Introduction

Today, landfills are substantially used for the removal of domestic solid waste.1–4 Domestic waste is the result of daily household activities. Such waste may include different kinds of organic chemicals with unknown living metabolisms. These substances display hazardous and risky features with regard to the continuity of living. Besides, these hazardous substances are mainly related to industrial and medical products used in the household with a tendency to increase day by day.3

In addition to industrial wastes, medical wastes such as human blood, blood products, pathological and microbiological wastes, medical needles from hospitals, health centres, sanatoriums and research institutes fall under the status of hazardous waste.5 Apart from these, products such as pesticides, paint products, varnishes, batteries and motor oil used in households are classified as hazardous waste according to their corrosiveness, combustibility, reactivity and toxicity.6–7

Like domestic solid wastes, hazardous solid wastes are disposed mostly into landfills. Leachate represents the first priority problem encountered in these fields. Treatment of the leachate is of vital importance in terms of environment and public health due to the fact that the leachate may include high levels of pollutants depending on the properties of the landfilled domestic and hazardous wastes.8,4

In recent years, the electrochemical methods that are generally used in the treatment of drinking water, domestic and various industrial wastewaters, have been encountered in some applications for the treatment of leachate.9–13

Under the heading of electrochemical methods, numerous processes have been developed so far. These processes may be used in a system together or separately. In these processes, pollutants are removed from wastewater by oxidation, adsorption, and by settling and/or flotation. Among the electrochemical treatment methods, electrocoagulation (EC) is the most commonly used method so far.

Treatment of wastewater by EC has been practised for most of the 20th century with limited success and popularity. In the last decade, this technol-
ology has been increasingly used in South America and Europe for the treatment of industrial wastewater containing metals. It has also been noted that in North America, EC has been used primarily to treat wastewater from pulp and paper industries and mining and metal-processing industries as well. EC can be considered the most important method, because it requires simple equipment and is easy to operate with sufficient operational latitude, negligible amount of chemicals and decreased amount of sludge.\(^{15-19}\)

EC is a complex process in which oxidation; coagulation, absorption, adsorption precipitation and flotation mechanisms occur simultaneously.\(^{20,21}\) The foundation of the process is related to the process of metal hydroxide flocks formation by loaded ion types and metal ions dissolving from anode under the influence of applied current. The progression of any EC is determined by the chemical features and the conductivity of the environment. Conductivity generally comprises the effect of the electrical field applied in consequence of the mobility of ions in the ambit.\(^{22}\)

In the present work, the effect of ion concentration on the conductivity in EC was examined. The influence of seawater with high ion concentration on the process efficiency was investigated with respect to the process parameters changes. Although seawater differs by region, depending on evaporation, it contains salt in high quantities. It is indicated that the average salt concentration in oceans and seas is approximately 3.5 %, and 3 % of this amount is composed of sodium (11 g kg\(^{-1}\)) and chlorine ions (19 g kg\(^{-1}\)).\(^{23}\)

There is a great deal of anions and cations, notably, Br\(^{-}\), SO\(_4^{2-}\), HCO\(_3^-\), F\(^-\), H\(_2\)BO\(_3^-\), Mg\(^{2+}\), Ca\(^{2+}\), Sr\(^{2+}\), K\(^+\) in seawater.\(^{24}\) The quantity and concentration of cations and anions cause a fall in the environment resistance. Thus, ions travel faster more easily and make up more flocks. This also accelerates the process of EC.

In ordinary EC, NaCl is added to the system due to its contribution to the pH and conductivity changes. It is necessary to supply chlorine ions to have at least 20 % of anions in the system, in order to make the process run efficiently.\(^{25}\) Since the study was performed with seawater fed externally to the system, addition of NaCl was not necessary. Nevertheless, the ions found in high concentrations in the seawater such as, Mg\(^{2+}\) and Ca\(^{2+}\) form hydroxite flocks by combining with hydroxyl ions. The coagulation increase makes the removal of pollutants more effective.

For this purpose, the leachate samples were taken from domestic and hazardous solid waste lots from the IZAYDAS Landfill (Izmit Domestic and Hazardous Solid Waste Regular Landfill), Kocaeli, and the study of their treatment was maintained by adding various proportions of seawater externally to the EC system. Wastewater and seawater were characterized and the effects of parameters, such as suspendend solids, phosphate, sulphate, color and turbidity on the treatment efficiency were investigated.

### Materials and methods

#### Description of the study area

IZAYDAS Landfill covers a surface area of 362.557 m\(^2\), assigned for the landfilling of domestic and hazardous wastes produced in the Kocaeli region. There are seven lots with a total volume of 4.132.919 m\(^3\). Six lots are planned for the landfilling of domestic wastes, and one for hazardous wastes.\(^{24,25}\) The area and volumes of domestic and hazardous solid waste lots are given in Table 1.

<table>
<thead>
<tr>
<th>Type of lots</th>
<th>Lot no</th>
<th>Area (m(^2))</th>
<th>Capacity (m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Domestic solid wastes</td>
<td>1,2,3,4,5,7</td>
<td>264392</td>
<td>3163000</td>
</tr>
<tr>
<td>Hazardous solid wastes</td>
<td>6</td>
<td>98165</td>
<td>969919</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>362557</td>
<td>4132919</td>
</tr>
</tbody>
</table>

Lot no. 6 for hazardous solid wastes is divided in itself into 5 cells with different volumes. Domestic and hazardous solid waste lots were prepared in compliance with the guidelines, and subsequent layers of clay, pebble, and synthetic polymers were laid out to enable sufficient permeability. Also, drain pipes and funnels were placed in the lots to drain the leachate and store gas out of the lot. The main sections of domestic and hazardous waste lots are given in Fig. 1.

As can be seen from Fig. 1, there is a two-stage leachate collecting system, and the additional clay and geomembrane layers are present in the hazardous waste lot. The solid wastes qualified as “domestic”, which come from the municipalities in the Kocaeli region, and industrial solid wastes that can be landfilled with domestic wastes are stored in the domestic solid waste lots. The hazardous wastes with calorific value below 2500 kcal, filter cakes and fly ash from the air pollution control equipment of the incineration plant, scum, and the inert wastes are landfilled into the hazardous waste lot (No. 6).

The study was conducted with the aim to observe the effect of seawater on the EC method. Seawater used in the reactor was provided from the Sea of Marmara. The Marmara Sea, Black Sea and Mediterranean Sea are mutually connected, whereas the salt rate of its waters, according to conductivity,
is less than that of the Mediterranean Sea and more than that of the Black Sea. The composition of the leachate samples taken from domestic and hazardous lots of IZAYDAS Landfill and the seawater used in the system are given in Table 2.

**Table 2 – Chemical composition of the leachates from IZAYDAS Landfill and seawater used**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Concentration</th>
<th>leachate from domestic solid waste lots (DSWL)</th>
<th>leachate from the hazardous solid waste lot (HSWL)</th>
<th>Seawater used (SW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended Solids (mg L⁻¹)</td>
<td>790</td>
<td>620</td>
<td>1350</td>
<td></td>
</tr>
<tr>
<td>Phosphate (mg L⁻¹)</td>
<td>181</td>
<td>5</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>Sulfate (mg L⁻¹)</td>
<td>224</td>
<td>1843</td>
<td>1433</td>
<td></td>
</tr>
<tr>
<td>Color (HZ)</td>
<td>2450</td>
<td>63</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>550</td>
<td>46</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>8.15</td>
<td>7.71</td>
<td>7.4</td>
<td></td>
</tr>
<tr>
<td>Conductivity (mS cm⁻¹)</td>
<td>21</td>
<td>18</td>
<td>32</td>
<td></td>
</tr>
</tbody>
</table>

**Analyses**

All chemicals of analytical grade were purchased from Merck/Germany (H₂SO₄, NaOH, BaCl₂, 2H₂O, KH₂PO₄), Fluka/Switzerland (Na₂SO₄), Baker/USA (MgCl₂, 6H₂O, KNO₃, CH₃COOH, (NH₄)₆Mo₇O₂₄·4H₂O, HCl), Carlo Erba/Italy (CH₃COONa·3H₂O) and Acros/USA (NH₄VO₃) and used without further treatment. The study performed for the assessment of the removal efficiency was carried out in compliance with 2540 B “Total Solids Dried at 103–105 °C” method for suspended solids (Sartorius Mechatronics Corporation, USA), 4500–P C “Vanadomolybdophosphoric Acid Colorimetric Method” for phosphate analysis, 4500–SO₄²⁻ E “Turbidimetric Method” for sulphate analysis specified in Standard Methods. A spectrophotometer (Merck-SQ118, Germany) was used in the spectrophotometric analyses based on the color and turbidity measurements. pH-meter (Solomat-520 °C, UK) was used in pH and conductivity measurements. Furthermore, 0.1 mol L⁻¹ H₂SO₄ and 0.1 mol L⁻¹ NaOH solutions were prepared for pH settings.

**Experimental**

The schematic view of EC used in the study is given in Fig. 2. The pilot unit is composed of a seawater supply tank, a leachate supply tank, an EC reactor and a tail water reservoir. The EC reactor has a volume of approximately 2L. In the EC unit, seawater and leachate were fed into the system from seawater and leachate supply tanks under optimum conditions determined previously.

The appropriate selection of the electrodes materials is very important. Due to the nature of the study, two different materials (iron and aluminum) were used for anode and cathode in the reactor. In the reactor, two groups of alternating electrodes (iron/aluminum) being cathodes and anodes (7 of
each type) are plates arranged vertically. The distance between neighboring anode and cathode is 3 mm. Prior to running the experiments, the electrodes were immersed in 1% HCl for 8 hours. The experiments were performed at room temperature.

In the study, the leachate samples were mixed with seawater in different proportions. Fe or Al plates were used as sacrificial electrodes. Domestic and hazardous waste leachates were subjected to the treatment by means of EC by mixing them with seawater in two different proportions, 1:1 and 1:3, respectively.

Current densities ranging from 2.81 to 6.88 mA cm$^{-2}$ at Fe plates, and from 2.69 to 6.54 mA cm$^{-2}$ at Al plates, were applied to the system for 15 minutes. During the treatment process, the leachate was left to rest for 20 minutes in order to let the flocks, formed at Fe electrodes in the pH range of 8.5–9.0 and at Al electrodes in the pH range of 7.5–8, settle and be removed by the water flow. The removal efficiencies observed in suspended solids, phosphate, sulphate, color and turbidity parameters were measured and evaluated in the samples.

The mechanisms of electroflocculation occurring in the electrochemical units have been studied well enough. When a direct current passes through the electrodes, metal ions release from the anode plates and react with OH$^-$ ions formed by the reduction of water on the cathode plates. Consequently, metal hydroxides are formed under appropriate pH level. This stage ends with the formation of colloidal particles. Hydroxides form the nuclei of the colloidal particles, and the adsorption layer of cations and anions is formed around the nuclei. Thus, nucleus and adsorption layer form a positively charged colloidal granule. Diffusion layer then occurs around the granule, and the particle becomes neutral. The metal hydroxides formed during the EC have a high adsorption capacity.

The adsorption volumes of the formed metal hydroxides are very high. Coagulated particles attract and absorb micro-colloidal particles and ions from the wastewater. Particle size, pH, and characteristics such as chemical constituent concentrations, influence the EC. The mechanisms of ion removal by EC will be explained in two specific examples with aluminum and iron anodes, since these two metals have been extensively used to clarify wastewater.$^{18,29}$

**Experimental results and discussion**

EC as a process that removes pollutants from water includes multiple mechanisms.$^{30}$ The process is combined of a few stages in which the electrodes participate in the coagulants formation through the electrolytic oxidation, the destabilization of pollutants, and subsequent flocks formation.$^{31}$

The selection of electrode material and the composition of the device are of vital importance to the efficiency of the system. Aluminum and iron are frequently used as electrolyte materials in electrocoagulation units because they are cheap, easily available and highly efficient in treatment.$^{10}$

The mechanism of ionizing the metals is complex enough and so far, not explained completely. However, according to contemporary views of the process, anodic dissolution of metals goes through the formation of a complex of metal and ions of the solution, which that happens in a few consecutive stages.$^{29}$

Specific adsorption of anions on the surface of the metal:

$$\text{Me} + \text{mA}^- = (\text{MeA}_m)^{\text{n}-} \text{(ads)} \quad (1)$$

Electrochemical phase that defines the velocity of the process, when the complex passes to the solution,

$$(\text{MeA}_m)^{\text{n}-} \text{(ads)} \leftrightarrow (\text{MeA}_m)^{\text{n-m}} \text{(sol)} + n e^- \quad (2)$$

The complex degradation to simple ions, or the products of hydrolysis

$$(\text{MeA}_m)^{\text{n-m}} \leftrightarrow (\text{MeA})^n + m \text{mA}^- \text{(sol)} \quad (3)$$

The anodic dissolution of Fe can be presented in accordance with a modified scheme (pH>2),

$$\text{Fe} + \text{OH}^- \rightarrow \text{FeOH}^+ + 2 e^- \quad (4)$$

$$\text{FeOH}^+ + \text{(ads)} + \text{OH} \rightarrow \text{Fe(OH)}_2 (\text{ads}) \quad (5)$$

$$\text{Fe(OH)}_2 (\text{ads}) \rightarrow \text{Fe(OH)}_2 (\text{sol}) \quad (6)$$

$$\text{Fe(OH)}_2 (\text{sol}) \rightarrow \text{FeOH}^+ + \text{OH}^- \quad (7)$$

$$\text{FeOH}^+ \rightarrow \text{Fe}^2^+ + \text{OH}^- \quad (8)$$
The process of specific adsorption of Cl ions with the consequent FeCl2 and FeCl3 formation can be presented by analogous equations. The influence of the ionic composition of seawater on the process of electrodes dissolution is of complex nature. Thus, aluminum anodes dissolve more intensively under higher Cl ions concentrations.29 In the presence of CO3\(^2\) ions, the anodic process passes slower.

Reactions on the Al-anode:

\[
\text{Al} - 3\overline{e} \rightarrow \text{Al}^{3+} \quad (9)
\]

\[
\text{Al}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{Al(OH)}^{2+} + \text{H}^+ \quad (10)
\]

\[
\text{Al(OH)}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{Al(OH)}_2^+ + \text{H}^+ \quad (11)
\]

\[
\text{Al(OH)}_2^+ + \text{H}_2\text{O} \leftrightarrow \text{Al(OH)}_3^+ + \text{H}^+ \quad (12)
\]

Anodic dissolution of Al produces hydrated ion \([\text{Al-H}_2\text{O}])^{3+}\ in acidic environment; hardly-soluble hydroxide \([\text{Al(OH)}_3\text{(H}_2\text{O}))_3]\ in low acidic and neutral environment; and hydrated ion \(\text{Al(OH)}_4^-\) in the basic environment.

Two different reactions occur in the process in which aluminum and iron are selected for the role of exhaustible electrode. The ions of the anode metal produce polymeric iron and aluminum hydroxide in wastewater, depending on the current applied. These polyhydroxy metallic compounds are coagulants that produce a forceful attraction to impurities suspended in water and keep forming as long as the current is applied to the system. It is presupposed that the growth of pH of environment from 4 to 7 promotes the growth of the polymerization degree for hydroxco-complexes of Al, according to the scheme.18,29

\[
\text{Al(OH)}^{2+} \rightarrow \text{Al}_{4}\text{(OH)}_{12}^{6+} \rightarrow \text{Al}_{10}\text{(OH)}_{22}^{8+} \rightarrow \text{Al}_{24}\text{(OH)}_{60}^{12+} \rightarrow \text{Al}_{54}\text{(OH)}_{144}^{18+} \quad (13)
\]

During the process, oxygen is produced at anode, and hydrogen is produced at cathode in the gas form, in addition to the electrodes dissolution. The bubbles of the gases are effective when removing pollutants in the system by the flocked pollutants flotation to the surface of water.29,31

It should be noted that in the electrochemical unit both metal ions transfer into the waste water and the reaction of active particles formation which participate in the process of disinfection occurs simultaneously.33 Some of the reactions are given in Table 3.

Table 3 – Some reactions on the surface of electrodes

<table>
<thead>
<tr>
<th>Anode</th>
<th>Catode</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2\text{H}_2\text{O} - 4\overline{e} \rightarrow 4\text{H}^+ + \text{O}_2)</td>
<td>(2\text{H}_2\text{O} + 2\overline{e} \rightarrow \text{H}_2 + 2\text{OH}^-)</td>
</tr>
<tr>
<td>(2\text{H}_2\text{O} - 2\overline{e} \rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+)</td>
<td>(\text{OH}^- \rightarrow e^- + \text{OH})</td>
</tr>
<tr>
<td>(2\text{H}_2\text{O}_2 - 3\overline{e} \rightarrow \text{HO}_2^- + 3\text{H}^+)</td>
<td>(\text{O}_2 + e^- \rightarrow \text{O}_2)</td>
</tr>
</tbody>
</table>
| \(\text{H}_2\text{O}_2 - e^- \rightarrow \text{HO}_2^- + \text{H}^+\) | |}

water decolourization. The mixture reacts with the chromophor groups and causes removal of colour from the solution.

It should be noted that under high current density, the active particles and radicals of chlorine can interact with dissolved organic compounds with some carcinogenic substances formation. The dependence of chlorine by-products generated species formation of the electrode material and applied charge is discussed in literature.32 In our experiments low current densities were applied, therefore the probability of forming such substances is very small.

**Experiments with iron anode**

The use of soluble anodes causes pH increase in the solution, and the most considerable pH changes occur in the reactor with iron anodes. pH value in the reactor during water electrolysis with dissolving iron anodes increases up to 9.5–10.0. Along with this, the final pH value of the solution depends not only on the concentration of the metal ions emitted, but on the initial pH of water as well.

The removal efficiencies of suspended solids, phosphate, sulphate, color and turbidity parameters for the domestic leachate are given in Fig. 3a, b, c, d and e respectively, in accordance with the content of the EC with iron electrodes participation.

In the experiments, the treatment was performed by mixing leachate with seawater in proportions of 1 : 1 and 1 : 3. Accordingly, the removal efficiencies of suspended solids, phosphate, sulphate, color and turbidity parameters for the domestic leachate in the proportion of 1 : 1 mixture were 51 %, 94 %, 66 %, 87 %, and 97 %, respectively, while the results of 1 : 3 mixture for the same parameters were determined as 55 %, 100 %, 54 %, 91 %, and 98 %, respectively.
The obtained data showed the best removal efficiency for phosphate, color and turbidity (ranging from 87 % to 100 %). Their maximum is found for Fe²⁺ in the range of 1.25–1.39 g L⁻¹. For suspended solids and sulfate, their removal efficiencies vary in the range of 51–66 %.

In the test made with hazardous waste leachate mixed with seawater in the same proportions, an increase was observed in the efficiencies of all parameters (except for sulfate), when the proportion of seawater was increased. For sulphate, the removal efficiency for the mixture of 1 : 1 was in the range of 22–56 %, while that for the mixture of 1 : 3 was in the range of 15–52 % (concentrations of Fe²⁺ are changing from 0.50 to 1.39 g L⁻¹).

The low percentage of SO₄²⁻ ions removal from wastewater (52–66 %) arises probably due to the formation of soluble salts of iron in the solution. To remove SO₄²⁻ from wastewater for the account of non-soluble compounds formation, its interaction with Ca²⁺ ion may be used. In contrast to this, phosphate ion forms hard-soluble salts with most of the metals in the base environment. As seen in Fig. 3b, the percentage of PO₄³⁻ ions removal is high and equals 72–100 %.

**Experiments with aluminum anode**

In the case of aluminum electrodes, the pH of the solution increases to 9.0–9.1, only, due to the amorphism of aluminum hydroxide being formed in the process of electrolysis. The removal efficiencies of suspended solids, phosphate, sulphate, color and turbidity obtained in the study with aluminum anodes are given in Fig. 4a, b, c, d, and e, respectively.

It was observed that the removal efficiency increased with the amount of Al used in the experiments. Also, it has been determined that, as in the experiments performed with Fe, the formation of flock becomes easier when the amount of seawater increases, thus in turn causing an increase in the pollutant removal efficiencies.

In the experiments with a HSWL : SW ratio of 1 : 1, it was observed that the removal efficiencies of suspended solids, phosphate, sulphate, color and turbidity were 66 %, 78 %, 55 %, 67 %, and 80 % respectively, whereas the experiments with a HSWL : SW ratio of 1:3 produced better removal efficiencies except for sulphate, as in the case of the experiments with Fe anode. High content of sulphate ions in the solution causes their less effective removal from DSWL and HSWL. Besides, it is known from literature that sulphate ions have an inhibiting effect on the anodic dissolution. Phosphate and chloride anions, in their turn, accelerate dissolution of Fe and Al anodes.

Fig. 3 – Removal efficiencies for (a) suspended solids, (b) phosphate, (c) sulphate, (d) color, and (e) turbidity for electro-coagulation with iron anodes
Analogously to the Fe-anode, the efficiency of \( \text{SO}_4^{2-} \) removal in the presence of the Al anode is also negligible, possibly due to the soluble aluminium salts formation as well. A negligible content of \( \text{Ca}^{2+} \) ions in the seawater under alkaline \( \text{SO}_4^{2-} \) does not guarantee full removal of the \( \text{SO}_4^{2-} \) ions.

**Conclusions**

The aim of the study was to determine the sensitivity of the system to conductivity in the treatment of leachates from domestic and hazardous landfill sites by means of EC process. For that purpose, the process using Fe and Al electrodes were fed externally with seawater. The removal efficiencies of suspended solids, phosphate, sulphate, color and turbidity parameters were determined according to the anode and leachate/seawater ratio used in the EC process.

In this study, experimental data showed the removal efficiencies of phosphate, color and turbidity parameters higher than suspendend solids and sulphate parameters’ efficiencies for each electrode. The results showed the same trend in the removal efficiencies in the experiments with Fe and Al anodes. However, with respect to leachate/seawater ratios, an increase in the efficiencies with the ratio of seawater increase was observed for all parameters except for sulphate, which showed the opposite trend. The reason for this controversy is thought to be the natural consequence of the high sulphate concentration in the seawater.

**ACKNOWLEDGEMENTS**

The authors wish to acknowledge The Scientific and Technological Research Council of Turkey (TÜBİTAK) for the financial support of this Project (Project Number: 106Y151).

**Abbreviations**

SW – seawater  
DSWL – domestic solid waste leachates  
HSWL – hazardous solid waste leachates  
EC – electrocoagulation  
SS – suspended solids (mg L\(^{-1}\))

**References**