

ORIGINAL RESEARCH PAPER

Chemical reducing conditions through the photo-assisted electrochemical process in the treatment of the urban rainwater

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ABSTRACT

BACKGROUND AND OBJECTIVES: Rainwater in the city of Tehran is regarded as a freshwater source; however, because of highly polluted air conditions, the rainwater quality could be seriously affected. Therefore, the treatment of it could be an attractive topic for assessment. The purpose of the present study was to treat Tehran rainwater by employing photoelectrocatalytic methods as one of the most powerful treatment methods. Also, this study aimed to find an easy laboratory procedure to create various redox environments and to assess a protocol for the release of metals.

METHODS: The photoelectrocatalytic process was achieved by using a photocatalyst (Titanium dioxide) as the photoanode for the treatment of Tehran rainwater. Sodium ascorbate was used as a reducing modifier to assess the effect of various redox potentials on the performance of the photoelectrocatalytic process.

FINDINGS: The positive redox potential, the 6 centimeter gap, and the sodium chloride concentration of 0.65 g/L resulted in a considerable increase of the chemical oxygen demand, iron, manganese and lead removals. On the other hand, the negative redox potential, the 12 cm gap, and the sodium chloride concentration of 0.65 g/L led to a noticeable increase in the removal of zinc. By employing the speciation and Pourbaix diagrams, the removal mechanisms of the PEC process were investigated. Chemical oxygen demand, iron and manganese by oxidation, lead, zinc and cadmium by precipitation were removed. Also, based on the cluster analysis, it was found that redox potential, dissolved oxygen and pH had a strong relationship.

CONCLUSION: This work provided evidence that the redox potential could be regarded as a critical parameter helping to better estimate the risks associated with the polluted sites.

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INTRODUCTION

Environmental contamination caused by the high chemical oxygen demand (COD) load with heavy metals in rainwater is a common problem (Igbinsosa and Aighewi, 2017). Most heavy metals belong to the group of permanent toxic materials. It has been reported that zinc (Zn), iron (Fe), manganese (Mn), lead (Pb), and cadmium (Cd) exist in rainwater (Agarwal, 2009). Excessive presence of these elements could cause notable health problems (Chen et al., 2013). More importantly, they cannot be completely destroyed by traditional treatment technologies which do not meet the strict discharge standard (Yao et al., 2015). Redox-active substances and reactions have recently been considered to serve as favorable ways for purification. This is due to their molecular eclectic and electronic tenability (Su et al., 2018). They could affect the structure of pollutants by with a rapid degradation rate (Jin et al., 2014). The basis of the photocatalytic process (PC), which is a renowned treatment process, is the occurrence of the redox reactions. It can lead to the ultimate mineralization of organic pollutants. Also, it can result in the conversion of metallic ions to less poisonous types or species that can be separated from the aquesystem (Litter, 2015). Through the PC process, a photon with an energy equal to or bigger than the photocatalyst's gap band is utilized. It can stimulate the semiconductor particles generating electron-hole pairs. These pairs ultimately participate in the detoxification of contaminants. The major drawback of this process is the recombination of electrons and holes, as well as the emission of the absorbed energy as heat. This can prohibit the redox reactions (Chowdhury et al., 2014; Ab Aziz et al., 2018). The usefulness of integrating PC with electrochemistry (EC), by employing a photo-assisted electrochemical process (PEC), has been proved (Seibert et al., 2020). Through the PEC process, the semiconductor particles are immobilized on the conducting substrates. The problem of recycling particles and the involved cost can be then solved. Also, applying a positive potential can drive the photogenerated electrons to the cathode, contributing to the separation of electron-hole pairs and production of oxidants; so, the photocatalytic efficiency is improved (Wang et al., 2011; Qin et al., 2016; Zou et al., 2020). The change of the oxidation state of the metals in the solution can occur through the electrolytic system (Williams,

2006). The feasibility of changing the redox of the metallic couples depends on the relative value of the redox potential (E) of the metallic couples, as compared with the conduction band (CB) and the valence band (VB) of the semiconductor (Chowdhury et al., 2014). Increasing the Redox potential (Eh) indicates that the redox status of the system is transformed from a low oxidizing level to a more oxidizing one. Although the thermodynamic importance of Eh has been doubted, studying systems under a range of redox levels is a prerequisite. This can help to better comprehend the fate and transport of metals in the environment (Williams, 2006). The control of Eh can play a decisive role during the electrolytic system. This is realized by influencing the reactions on the surface of the electrodes, the speciation and oxidation state of the metals and consequently, the redox behavior. Such a control is commonly a composite function of dissolved oxygen (DO) and pH control. It can be obtained by using convenient chemicals such as potential modifiers (Chimonyo et al., 2017). The chemical modifiers or reducing agents include agents to achieve the reducing conditions, as well as changing the oxidation/reduction reactions. Many chemicals have been utilized, such as sodium ascorbate, ascorbic acid, ammonium thiosulfate, hydroxybenzene and sodium borohydride (Williams, 2006). Among these chemicals, Sodium ascorbate (NaAsc) has been widely employed. This is because it is a mild reducing reactant with a redox potential of +0.39V. vs NHE. It can display a significant range of reducing conditions, serving as a rapid means to achieve several redox environments (Chatain et al., 2005). Sodium ascorbate has been proposed to be an appropriate redox reactant for the Eh control. Bai et al. (2016) have reported that copper-containing metal-organic nanoparticles (MONPs) are easily characterized via the Cu²⁺-mediated intramolecular reaction of the aspartate containing polyolefins in pure water. Therefore, in-situ, 2.5 mg of sodium ascorbate in 0.5 mL of water was utilized at 50 °C for 24 h to reduce Cu²⁺ to Cu⁺¹ in the MONPs. Berardo et al. (2016) investigated the effects of sodium ascorbate on the protein oxidation. According to the results, sodium ascorbate could affect protein oxidation in different ways. It could reduce the formation of malondialdehyde, acting as a pro-oxidant in the presence of metal ions. Pareuil et al. (2008) also

established several reducing levels using sodium ascorbate solutions. This was to investigate the solubilization of metallic elements from soil samples. The results displayed that metallic mobilization was extremely raised with decreasing the redox potential within a limited and so, critical range. [Chatain et al. \(2005\)](#) also studied the effect of the reducing conditions on the Arsine release from pollutant sites, manipulating Eh and pH in the soil slurries. The addition of different concentrations of sodium ascorbate supplied various reducing conditions (from -7 to +345mV vs. NHE). According to the removal technique utilized, conflicting data have been determined. For example, a simultaneous increase in the mobility of metals was observed when the redox potential Eh was increased and decreased. However, very few researchers have examined the impact of sodium ascorbate on the reducing conditions and the mobility of the metals in water. In this context, the main aim was to suggest a chemical experimental process originating from a range of redox conditions by adding different concentrations of sodium ascorbate. This was to understand the impact of the reducing conditions on the PEC efficiency in the organic and metallic agents' removal for the treatment of Tehran rainwater. Because of the complexity of using sodium ascorbate under the current experiments, to check the changes in the oxidation state, speciation and solubilization of metals, the Pourbaix (Eh/pH) diagrams could be drawn by applying the HSC Chemistry software. To investigate the behaviors and the relationships between quality parameters and contaminants, cluster analysis was employed. The removal mechanisms were assessed during the PEC process and their conformity to the results was obtained from the study of metal species. The secondary aim was to optimize the PEC conditions and the experimental design parameters. The monitored parameters were the redox potential, the gap between electrodes, and the concentrations of the electrolyte. They were chosen due to their influence on the purification performance of the PEC process. For the PEC process, the procedures were followed by using Ti/TiO₂ and graphite (Gr) as the electrodes. These electrodes have recently received much attention. In the current study, Ti/TiO₂ was selected due to such advantages as high oxidizing ability, nontoxicity, chemical stability, corrosion resistance and low cost. Its properties could

lead to apparent photocatalytic activity developments ([Zhou et al., 2015](#); [Shariffard et al., 2018](#); [Cheng et al., 2020](#)). Employing graphite as the cathode for oxygen reduction could lead to the generation of the hydrogen peroxide (H₂O₂). H₂O₂ serves a significant role as an electron acceptor. Thus, it can contribute to the separation of the electron-hole pairs and the increase of the production rate of radical hydroxyl (\cdot OH). This radical could be formed by the oxidation of water molecules (H₂O) or hydroxides ions (OH⁻) on the electron vacancy (a hole) ([Zhao et al., 2014](#); [Yao et al., 2019](#)). The current work is a comprehensive chemical study of rainwater using a reducing modifier, speciation and statistical analysis. The PEC performance was evaluated by using COD and Zn, Fe, Mn, Pb, and Cd metals (which commonly exist in rainwater) as the target compounds. The aim of the study was to simultaneously remove metal and organic pollutants from Tehran rainwater by employing the photoelectrocatalytic method and to assess the impact of Eh on the removal mechanisms. This study was carried out in Tehran, Iran, in 2020.

MATERIALS AND METHODS

Sampling of Tehran rainwater

The rainwater samples were collected from the Kan canal, in the south of Tehran, near Azadi Highway, in 2020. Kan canal gathers the rainwater from different areas of the city and flows along with various pollutants from the north to the south of Tehran. Thus, it could guarantee that our samples were typical, representing all kinds of contaminants existing in Tehran rainwater. Before collecting the samples by polyethylene containers, some intensive agitation was done to ensure the similarity of the tested samples. The samples were transferred to the laboratory and saved under cooling (4°C). They were analyzed; their chemical and physical quality parameters were measured before and after PEC treatment. The Tehran rainwater characteristics are shown in [Fig. 1](#).

Set-up and photo-assisted electrochemical experiments

The batch photo-electro-catalytic cell was according to [Fig. 2](#). Ti/TiO₂ served as a working (photoanode) electrode with 5.0 × 10 cm². Graphite with the same active area was used as a cathode. The electrodes were purchased from Chinese plants and

The photoelectrocatalytic process for the treatment of the urban rainwater

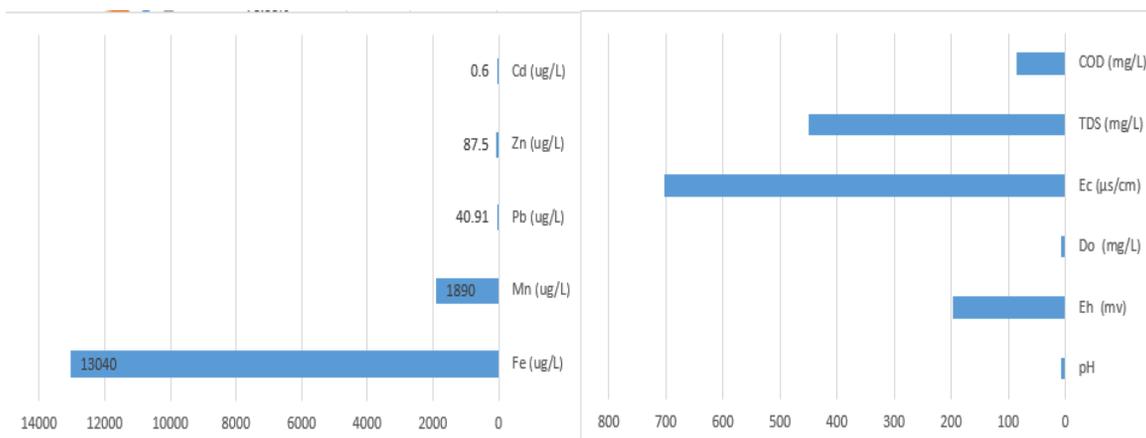


Fig. 1: Characteristics of Tehran rainwater in Kan canal in Tehran, Iran

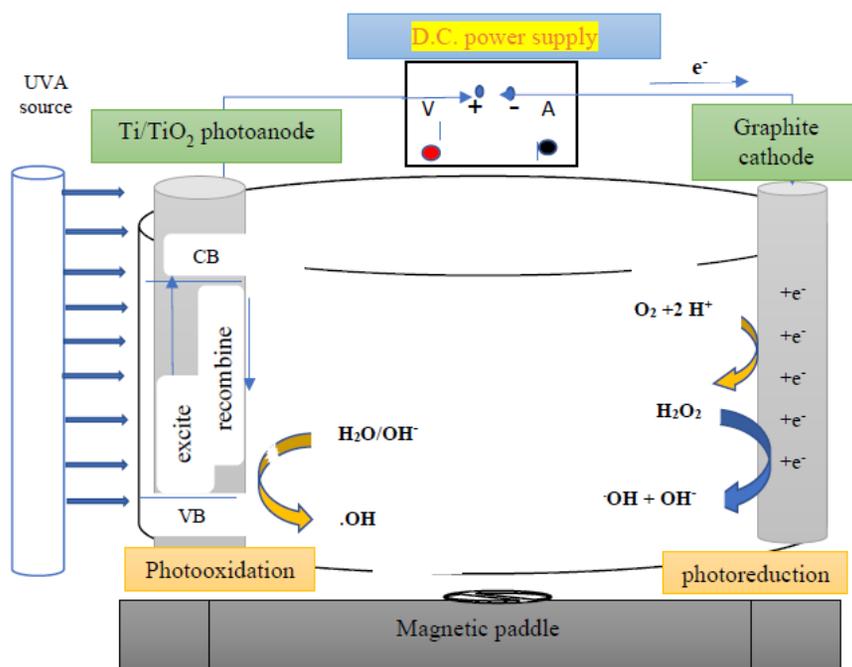


Fig. 2: Schematic diagram of the PEC reactor system

put in a Pyrex glass beaker and submerged in parallel. One anode/cathode potential (voltage) was applied between the electrodes (2.5 V). It was supplied by a DC-regulated power supply (UTP3704S UNI-T). A UVA lamp (Philips Actinic BL TL, 8 W) served as the light source; it was kept outside of the photo-cell. Its main wavelength was 380 nm. This could guarantee

providing the energy needed to overcome the band gap ($E = 3.2$ eV) of TiO_2 , as well as motivating the electrons and generating the electron-hole pairs for the oxidation and reduction reactions (Montenegro-Ayo *et al.*, 2019). The photo-anode was put 3 cm from the center of the UV lamp to avoid light attenuation. Doubly distilled water and alcohol (90 %) were used

before each experiment for electrodes cleaning. To reach the thermodynamic equilibrium conditions and to attain adsorption–desorption, a magnetic agitator was employed for 5 min for the solution stirring. This occurred without using any voltage. Also, the procedures were done in dark conditions and without any irradiation to prohibit the entry of the non UV lighting (Pareuil *et al.*, 2008; Cheng *et al.*, 2020). Although the experiments were performed at a laboratory temperature, the temperature of the solution after the PEC process was raised. This was because of the heat gained from the UV lamp.

To identify the condition of the typical system and examine the influence of the redox potential, NaCl concentration and the gap between electrodes on the photodegradation of the pollutants, two sets of tests were conducted. These sets could offer a chemical experimental method creating a different range of redox potential; it could also help to study the effect of the change of oxidation states on the metals purifications. Two tests were involved in the first set. They were achieved by fixing the anodic bias potential in each test. Every test had different gaps, but a specific redox potential. In the same order, two tests were included in the second set. In each test, the anodic bias potential was fixed. Every test had different concentrations of the NaCl electrolyte, but a specific redox potential. In the current study, NaCl was selected to be an electrolyte due to cheapness, availability, and its ability to increase the ionic strength. Most importantly, this was due to its capability to generate the holes, ·OH and reactive chlorine species (RCS) at the photoanode. They are strong oxidants and mediators for indirect oxidation (Vahidhabanu *et al.*, 2015; Zarei and Ojani, 2017; Komtchou *et al.*, 2020). The major characteristics of the photo-reactor were chosen as the desired parameters for the organic and metal removal, which were close to the literature (Liu *et al.*, 2016). In this work, each experiment was repeated twice and each value was the average of two repeated analyses.

Analytical techniques and chemical measurements

The indispensable parameters at the sampling site were analyzed; these included temperature (by a normal mercury thermometer), pH, Eh, DO and electrical conductivity (EC) (via a portable multi-parameter probe). COD, which is a significant index for controlling the wastewater purification

and estimating the water quality, was measured in duplicate, according to the standard methods APHA. To monitor the COD change, a spectrophotometer (DR 5000- Hach) was employed. An inductively coupled plasma-mass spectrometer (ICP-MS) was also chosen to quantify the concentration of the metals (Fe, Mn, Zn, Cd, and Pb). This was because of its distinctive properties, such as high thoroughness, suitable detection limits and its ability to measure many elements at the same time (Wilschefski and Baxter, 2019). Each test typically began with 2L. After 120 minutes, 0.1 L of the samples was separated and kept in the sulfuric acid solution (98%) (Until pH < 2) for the measurements of COD. On the other hand, 1 L samples were separated and kept in nitric acid (until pH < 2) for the measurements of metals. The metals and COD were removed from rainwater samples by the PEC purification. So, the remaining concentrations of these pollutants in the solution were measured after a 120 min interval. The COD and metals removal efficiency (RE) were determined using Eq. 1 (Le *et al.*, 2019).

$$RE(\%) = \left(\frac{C_0 - C_t}{C_0} \right) * 100 \quad (1)$$

Where, C₀ is the initial concentrations and C_t is the final concentrations (after PEC purification) of the pollutants.

By applying the HSC chemistry software (version 5.1), we could provide detailed information on the solubility class, chemical species, and the oxidation state of the electrodeposited metals on the electrodes. This software needs distinct parameters such as pH, T, Eh, pressure, and the concentration of the element to draw Eh/pH diagrams (Alabdeh *et al.*, 2019). The chemical dominant speciation diagrams of the rainwater after 120 min of treatment and during different redox potentials were drawn. Employing multivariate statistical methods such as cluster analysis could help to classify a large number of water quality factors into meaningful hydrochemical clusters. In the cluster analysis, no assumption was made about the number of groups or their structure and each sample could form a cluster itself (Johnson and Wichern, 2002). In this work, it was used to assess the validity of the results obtained from the Eh/pH diagrams. According to the correlation coefficient and similarities in the behavior of the physicochemical parameters and the pollutants,

Table 1: The summary of the experimental conditions and development of several quality parameters of rainwater (after PEC) with the initial anodic potential (2.5V); Ec (703 $\mu\text{s}/\text{cm}$); pH (7.3); electrode material: Ti/TiO₂-Gr

Experiment	Test	Initial redox potential (mV)	Gap between electrodes (cm)	NaCl electrolyte (g/L)	Eh mV	pH	DO mg/L	Ec $\mu\text{s}/\text{cm}$
1 st set	Test 1	+50	6	Not added	152	6.76	4.53	933
		+50	9	Not added	99	6.78	4.47	937
		+50	12	Not added	96	6.81	4.3	941
	Test 2	-50	6	Not added	-35	4.28	3.32	973
		-50	9	Not added	-44	4.67	3.29	976
		-50	12	Not added	-65	4.68	2.01	1063

the treatment mechanisms that took place through PEC were examined. Also, for effective water quality management, the parameters affecting the pollutant removal were identified. The Weighted pair group (WPG) approach, which is the most popular clustering technique in the environmental works, was employed in the current study. It was chosen due to its ability to identify the clustering tendencies among several samples (Karbassi *et al.*, 2008(a)).

RESULTS AND DISCUSSIONS

The PEC efficient was affected by the redox potential and the gap between electrodes. To investigate the influence of different values of the redox potential and the gap between cathode and anode on the degradation of COD and metals by the PEC method, the first set was accomplished. This set had the same anodic potential (2.5 V), EC (703 $\mu\text{s}/\text{cm}$) and pH (7.3). Each test of the current set involved three separated analyses. Every three analyses had various gaps of 6, 9 and 12 cm, and the same redox potential +50 or -50 mV, in the tests 1 and 2, respectively. Table 1 summarizes the obtained experiments. These could show the impact of various redox potentials (different reduction conditions) and gaps between electrodes on EC, Eh, pH and DO. As a result, their impact on the oxidation-reduction reactions and mobility of the studied metals could be verified as well.

By examining the information in Table 1, it could be seen that in the test 1, with increasing the gap, pH was slowly raised from 6.76 to 6.81 because of the small decrease of DO from 4.53 to 4.3 and the considerable decrease of Eh from 152 to 96 mV, as well as the rise of conductivity from 933 to 941 $\mu\text{s}/\text{cm}$. Likewise, in the test 2, with increasing the gap,

pH was increased from 4.28 to 4.68 because of the decrease of DO from 3.32 to 2.01 and Eh from -35 to -65 mV, as well as the rise of conductivity from 973 to 1063 $\mu\text{s}/\text{cm}$. By inspecting the values in tests 1 and 2, Eh values, especially for the gap of 12 cm, were declined as the initial redox potential was decreased. It could adversely affect the degradation rate of COD and some metals such as Fe, Pb, and Mn by discouraging the oxidizing potential (Chimonyo *et al.*, 2017). A decline in the Eh values led to a great increase of the mobility of specific metals due to the prevalence of the reduction conditions in the system (Haratifar *et al.*, 2011). In the six samples, the pH values at the end of the reactions were measured. They were decreased after treatment. The final pH depended on the initial redox potential: the lower the redox potential, the lower the pH, with clear variations between +50 and -50 mV. This could be attributed to the addition of sodium ascorbate to the samples before the PEC occurrence (Pareuil *et al.*, 2008). The decrease of pH values could also be because of the increase of acidic products such as oxalic acid and formic acid generated by oxidizing the organic compounds (Li and Liu, 2005; Yurdakal *et al.*, 2020). To get Eh= +50 and -50 mV conditions, 0.05 and 0.19 g/L sodium ascorbate were added, respectively. When more sodium ascorbate was added, the decrease of Eh, pH and DO was higher. So, Eh values could vary with varying the concentrations of the reluctant in solution (Li and Bishop, 2004). Based on Fig. 3, the variation of rainwater parameters with the variation of experiment variables could be observed. Also, the different removal performance of COD and metals by the PEC method is clearly shown.

Based on Fig. 3, the degradation rate of the pollutants was gradually decreased with increasing the

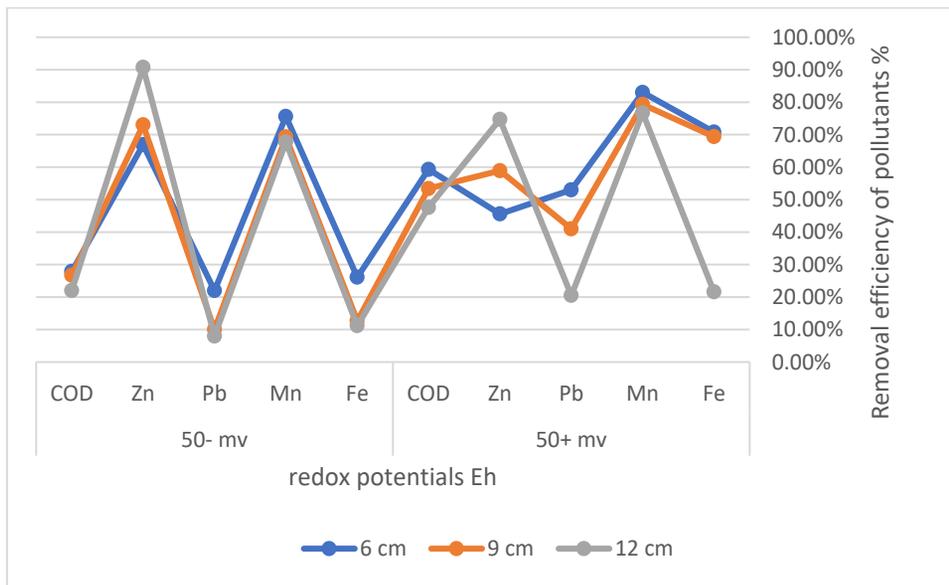


Fig. 3: Removal effectiveness of the pollutants by the PEC treatment according to the first set of analysis

gap between electrodes. This could be attributed to the decreasing current density with the gap decrease (Biswal *et al.*, 2019). The experiments showed that Fe, Mn, Pb and COD concentrations were increased with decreasing the redox potential and raising the gap. The remaining concentrations of COD changed from 35 to 45 mg/L, of Fe from 3794 to 1071 µg/L, of Mn from 320 to 440 µg/L, and of Pb from 19.2 to 32.5 µg/L by raising the gap from 6 to 12 cm, respectively. This proposed that the most suitable effect of the integrated photo- and electrochemical catalysis for COD, Fe, Mn and Pb occurred at the positive redox potential (+50 mV). This was demonstrated by the fact that the Eh decrease indicated that the oxidation status of the rainwater samples had been altered from a higher oxidizing level to a lower oxidizing one. This caused the decline of the species oxidation. The opposite was also true (Haratifar *et al.*, 2011). At this point, it is important to highlight that the oxygen whose concentrations in test 1 were higher than those in test 2, especially in the gap of 6 cm, is an electron acceptor. It serves an important role in the separation of the electron-hole pairs. It can react with two atoms of hydrogen and two electrons, being reduced to H₂O₂. That is the main reason for the production of ·OH. So, oxygen is responsible for the

rise of the photooxidation rate of COD and Fe, Pb, and Mn in test 1 (Barrera-Díaz *et al.*, 2014; Ensaldor-Rentería *et al.*, 2018). Therefore, the positive redox potential of +50 mV and the cathode and anode gap of 6 cm could be suggested in the current work for the efficient removal of the COD, Fe, Pb and Mn. This was in agreement with the results obtained by Li and Bishop (2002) for the COD removal. Their findings showed that the redox potential and COD removal were following a good linear relationship. Additionally, Chimonyo *et al.* (2017) gave an account that at a constant pH, raising the Eh values resulted in a considerable increase in the removal efficiency of COD. By using appropriate chemicals, an increase of Eh in the range of 500–600 mV was achieved. The redox potential of -50 mV and the gap of 12 cm were suggested in this work for the Zn removal. This could be related to the low Eh and DO resulting from adding extra sodium ascorbate. As a result, sodium ascorbate elevated the reduction conditions in these experiments. The decrease in the Eh values can be illustrated by the fact that the operating foundation of a potential modifier is to produce the electrons required to reduce species. This has been confirmed by the findings of several researches (Smith and Pierson, 1979; Williams, 2006; Herbel *et al.*, 2007).

Table 2: The summary of the experimental conditions and development of several quality parameters of rainwater (after PEC) with the initial anodic potential (2.5V); gap (12 cm); pH (7.3); electrode material: Ti/TiO₂- Gr

Experiment	Test	Initial redox potential (mV)	Gap between electrodes (cm)	NaCl electrolyte (g/L)	Eh mV	pH	DO mg/L	Ec μ s/cm
2nd set	Test 1	+50	12	0.4	97	7.58	5.16	2180
		+50	12	0.65	88	7.65	4.69	3150
		+50	12	1	20	7.69	4.45	3360
	Test 2	-50	12	0.4	-20	6.15	2.85	1613
		-50	12	0.65	-28	6.59	2.67	2720
		-50	12	1	-33	6.88	2.1	3900

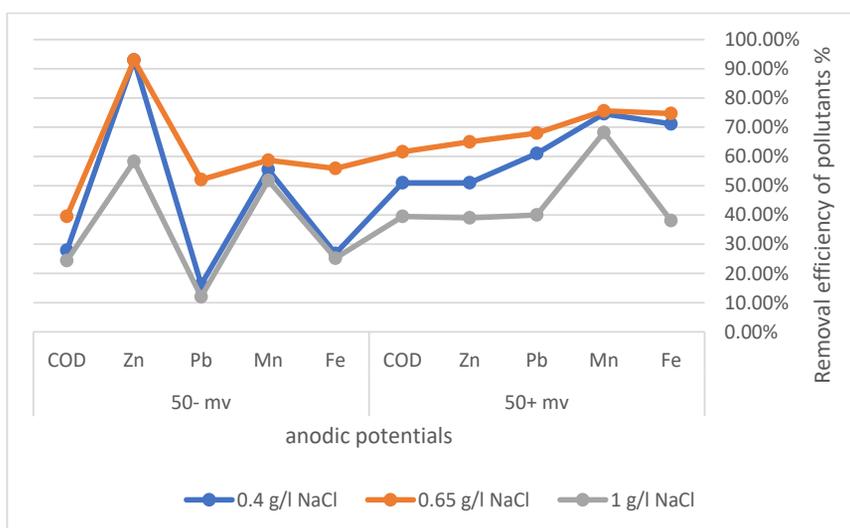


Fig. 4: Removal effectiveness of the pollutants by the PEC treatment according to the second set of analysis

The PEC efficiency affected by the redox potential and NaCl electrolyte concentrations

To investigate the impact of various values of redox potential and the concentration of electrolyte on the COD and metals removal by the PEC process, the second set was accomplished. This set had the same gap (12 cm), anodic bias potential (2.5 V), and initial pH (7.3). The two tests of the current set involved three analyses. Each of three analyses had various NaCl concentrations of 0.4, 0.65, and 1 g/L (showing variation in the initial ionic strength (EC) and the same redox potential of +50 or -50 mV in tests 1 and 2, respectively). The experimental conditions are presented in Table 2.

According to the data in Table 2, the conductivity after PEC treatment ranged from 1613 to 3900 μ s/cm. In test 1, by adding a concentration of NaCl, pH

was increased from 7.58 to 7.69. It was because of the decline of DO from 5.16 to 4.45, Eh from 97 to 20 mV, and the increase of conductivity from 2180 to 3360 μ s/cm. Also, in test 2, by adding a higher concentration of NaCl, pH was raised from 6.15 to 6.88 because of the decline of DO from 2.85 to 2.1, Eh from -20 to -33 mV, and the increase of conductivity from 1613 to 3900 μ s/cm. By comparing the data from tests 1 and 2, Eh and pH values were decreased as the sodium ascorbate concentrations were increased, which could adversely affect the removal rate of COD, Fe, Pb and Mn by reducing the oxidizing potential of the PEC technique. Conversely, it could improve the reduction potential of other metals such as Zn and Cd considerably; as shown in Table 2 and Fig. 4. When DO values in test 2 were lower than those in test 1, the change of Eh to the negative values occurred in

test 2. This linearly decreased COD, Fe, Mn, and Pb removal efficiencies in test 2. Also, an increase of the Zn removal efficiency in test 2 could be noticed. The decrease of the oxidation efficiency and the increase of the reduction efficiency could be attributed to the decrease of the redox potential. Based on Fig. 4, the experiments showed that the remaining COD, Pb, Fe, and Mn concentrations in test 1 declined, but the remaining Zn concentrations were elevated during the positive redox potential.

Based on Fig. 4, the increase was slight for Fe, Mn and Pb removal in test 1, with Eh= +50 mV; as a result, the higher the NaCl concentration, the greater the pollutant removal rate. This could be due to the increase of the ionic strength and production of the oxidants reagent electro-produced from the supporting electrolyte such as HOCl, ClO⁻, Cl[•] and Cl^{•-}. They were formed by the oxidation of Cl⁻ on the holes. They had the ability to indirectly oxidize the organic compounds and metals. They could also activate and speed up the migration rate of electrons and mass transfer between electrolyte and the surface of the electrode (Yao *et al.*, 2019). Similar findings were reported by Vahidhabanu *et al.* (2015), who proved the efficiency of adding 1 g/L NaCl as a supporting electrolyte to the PEC photo-reactor for pharmaceuticals oxidation. On the other hand, when the concentration of NaCl was raised from 0.65 to 1 g/L, the COD, Fe, Mn, Pb, and Zn removal

was reduced. These phenomena could be attributed to the competition between Cl⁻ and H₂O or OH⁻ to oxidize on the photogenerated hole. It could reduce the generation of ·OH. Also, it could be attributed to the RCS ability to participate in the decomposition of H₂O₂. They could negatively affect H₂O₂ and ·OH generation. This could lead to the loss of the oxidation potential of PEC, especially on the cathode (Park *et al.*, 2009). It is worth mentioning that the low concentrations of pollutants in the Tehran rainwater affected the efficiency of the PEC process. This is because of their impact on the number of oxidants produced on the anode and cathode. These pollutants could act as electron donors and acceptors, actively separating hole- electron pairs (Subramaniam *et al.*, 2019). The redox potential of +50 mV and the NaCl concentration of 0.65 g/L were recommended in this work for organic agents, Fe, Pb and Mn removal, with the same NaCl concentration, but a redox potential of -50 mV was found for the Zn removal. It should be noted that in tests 1 and 2 of the current set, adding 0.65 g/L of NaCl could make the studied samples reach the typical conductivity.

The HSC Chemistry results and the speciation of the studied metals in Tehran rainwater

Based on the Eh/pH diagrams obtained by applying the HSC chemistry software (Figs. 5 and 6), when the rainwater samples had an acidic pH, all of

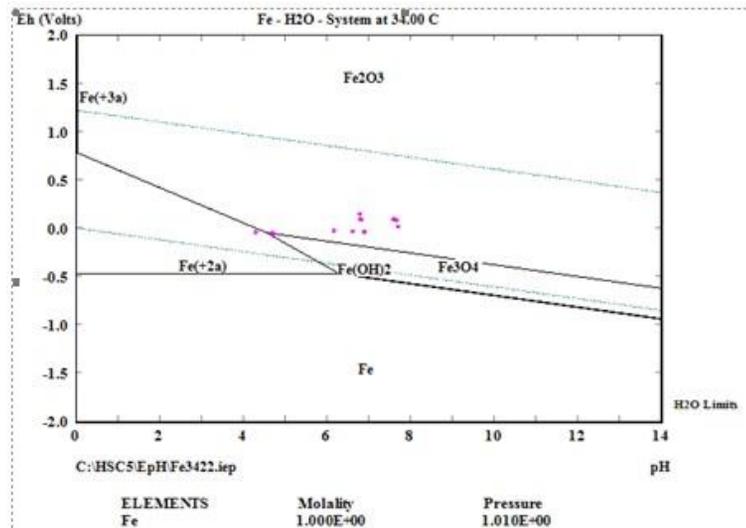


Fig. 5(a): Speciation of Fe in different Eh values in Tehran rainwater samples after the PEC process

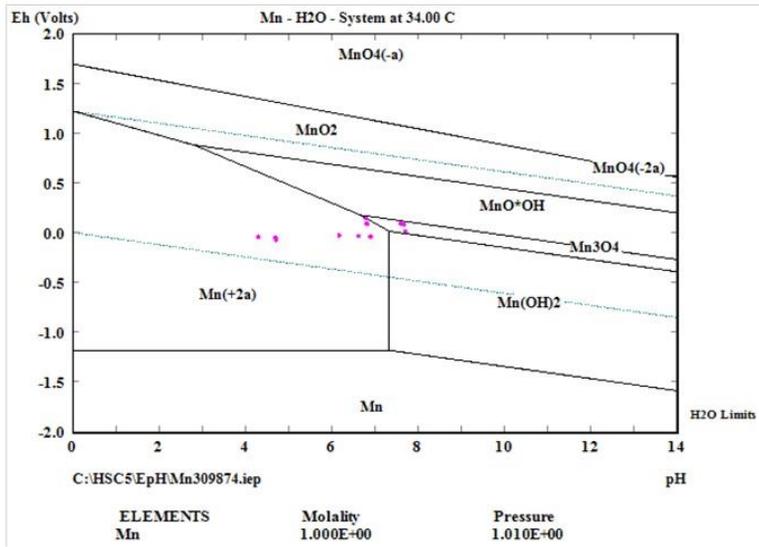


Fig. 5(b): Speciation of Mn in different Eh values in Tehran rainwater samples after the PEC process

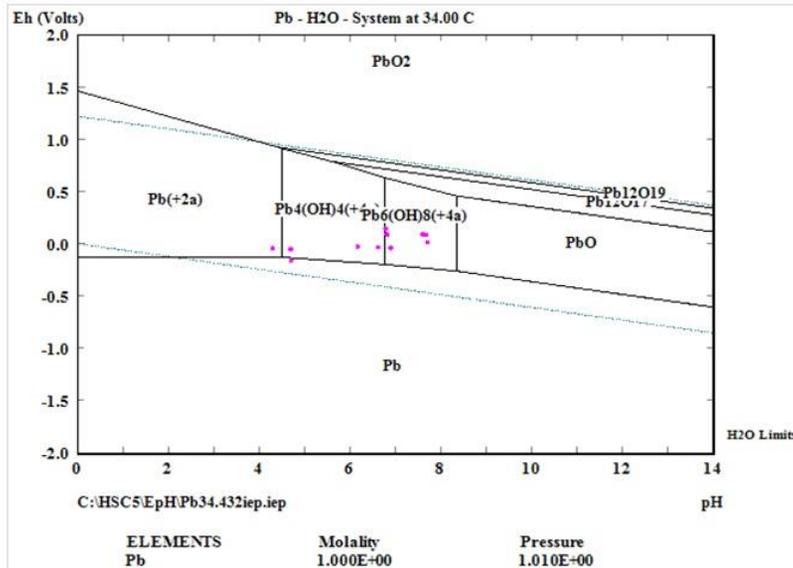


Fig. 5(c): Speciation of Pb in different Eh values in Tehran rainwater samples after the PEC process

the studied metals were present as bioavailable and soluble ions: Fe^{2+} , Mn^{2+} , Pb^{2+} , Zn^{2+} and Cd^{2+} . In the acidic conditions, especially lower than the pH_{pzc} of TiO_2 (point of zero charge = 6.3), the adsorbent surface of TiO_2 was positively charged. A repulsion strength between cationic compounds and the photo-catalyst

electrostatically predominated. This could reduce the removal extent. The polarity of the TiO_2 photo-anode surface changed according to the pH values. Hydroxyl groups on the surface of TiO_2 underwent a suilibrium reaction. It can be explained by Eq. 2 (Wahyuni et al., 2015; Zarei, 2019).

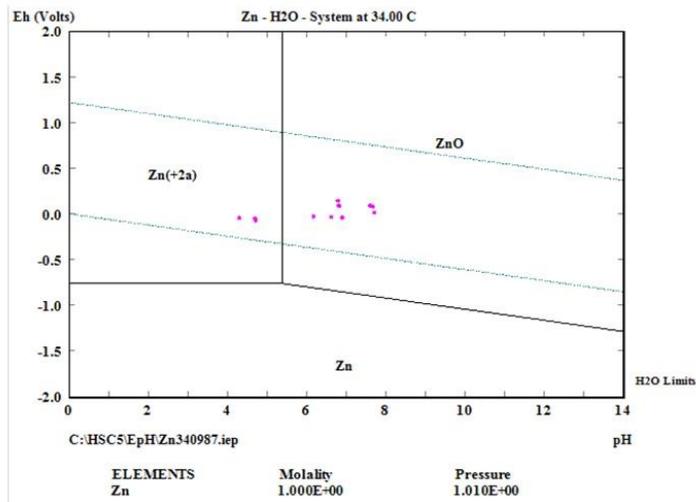


Fig. 6(a): Speciation of Zn in different Eh values in Tehran rainwater samples after the PEC process

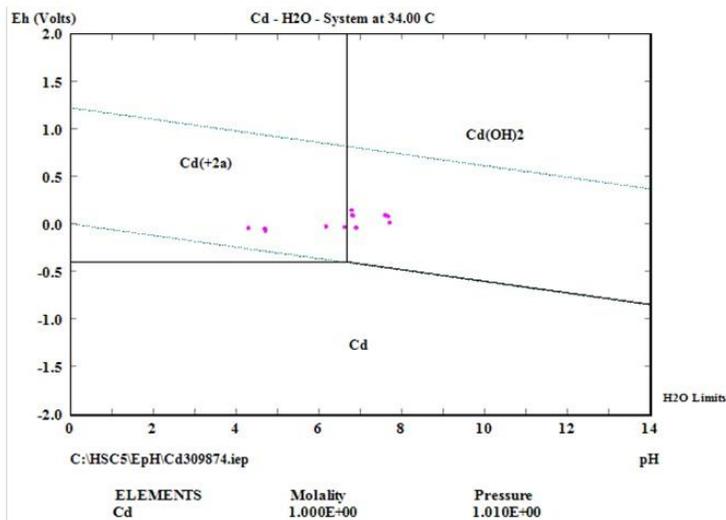
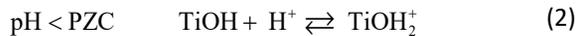


Fig. 6 (b): Speciation of Cd in different Eh values in Tehran rainwater samples after the PEC process



In this situation, these ions, which have divalent oxidation states, cannot be absorbed by the positive TiO_2 surface. According to Eq. 2, TiOH on the TiO_2 surface is transformed to TiOH_2^+ . So, TiOH is not enough to provide the electrons and $\cdot\text{OH}$ needed to remove the pollutant through the PEC process. In alkaline conditions and higher pH values, especially near pH_{pzc} , TiOH was abundantly formed. Here,

adsorption, by charging the TiO_2 surface with negative charge, was enhanced. The equilibrium reaction of the hydroxyl groups can be explained by Eq. 3 (Zarei and Ojani, 2017).



According to Figs. 5 and 6, Fe^{2+} , Mn^{2+} and Pb^{2+} at high pH were oxidized to iron oxide (Fe_2O_3), (Fe_3O_4), manganese oxide (Mn_3O_4), (MnO_2), manganese

oxohydroxide (MnO^*OH) and lead oxide ($\text{Pb}_{12}\text{O}_{19}$, $\text{Pb}_{12}\text{O}_{17}$); they were precipitated and converted to iron hydroxide ($\text{Fe}(\text{OH})_2$), manganese hydroxide ($\text{Mn}(\text{OH})_2$), lead hydroxyl complex ions ($\text{Pb}_4(\text{OH})_4(+4)$) and ($\text{Pb}_6(\text{OH})_8(+4)$). According to Figs. 5 (a), 5 (b), 5 (c), the dominant species of Fe, Pb, and Mn after PEC purification were Fe^{2+} , Fe_2O_3 , Pb^{2+} , $\text{Pb}_4(\text{OH})_4(+4)$, $\text{Pb}_6(\text{OH})_8(+4)$, Pb, Mn^{2+} and Mn_3O_4 . This could be due to the ability of Fe, and Mn to oxidize on the photo-anode by $\cdot\text{OH}$ at the positive Eh value (+50 mV). Pb not only existed as free and soluble ions, but also as $\text{Pb}_6(\text{OH})_8(+4)$, $\text{Pb}_4(\text{OH})_4(+4)$, and Pb that had an ability to precipitate on the surface of the cathode. In the case of Cd^{2+} and Zn^{2+} (Figs. 6 (a) and 6 (b)), at the high pH, they were reduced to Cd(s) and Zn(s) elements, precipitating as cadmium hydroxide ($\text{Cd}(\text{OH})_2$) and zinc oxide (ZnO). The speciation of Cd and Zn after the PEC process fell within Cd^{2+} , $\text{Cd}(\text{OH})_2$, Zn^{2+} and ZnO classes. This indicated the separation of these metals from rainwater by precipitation as happened in $\text{Pb}_6(\text{OH})_8(+4)$, $\text{Pb}_4(\text{OH})_4(+4)$, and Pb. In the rainwater treated by the PEC process, Cd and Zn never had the ability to oxidize by $\cdot\text{OH}$ or the hole. Also, they never had the ability to reduce even in the reducing conditions. This was because Cd^{2+} and Zn^{2+} had a negative standard reduction potential ($E^\circ = -0.403$ and -0.76V vs. NHE) to reduce to Cd^0 and Zn^0 . These potentials were just below (-0.5 V vs. NHE) of the conduction band of TiO_2 at pH 7. Cd^{2+} and Zn^{2+} reductions were not thermodynamically reasonable, thus demanding sacrificial agents at the beginning of the process (Chowdhury et al., 2014). The removal rate of Cd and Zn could be because of the reaction with OH^- ions and oxygen, respectively, and the precipitation on the graphite cathode. The adsorption and precipitation of these ions occurred on the cathode surface that had more electrons. The removal of the Cd and Zn present in the solution could be attributed to the pH value (>6) required, as represented in the speciation diagrams. These findings are in agreement with those obtained by Le et al. (2019). They had proved that Cd could not be reduced by a reduction on the surface of the photocatalyst; it could only be adsorbed. Although Zn and Cd were not reduced in the reduction conditions and at low Eh (-50 mV), these metals were removed at a high rate. These could be attributed to the increase in the ability of these elements to precipitate in anoxic conditions and the low Eh. Also, it has been proved

that in the oxidation conditions, they can be released into a solution (Biati et al., 2010). The decline of Fe and Mn concentrations was due to the photocatalytic oxidation. Also, a number of free ions remained in the reducing conditions. It has been proved that these metals are released in low amounts and oxidized in the high Eh. The low redox potential supported the decline of the insoluble iron and manganese oxides, resulting in the rise of iron and manganese solubility (Nadaska et al., 2018). The initial pH (7.3) was monitored in rainwater samples, making the absorption of cationic metals such as Fe and Mn on the negative TiO_2 surface possible. The standard reduction potentials of Fe^{2+} and Mn^{2+} ($E^\circ = -0.77$ and -1.7V vs. NHE) were to anodically oxidize to Fe^{3+} and Mn^{3+} (El Jamal, 2008; Khan et al., 2018). These potentials were less positive than (3.5 V vs. NHE) of the valence band of TiO_2 at pH 7. It indicated the thermodynamic ability of the photo-generated holes and $\cdot\text{OH}$ to oxidize Fe^{2+} and Mn^{2+} on the TiO_2 surface. On the other hand, the standard reduction potential of Pb^{2+} ($E^\circ = -0.67\text{V}$ vs. NHE) to oxidize to Pb^{4+} should be noted (Wahyuni et al., 2015). This means that photo-generated holes and $\cdot\text{OH}$ can oxidize Pb^{2+} . However, Pb^{2+} in Tehran rainwater after the PEC purification existed as free ions, precipitate hydroxide and element. These findings, therefore, seem to indicate that by adding sodium ascorbate, the anodic potential of 2.5 V and the obtained redox potentials of +50 mV and -50 mV were not appropriate for oxidizing the Pb^{2+} ions on the TiO_2 surface.

The results obtained by cluster analysis and MVSP software

This study attempted to investigate the findings obtained from Eh/pH diagrams by employing the cluster analysis method. This method by drawing a dendrogram could be a helpful tool to interpret the relationship between the studied parameters (DO, Eh, TDS, EC, and pH) and pollutants and their behaviors. The clustering results are graphically represented in the form of a dendrogram (Fig. 7).

As shown in Fig. 7, the dendrogram has two individual clusters, namely, A and B. Cluster "A" consists of Eh, Zn, DO and pH. It presents that pH and DO had a relatively strong (0.88) correlation coefficient and joined to Zn and Eh in lower (0.72 and 0.53) correlation coefficients. These parameters had a strong relationship, such that Eh and DO were

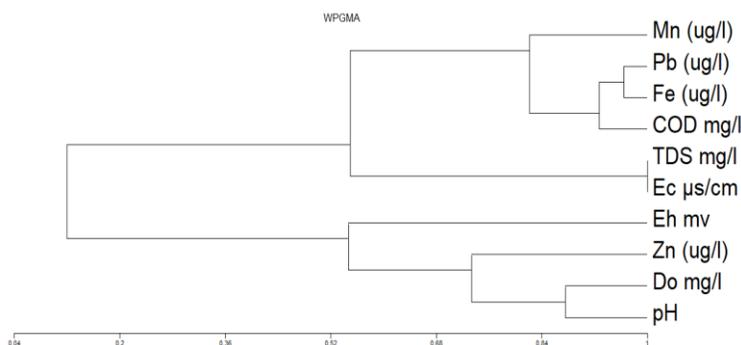


Fig. 7: The dendrogram obtained by the MVSP of Tehran rainwater after PEC treatment

decreasing along with the decline of pH. This was due to the addition of sodium ascorbate. It was in agreement with the results of one study (Deng, 1997). Also, they had a strong relationship with the Zn element. It means that pH and DO (with a higher impact), and Eh (with a lower impact) can control the Zn precipitation during the PEC method. This is also in agreement with the findings of some researches (Karbassi et al., 2008(b); Karbassi et al., 2011). These studies, based on cluster analysis, proved that pH could affect the Zn removal. Cluster “B” involves COD, Fe, Mn, Pb, TDS and EC. It showed that TDS and EC had the highest (1) correlation coefficient. Fe and Pb were joined in a lower (0.95) correlation coefficient. They were connected to COD and Mn in the correlation coefficients of 0.89 and 0.8. In this cluster, TDS and EC (as a result of NaCl concentrations) could control the Mn, Fe, COD, and Pb removal by the PEC method. COD, Mn, Fe, and Pb had similar behaviors. This is also in agreement with the findings of this study. Fe, Mn, Pb, and COD had the ability to oxidize by $\cdot\text{OH}$ through PEC photooxidation. All these mentioned metals in this cluster had higher removal efficiency in the positive Eh value = +50 mV, and a higher ability to release in the negative Eh value = -50 mV. This was the opposite of what happened to Zn; this could explain why Zn fell into a cluster by itself. Importantly, the two clusters could be joined at a positive and low (0.11) similarity coefficient. This means that the investigated pollutants in each cluster were influenced and controlled by the parameters in the other cluster through the PEC process. Cd concentrations before and after treatment were low, so Cd was not involved in the dendrogram.

CONCLUSION

Based on the results of the current study, one can conclude that the experimental arrangement is a powerful way to optimize the PEC conditions. Also, it can provide a better understanding of the parameters affecting the purification performance. This research emphasizes the significance of the knowledge of the Eh for correct risk estimation. Further, the ability of chemical potential modifier, sodium ascorbate, to create various redox environments in the rainwater samples was studied. The findings showed that the increase in the reducing conditions could display a decrease in the mobility of Zn and Cd. Conversely, the decline of these conditions could lead to a decline in the mobility of Fe, Mn and Pb during the PEC treatment. This study made an attempt to confirm the results by studying the speciation and mobility of the studied metals and by investigating the relationship with the behavior of them through cluster analysis. The results also proved the effectiveness of these approaches for assessing the removal mechanisms of the PEC purification. The mechanisms present in the removal of the COD, Fe and Mn from the Tehran rainwater, was oxidation in the positive Eh values, forming Fe_2O_3 and Mn_3O_4 on the photoanode. However, in the removal of Cd and Zn, the mechanism was precipitation in the negative Eh values, forming insoluble $\text{Cd}(\text{OH})_2$ and ZnO , as realized by electrolysis. The Cd removal rate was low because of its low concentration in Tehran rainwater. The results of the dendrogram were identical to those obtained from the Eh/pH diagrams. Eh and pH had a strong effect on the studied pollutants, which had a similar behavior through changing Eh values during

PEC, except Zn. The present work tried to present an advanced treatment technique for the organic and metallic agents' removal. PEC process can also be employed for the removal of other metal ions such as Cr, Cu, Hg, etc, as well as other pollutants from Tehran rainwater.

AUTHOR CONTRIBUTIONS

Gh. Ebraheim conducted the literature review, planned the experimental design, and analyzed and interpreted the information, in addition to writing the manuscript. A.R. Karbassi and N. Mehrdadi supervised and helped in the literature review and the manuscript preparation.

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CONFLICT OF INTEREST

The authors declare no potential conflict of interest regarding the publication of this work. In addition, the ethical issues including plagiarism, informed consent, misconduct, data fabrication and, or falsification, double publication and, or submission, and redundancy have been completely observed by the authors.

ABBREVIATIONS

<i>OH</i>	Hydroxyl radical
$\mu\text{s}/\text{cm}$	Microsiemens per centimeter
<i>CA</i>	Cluster analysis
<i>CB</i>	Conduction band
<i>Cd</i>	Cadmium
$\text{Cd}(\text{OH})_2$	Cadmium hydroxide
<i>COD</i>	Chemical oxygen demand
<i>DO</i>	Dissolved oxygen
<i>EC</i>	Electrical conductivity
<i>Eh, E</i>	Redox potential
<i>eV</i>	Electron volt
<i>Fe</i>	<i>Iron</i>
Fe_2O_3	Iron oxide
H_2O_2	Hydrogen peroxide
<i>ICP-MS</i>	Inductively coupled plasma mass spectrometry
<i>Mn</i>	Manganese

Mn_3O_4	Manganese oxide
MnO_2	
<i>mV</i>	Mele volte
<i>MVSP</i>	Multivariate statistical package
<i>NaAsc</i>	Sodium chloride
<i>NaCl</i>	Sodium chloride
<i>NHE</i>	The standard hydrogen electrode
<i>OH⁻</i>	Hydroxides ions
<i>Pb</i>	Lead
<i>PC</i>	Photocatalyst
<i>PEC</i>	Photoelectrocatalytic
<i>pzc</i>	point of zero charge
<i>RCS</i>	Reactive chlorine species
<i>RE</i>	Removal efficiency
<i>TDS</i>	Total dissolved solids
<i>Ti</i>	<i>Titanium</i>
TiO_2	Titanium dioxide
<i>UV</i>	Ultraviolet
<i>VB</i>	Valence band
<i>WPG</i>	Weighted pair group
<i>Zn</i>	Zinc
<i>ZnO</i>	Zinc oxide

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