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Investigating the Level of Metal's Toxicity in Used Cell Phone Batteries by TCLP and WET Methods

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ABSTRACT

Introduction: Batteries are widely used in all kinds of electrical and electronic equipment. These batteries contain several metals that lead to the leakage of metals into the soil and underground water in the burial places, which pose serious risks to human health and the environment.

Materials and Methods: In this study, the concentration of 15 metals (Ag, Al, As, Ba, Cd, Co, Cs, Cu, Fe, Li, Mn, Pb, Sr, Zn, Ni) in different components of 7 used battery models was investigated using Waste Extraction Test (WET) and Toxicity Characteristic Leaching Procedure (TCLP) toxicity. The concentration of metals was measured by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Metal concentrations were compared with the United States Environmental Protection Agency (USEPA) and California Department of Toxic Substances Control (CDTSC) standards.

Results: The results showed that the average concentration of metals in both WET and TCLP methods was high, but the concentration of most metals in WET method was relatively higher than in TCLP method.

Conclusion: The results showed that the recovery of metals from batteries is necessary, moreover safe burial of batteries is essential to reduce environmental risks.

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Introduction

The widespread use of batteries in a variety of electrical and electronic equipment such as watches, calculators, cell phones, laptops, hearing aids, medical devices, toys, vehicles, etc. has made it difficult to find an area without the use of batteries [1, 2]. In batteries, metals such as As, Hg, Cd, Pb, Ni, Zn, Cu, Al, Co, and Mn are used as electrodes or to

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increase the life of batteries [3]; however, all these metals are detrimental to human health and able to make environmental risks[4, 5]. Environmental risks caused by uncontrolled disposal of used batteries are increasing worldwide. Used batteries contain various metals that can cause poisoning of leachate in sanitary landfills, emissions from waste incinerators, and ash left over from incineration and composting [3, 6, 7]. In landfills, metals have the potential to slowly seep into soil and groundwater or surface water due to pH reduction [6]. Due to the hazardous potential of metals in batteries for the environment and human health, recently, special attention has been paid to these waste products. The USEPA has classified batteries as hazardous waste. In Europe, there are strict laws that control the production, consumption, collection, recovery, and disposal of batteries [4, 7]. Various methods have been proposed and implemented by various regulatory agencies to investigate the toxicity of waste [8]. The TCLP is designed to simulate the worst leaching conditions that may occur if the waste is disposed of in a municipal solid waste (MSW) landfill. Also, the TCLP method is the main method used to determine the toxicity characteristics of electrical and electronic waste. In this method, acetic acid is used as an extraction fluid, which represents the conditions of organic acid produced by anaerobically decomposed waste in the landfill. This method is established by the US-EPA [8-10]. However, the California Department of Toxic Substances Control (CDTSC) also recommends the waste extraction method (WET) to measure the toxicity of E-waste [8]. TCLP and WET are used to simulate landfill scenarios and metal toxicity leakage from electronic waste such as batteries in laboratory conditions [11]. In each of the TCLP and WET methods, different washing solutions are used, as a result of which each method can identify the toxicity of some metals [12]. Toxic metals are used in the manufacture of batteries, are considered hazardous waste. On the other hand, burying batteries together with urban waste in burial sites can cause these metals to leak into water and soil and cause environmental pollution [11, 12]. Studies conducted on other electronic waste, such as Singh et al.'s study, which investigated the trend of metal toxicity in worn-out mobile phones, showed that the relative mass of toxic metals in worn-out mobile phones has increased over a decade. Moreover, the danger of toxicity in mobile phones have not decreased with the advancement of technology [13]. Chen et al., examined the toxicity caused by waste printed circuit boards (WPCBs) over a decade, using standard leaching tests; it showed that this type of waste is dangerous for human health and the environment, and with the advancement of technology, the use of precious metals such as gold has declined [14]. In the study by Seung et al., the potential effects of sources and toxicity of metals in electronic waste were examined; it demonstrated that the recycling of Pb, Ag, Cu, and Sb metals can affect the resources, and Pb, Ni, Hg, and Zn metals affect health [15]. Therefore, measuring the toxicity and number of heavy metals in used batteries is effective and necessary for planning of hazardous waste management and preventing environmental pollution.

The novelty of this study was about comparison between two methods to analyze metals. The purpose of this study is to investigate the toxicity level of heavy metal leakage in used batteries (coin battery, pen battery, lithium polymer battery) using TCLP and WET methods.

Materials and Methods

The used batteries were randomly selected from Yazd city, taking into account the variety of brands, the accessibility of batteries, and the selection of dominant batteries in the market which are used by people. Three types of batteries (coin battery, pen battery, lithium polymer battery) and a total of 7 batteries were selected. The specifications of these batteries and the corresponding codes are shown in Table 1. Code W1 to W7 corresponds to 7 batteries by WET analysis method and code T1 to T7 corresponds to the same 7 batteries by TCLP analysis method. Each of the collected batteries was broken into small pieces. For TCLP test, the batteries were broken about 9 mm, and for the wet test, the batteries were broken about 1 mm.

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Table 1: Characteristics of batteries used in the WET and TCLP

Code WET	Code TCLP	Battery type	Factory type	Model	Year of construction
W1	T1	Coin battery	MAXBII	MAXBII	-
W2	T2	Mobile	LG	BL-48TH	2014
W3	T3	Mobile	SAMSUNG	EB464358VU	2014
W4	T4	Mobile	HUAWEI	HB3543B4EBW	2013
W5	T5	Ni-Cd	Ni-Cd	ADO1SA2A	-
W6	T6	AA batteries*	C.F.L.	AA Ni-MH	-
W7	T7	AA batteries*	PANASONIC	P-130SCR	-

* AA: batteries is a single cell cylindrical dry battery of standard size.

In TCLP test, crushed samples (9 mm) were mixed with a buffer solution (mixed with 5.7 mL of glacial acetic acid and 64.3 mL of NaOH mol L^{-1}) at pH 5 in a 1-liter wide-mouth bottle with a solid-to-liquid ratio of 1:20. Then, this material was blended with a rotary shaker for 18 hours at a speed of 30 rpm. The mixed solution was passed through a filter paper under pressure with a pore size of 0.45 µm and stored in a plastic bottle for metal analysis. The concentration of 15 metals (Ag, Al, As, Ba, Cd, Co, Cs, Cu, Fe, Li, Mn, Pb, Sr, Zn, Ni) was measured by inductively coupled plasma emission spectrometry (ICP-OES). Concentration metals were compared with the standard US EPA for hazardous waste classification mg L^{-1} specified for 8 metals (Ag, Ba, Cd, Cr, Cu, Pb, Zn, Ni) [8].

For WET test, the crushed samples (1 mm) were mixed with a buffer solution (0.2 mol L^{-1} citric acid and 4 mol L^{-1} sodium hydroxide) to pH 5 with a ratio of 10:1 liquid (buffer) to solid (broken batteries). These materials were blended for 48 hours at a speed of 30 rpm using a rotary shaker. Then, they were filtered using a membrane as in TCLP method, and metal concentrations were measured by an ICP-OES device. The concentration of metals was compared with standard DTSC for hazardous waste classification mg L^{-1} ,specifying 8 metals (Ag, As, Ba, Cd, Cu, Pb, Zn, Ni) [8]. The graphical summary of WET and TCLP methods is shown in Figure 1.

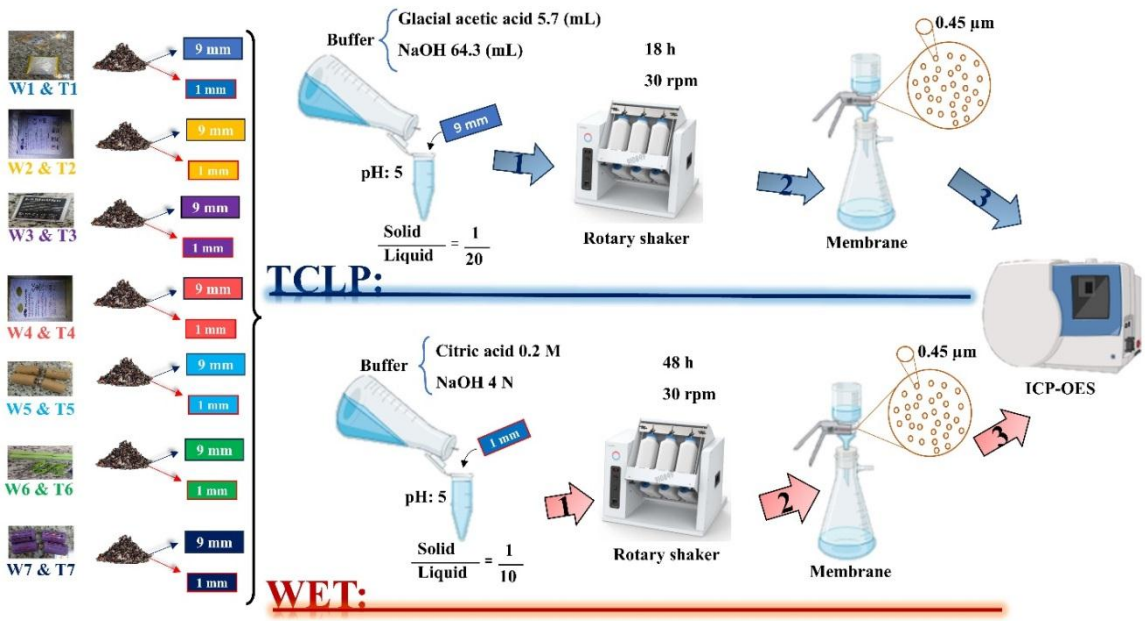


Figure 1: Graphical summary of WET and TCLP methods

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Results

Table 2 shows the average concentration of Metals leaked from the studied batteries by WET method. Also, to compare the average concentration of metals with standard values and determine the toxicity of these metals, the standard concentration of these metals based on the standards of DTSC Limits mg L^{-1} and US-EPA Limits for hazardous waste classification mg L^{-1} in Table 2 and Figure 2 show the comparison of the concentration of metals in the studied batteries by WET method. The results showed that the average of Cd in batteries coded W1, W3, W5, W6, and W7 mg L^{-1}, respectively equal to 81.20, 4.75, 8970, 12.47, 11560 was higher than the standard. The average of Cu mg L^{-1} in batteries coded W2, W3, and W4 (182.60, 50, and 469.80 mg L^{-1}, respectively) was observed to be higher than the standard. The average Pb mg L^{-1} in batteries coded W2, W4, and W6, respectively 5.83, 78.5, and 22.9 was higher than the standard. The average Zn mg L^{-1} in batteries coded W1 and W6 (4430 and 13530) was also higher than the standard. Finally, the average Ni mg L^{-1} in batteries coded W5, and W7, respectively 96.50, and 202.20 was above the standard limit.

Table 2: The average concentration of metals in the analysis of leakage from different batteries by WET

	Metals (mg L^{-1})														
	Ag	**As**	**Ba**	**Cd**	**Cu**	**Pb**	**Zn**	**Ni**	**Al**	**Cs**	**Co**	**Fe**	**Li**	**Mn**	**Sr**
Limits *	5	5	100	1	25	5	250	20	NL	NL	NL	NL	NL	NL	NL
ID															
W1	0.01	0.06	0.06	81.20	23.60	0.13	4430	2.40	1.77	0.09	2.07	11.83	445	1332	0.22
W2	0.01	0.06	0.57	0.32	182.60	5.83	16.88	1.20	1158	BDL**	2335	14.42	766	25.34	0.47
W3	0.01	0.33	0.22	4.75	50	0.40	5.11	1.20	2331	BDL	1355	12.69	937	10.25	20.24
W4	0.01	0.10	0.68	0.79	469.80	78.5	130	1.00	2139	BDL	2854	11.37	596	121	0.59
W5	0.01	0.05	0.03	8970	0.51	0.06	2.68	96.50	3.48	BDL	46	0.21	27.00	2.81	0.25
W6	0.04	0.07	8.22	12.47	2.72	22.9	13530	0.70	18.72	BDL	2.94	184.4	1.00	721	1.74
W7	0.01	0.04	0.04	11560	0.05	0.03	23.92	202.20	0.38	BDL	279	0.43	17.00	1.17	0.16

NL: No limit given by the California Department of Toxic Substances Control (CDTSC)
BDL: Below detection limit

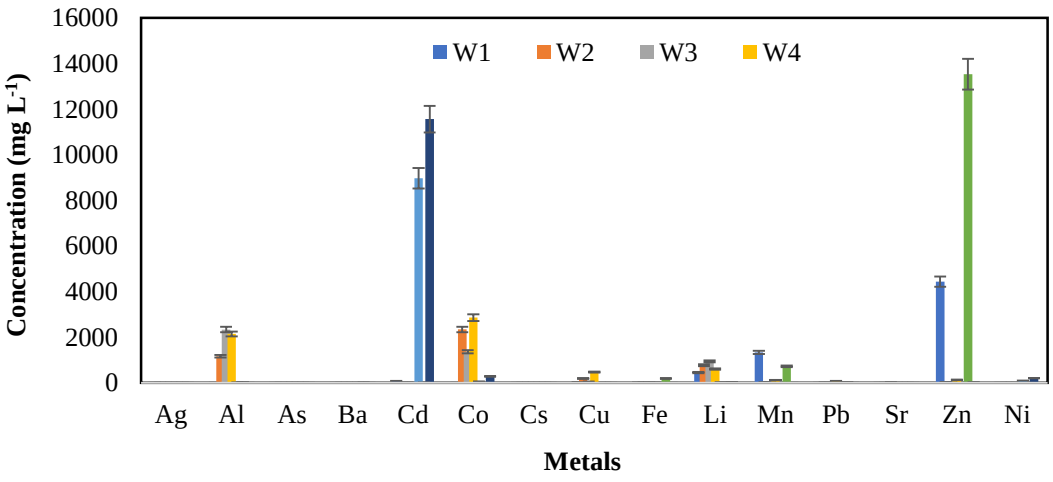


Figure 2: Comparison of metals concentration with WET

Table 3 shows the average concentration of metals leaked from the studied batteries by TCLP method. In addition, to compare the average concentration of metals with standard values and determine the toxicity of these metals, the standard concentration of these metals based on the standards of DTSC Limits mg L^{-1} and USEPA Limits for hazardous waste classification mg L^{-1}

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was provided in this Table. The results showed that the average Cd mg L^{-1} in all the studied batteries was higher than the standard. The average Co mg L^{-1} in batteries coded T2, and T4 mg L^{-1} 1146, and 1320 respectively was more than the standard. The average Cu mg L^{-1} in batteries coded T3, and T4 mg L^{-1} 764.90, and 60.20 respectively was higher than the standard. The average Pb mg L^{-1} in batteries coded T3, T6 189.9, and 6.53 mg L^{-1}, respectively was above the standard. The average Zn mg L^{-1} in batteries coded T1, and T6 mg L^{-1} 780, and 4050 respectively was also higher than the standard, and the average Ni mg L^{-1} in batteries with code T5 mg L^{-1} 39.6 was observed higher than the standard. Figure 3 shows the comparison of the concentration of metals in the studied batteries by TCLP method.

Table 3: The average concentration of metals in the analysis of leakage from different batteries by the TCLP

	Metals (mg L^{-1})														
	Ag	**Ba**	**Cd**	**Co**	**Cu**	**Pb**	**Zn**	**Ni**	**Al**	**As**	**Cs**	**Fe**	**Li**	**Mn**	**Sr**
Limits *	5	100	1	80	25	5	250	20	NL	NL	NL	NL	NL	NL	NL
ID															
T1	0.06	0.74	76.85	2.49	0.55	0.87	780	1.20	0.79	0.02	0.02	1.76	137	392	0.19
T2	0.01	0.12	6.86	1146	0.86	0.07	13.94	0.40	0.43	0.01	BDL	0.18	494	5.46	0.11
T3	0.06	0.13	10.15	8.18	764.90	189.9	3.08	17.6	74.55	0.02	0.01	0.06	298	895	0.03
T4	0.02	0.09	2.07	1320	60.20	0.81	3.22	0.10	48	0.01	BDL	0.12	387	5.06	0.21
T5	0.11	0.68	1964	4.03	0.45	2.74	0.52	39.6	0.27	0.01	BDL	0.05	21	0.52	0.06
T6	0.08	2.52	8.28	1.42	0.19	6.53	4050	3.10	0.20	0.02	BDL	0.08	1.00	81.68	0.8
T7	0.01	0.25	3038	7.73	0.07	0.98	6.95	12	0.14	0.01	BDL	0.06	7.00	0.31	0.05

NL: No limit given by USEPA
BDL: Below detection limit

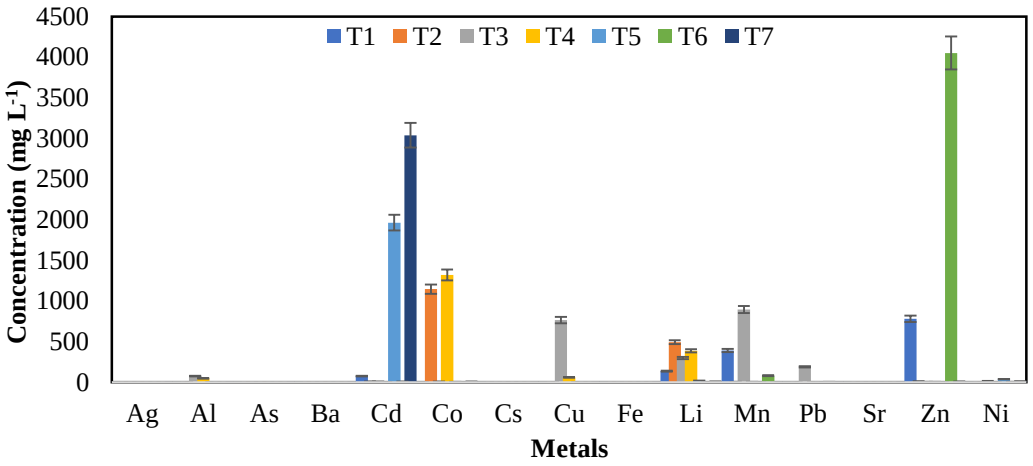


Figure 3: Comparison of metals concentration with the TCLP

Discussion

The concentration of leakage caused by heavy metals in used batteries was investigated using TCLP and WET toxicity evaluation methods. Limited studies have investigated the toxic leakage caused by metals in batteries by TCLP and WET methods. Karnchanawong et al., used leaching method and lysimeter tests and investigated the toxicity of 36 spent batteries that were buried in the landfill for up to 3 years. The results of their study showed that the concentration of leached metals was different in each type of battery, and their results also showed that most metals leaked from batteries included Mn and Zn. Based on the current study, the consumption of batteries together with urban waste can increase the amount of heavy metals in leachate

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[6]. In addition, in the study by Yadav et al., conducted by measuring the toxicity of metals from mobile batteries using TCLP and WET methods, the concentration of Pb metal with TCLP method and the concentration of Cu and Co metals with WET method was higher than the standard limit [12]. Similarly, in this study, the concentration of Cd mg L^{-1} in all the batteries studied by TCLP method and most of the batteries by WET method was higher than the standard limit (1 mg L^{-1}). The redox potential and the presence of other metals can lead to an increase in the concentration of Cd. Management of used batteries in terms of recycling valuable metals such as Cd is very important from two points of view. On the one hand, there is environmental concern that cadmium is especially important among metals because the roots of plants absorb it and the toxicity of Cd [16], and it is easily leached through the soil; on the other hand, it leads to kidney dysfunction, bronchitis, lung cancer, bone fragility, increased blood pressure, and digestive system disorders in humans [17, 18].

Based on TCLP test in Table 3, the concentration of Co metal in T2 (1146 mg L^{-1}) and T4 (1320 mg L^{-1}) samples was higher than the standard (80 mg L^{-1}). Co metal was quickly and easily converted into a soluble form [19], As a result, its concentration was higher than other metals.

Based on WET test, the concentration of Zn metal in W1, W6, T1, and T6 samples was above the standard limit (250 mg L^{-1}). Maragos et al. investigated the leakage of toxic metals in 24 types of waste cell phones. They measured the metals Cd, Cr, Cu, Fe, Hg, Ni, Pb, and Zn in plastic and LCD cell phones. Their results indicated that the concentration of these metals exceeds the standard levels [20]. Zn metal is a micronutrient necessary for growth and development of humans and other organisms. Zn metal has a regulatory, catalyst, and structural role in body [21, 22]. Studies show that high exposure to Zn can disrupt the nervous system and cause skin problems in humans. Exposure of plants to Zn leads to chlorosis in the plant, which results in reduced growth of the plant's roots, stems, and leaves [23, 24].

The concentration of Pb in some samples of T3, T5, T6, W2, W4, and W6 was higher than the standard limit (5 mg L^{-1}) in both TCLP and WET methods. Based on Pb toxicity studies, the nervous system would be affected as the most important side effect [25]. Other effects on human health included fatal encephalopathy in newborns, abortion in pregnant women, mental retardation in children, damage to the organs of sperm production, congenital paralysis, and deafness that occurs in case of abuse [10, 26, 27].

The results showed that in samples W5, W7, and T5, the concentration of Ni with TCLP and WET methods was higher than the standard limit (20 mg L^{-1}). Ni is known as an essential nutrient for some microorganisms, plants, and animal species. It is essential for proper growth and development of plants and plays a vital role in a wide range of morphological and physiological functions such as seed germination and productivity. However, at high levels, Ni alters metabolic activities of plants and inhibits enzyme activity, photosynthetic electron transport, and chlorophyll biosynthesis. Depending on the dose and duration of exposure, Ni can cause various effects on human health, such as contact dermatitis, cardiovascular diseases, asthma, lung fibrosis, and respiratory tract cancer [28].

In samples T3, T4, W2 and W4, the concentration of Cu metal with TCLP and WET methods was higher than the standard limit (25, mg L^{-1}). Cu is an essential nutrient for humans, animals, and plants, but high exposure to it can cause risks to human health such as cardiovascular risks and damages to immune system and bones [29, 30]. Toxic metals can also reduce or destroy the soil microbial population. The metals with the highest absorption in the soil include Cd, Cu, and Pb, which can lead to poisoning or death of the plant if the plant is exposed to these metals for a long time [31]. Therefore, it is necessary to manage such wastes in terms of reducing environmental effects.

Conclusion

TCLP and WET methods are suitable solutions for assessing the risk of metals in used batteries. The concentration and type of metals measured in

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the types of batteries studied are different. The results showed that in TCLP method, the concentration of Cd, Co, Cu, Pb, Zn, and Ni was higher than the standard, and in the WET method, the concentration of Cd, Cu, Pb, Zn, and Ni was higher than the standard. However, the measured concentration of most of the metals in WET method was higher than TCLP method, which indicated that WET method was more aggressive. The concentration of most of the metals was higher than the permitted standard set by the EPA and CDTSC; accordingly, used batteries are hazardous pollutants for the environment. It should be noted that sustainable management of used batteries has not yet been resolved, and increasing the lifespan of batteries and efficient collection is one of the sustainable management solutions. The results of the present study can help designers, manufacturers, and recyclers worldwide to reduce the use of toxic metals in batteries by raising awareness. Also, the results of the present study showed the increasing importance of monitoring the process of using materials for the production of batteries, that the increase in demand for the use of batteries in electronic devices, if not properly collected and recycled, can be a serious risk to human health and the environment. The present study calls for improving the international management of used batteries and encouraging designers and manufacturers to implement sustainable material management by replacing toxic materials with green materials in batteries.

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Conflict of Interest

The authors declared no conflict of interests.

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Ethical considerations

The authors obtained permission from the Ethics Committee of Shahid Sadoughi University of Medical Sciences

Code of Ethics

The code of ethics was IR.SSU.SPH.REC. 1397.098.

Consent to participate

Not applicable

Consent to Publish

Not applicable

Data availability

The supporting data are available from the corresponding authors upon reasonable request.

Authors' contributions

All the authors contributed to the study's conception and design. Material preparation, data collection, and analysis were performed by Ali Asghar Ebrahimi, Maryam Gholami, Maryam Khashij, Zahra Shamsizadeh, and Habibeh Nasab. The first draft of the manuscript was written by Maryam Gholami, Maryam Khashij, Habibeh Nasab, and all the authors commented on the previous versions of the manuscript. All the authors read and approved the final manuscript. Conceptualization was performed by Maryam Gholami; methodology by Keywan Weysi and Mohsen Pourafshar; formal analysis and investigation by Zahra Shamsizadeh and Habibeh Nasab; draft preparation by Maryam Gholami, Maryam Khashij, Zahra Shamsizadeh, and Habibeh Nasab; and review and editing by Ali Asghar Ebrahimi and Mohammad Hassan Ehrampoush.

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