.77	10
0.22 ± 0.08	0.94 ± 0.41	1.012 ± 0.6	20
0.3 ± 0.07	0.355 ± 0.11	0.58 ± 0.21	30
0.19 ± 0.06	0.38 ± 0.19	0.52 ± 0.15	40
0.17 ± 0.05	0.23 ± 0.07	0.42 ± 0.15	50
0.13 ± 0.03	0.17 ± 0.04	0.28 ± 0.05	60

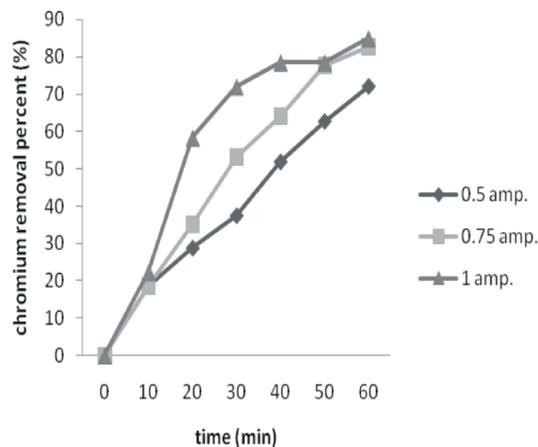


Fig. 2: Missing

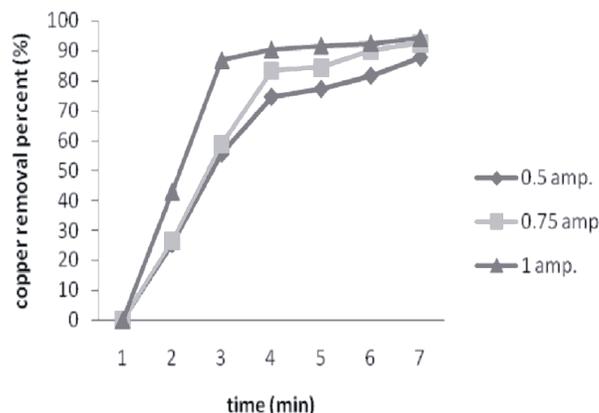


Fig. 3: Missing

The highest current density was 1A, which led to removal of nearly 85% Cr and some 94% of Cu within 60 min. According to the removal rate the investigated metals ranked in the following order: Cu > Cr. the obtained results were showed in Table 2, 3.

This is ascribed to the fact that at high current, the amount of iron oxidized increased, resulting in a greater amount of precipitate for the removal of pollutants. In addition, it was demonstrated that bubbles density increases and their size decreases with increasing current density, resulting in a greater upwards flux and a faster removal of pollutants and sludge flotation [31,32].

As the current decreased, the time needed to achieve similar efficiencies increased and the results of this research confirm this fact. This expected behavior is explained by the fact that the treatment efficiency was mainly affected by charge loading ($Q = It$), as reported by Chen [20,33].

CONCLUSION

The electrochemical process is currently the most effective process for treating leachate containing heavy metal ions, but its removal efficiency was significantly affected by various parameters including the current density, initial pH and electrolysis time.

The Results showed when current density and time reaction increased, removal efficiency of heavy metals such as chromium and copper increased. at initial pH = 7, density 1A and reaction time 60 minutes, Cu and Cr, respectively up to 94 and 84% were removed.

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