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Extraction of Manganese Element from Electric Arc Furnace Steel Slag (EAFS) by Liquid-liquid extraction (LLE) method

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ABSTRACT

This research investigates manganese (Mn) extraction from Electric Arc Furnace Steel Slag (EAFS) by using the Liquid-liquid extraction (LLE) method. The chemical analysis was done on the slag using X-ray fluorescence, X-ray diffraction, and atomic absorption spectroscopy. This work consisted of two parts: the first was an extensive study of the effect of variables that can affect the leaching process rate for Mn element from slag (reaction time, nitric acid concentration, solid to liquid ratio, and stirring speed), and the second part evaluates the extraction of Mn element from leached solution. The results showed the possibility of leaching 83.5 % of Mn element from the slag at a temperature of 25°C, nitric acid concentration 2 M, time 90 min, S / L ratio 1/100, and stirring speed 700 rpm. 94.7% extraction of Mn was accomplished from nitric acid solutions by using Octyl Pyro Phosphoric Acid (OPPA) in kerosene at contact time for 12 min, 50%OPPA -kerosene, stirring speed 900 rpm, and organic to the aqueous phase (O/A) of 4/1. Kerosene was the most important diluting agent in extracting Mn, compared to benzene and toluene.

Keywords: Liquid-liquid Extraction, Electric Arc Furnace Steel Slag, Mn element.

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استخلاص عنصر المنغنيز من الخبث الفولاذي لفرن القوس الكهربائي بطريقة الاستخلاص السائل-السائل

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الخـلاصـــــــــــــة

في هذا البحث تم دراسة استخلاص عنصر المنجنيز من الخبث الفولاذي لفرن القوس الكهربائي (EAFS) باستخدام طريقة الاستخلاص السائل السائل .(LLE) تم إجراء التحليل الكيميائي على الخبث باستخدام مضان الأشعة السينية ، حيود الأشعة السينية ، والتحليل الطيفي للامتصاص الذري. يتكون هذا العمل من جزأين: الأول عبارة عن دراسة شاملة لتأثير المتغيرات التي يمكن أن تؤثر على معدل عملية الترشيح لعنصر المنغنيز من الخبث (نوع الحامض ،وقت التفاعل ، وتركيز حمض النيتريك ، ونسبة الصلب إلى السائل ، وسرعة التحريك) ، و الثاني هو تقييم استخلاص عنصر المنغنيز من محلول النض. أظهرت النتائج ترشيح 83.5٪ من عنصر المنغنيز الذي تم الوصول إليه عند درجة حرارة 25 درجة مئوية ، وتركيز حامض النيتريك 2 م ، والوقت 90 دقيقة ، ونسبة الصلب الى السائل 100/1 ، وسرعة التقليب 700 دورة في الدقيقة. تم الحصول على 94.7٪ من المنغنيز من محاليل حامض النيتريك باستخدام حمض الفوسفوريك أوكتيل بايرو (OPPA) في الكيروسين في وقت التلامس لمدة 12 دقيقة ، 50٪ كيروسين OPPA ، سرعة التحريك 900 دورة في الدقيقة ، والعضوية في الطور المائي 1/4. كان الكيروسين أهم عامل مخفف في استخلاص المنغنيز مقارنة بالبنزين والتولوين.

الكلمات الرئيسية: استخلاص سائل-سائل, الخبث الفولاذي لفرن القوس الكهربائي, عنصر المنغنيز

1. INTRODUCTION

The steelmaking process in electric arc furnaces generates up to 15 % of slag per ton of steel. Major components of steel mill slag include Ca-silicates, Ca-Al-ferrites, and molten oxides of calcium, iron, magnesium, and manganese. The composition of slag varies on the type of furnace and charge, the desired grade of steel purity, and the furnace operating conditions. Materials to be added to the steel melt directly before the end of the reheating process are not fully embedded in the slag structure, so they can be found in the slag as “free“oxides (CaO, MgO) **(Tsakiridis et al., 2008).** Manganese is one of the most important and common alloying elements. The addition of manganese improves the mechanical properties of the steel (tensile strength, hardness, hardenability, toughness). The presence of manganese also helps to eliminate detrimental sulfur **(Borovsky et al., 2012).** Ferromanganese is a very common alloying input, but it is expensive.

Moreover, after adding the liquid steel, it cools down the melt. This results in higher energy consumption. It is possible to achieve partial ferromanganese savings by reducing manganese from the MnO-bearing slag in the electric arc furnace, for example, by adding cheaper manganese ores and wastes from manganese production, etc. **(Borovsky et al., 2012).** Thanks to this, the fluidity of EAF slag could be improved too. The ideally suitable option could be the utilization of existing Mn from the EAFS charge and reducing MnO within the de-phosphorized steel melt in the decarburization stage **(Jung, 2003).** MnO is known as a basic substance and that is why it does not form stable compounds in the EAFS of basic character. This oxide is very similar to FeO, so sum (%MnO + %FeO) is often used within steelmaking slags. MnO is more basic than FeO, and the activity of MnO in the slag increases with the basicity. In contrast, the activity of FeO in the slag behaves in the opposite manner **(Mohd,2015).** The manganese oxide is unstable. It greatly depends on the temperature, i.e., the increase in temperature results in MnO decomposition.

Alumina has no adverse effect on Mn yield. Silica reacts with MnO and thus lowers Mn yield. The diffusion of Mn from metal to the slag-metal interface is the rate-limiting step in the kinetics of manganese oxidation **(Borovsky et al., 2012).** Oxidizing effect of FeO is even accelerated with basicity growth **(Yusuf et al., 2013).** The reduction rate of manganese oxide is intensified by increasing MnO activity in the EAFS and a rise in temperature **(Borovsky et al., 2012).** Many methods have been used for the extraction of elements from ore. These treatment methods are solvent extraction, ion exchange, bioremediation, precipitation and coagulation, membrane filtration, and adsorption **(Gunatilake, 2015)**. Liquid-liquid extraction (LLE), sometimes called solvent extraction, is a common process used to separate the concentrating metals selectively. Where LLE is conducted utilizing an organic extractant dissolved in an organic solvent. This approach is the most effective and attractive for separating metals because, in this method, the separation is almost complete compared with the precipitation method. The operating time is much less compared to the ion-exchange method **(Muharrem and Kaplan, 2019).** This research aims to exploit the waste of electric arc furnaces to recover manganese by metallic methods to reach the identification of process variables that are better from locally available raw materials. The exploitation of solid and liquid waste by metallurgical methods does not solve the problem of dangerous pollution as it occupies large land areas. Still, it is also an important source of minerals.

2. EXPERIMENTAL

2.1 Materials

The representative working sample was the Iraqi geological survey that provided the steel slag. The sample was dried, crushed, and sieved, and a particle size fraction of 150–63 μm was selected as powder particle size for the subsequent experiment. The drying of sieved samples was done in an oven at 100 °C. These samples were brought to ambient temperature and were kept in well-dried plastic jars. The chemical analysis of the representative working sample is shown in **Table. 1.** The Mineralogical composition was obtained by powder X-ray diffraction (Shimadzu 7000 model) to define the mineralogical structure, which is illustrated in the X-ray diffraction pattern **Fig. 1.** The XRF analysis of bauxite ore was carried out in the Iraqi-Germany laboratory, College of Geology, at the University of Baghdad. The chemical analysis was achieved by X-ray fluorescence (Shimadzu 1800, XRF). The atomic absorption spectroscopy type (nova AA 350). It was used to determine the dissolved Mn element in the solution at the laboratories of Ibn-Sina state Company. XRD pattern confirms that the main mineral phases of the steel slag sample match the XRD pattern, which shows that the main mineral phases of the steel slag sample contain manganese bound with silica ($MnO_2.SiO_2$), and alumina ($MnO_2.Al_2O_3$), with the presence of manganese alone in small proportions. As for the oxides of iron, calcium, and magnesium, despite their presence in proportions (7.1, 7.87, and 14.8), respectively, as shown in **Table. 1**. They do not appear as crystalline peaks, and this may be because of the calcium silicate ($CaO.SiO_2$) and ($FeO.SiO_2$) formed during the melting process are fused with each other.

Table 1. Chemical analysis of steel slag.

SiO_2 %	Al_2O_3%	MgO%	Mn%	CaO%	Fe_2O_3%
32.56	3.2	14.8	24.7	7.87	7.1

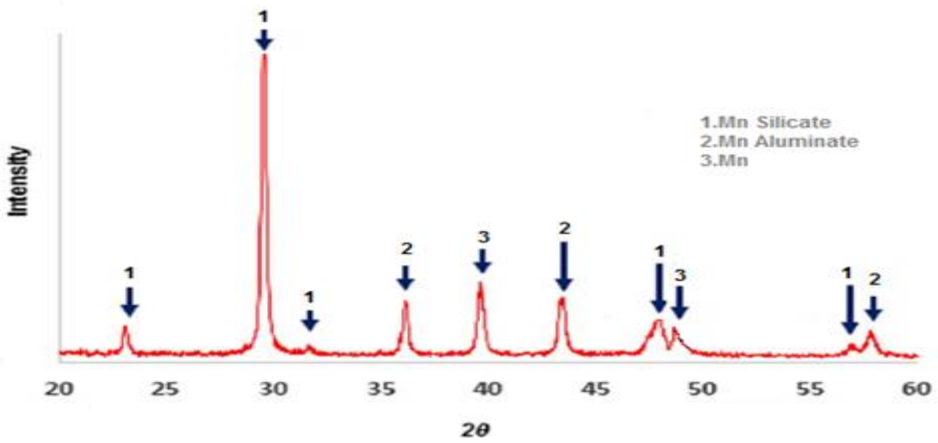

Figure 1 . XRD pattern of steel slag.

2.2 Procedure

Leaching experiments were conducted at atmospheric pressure using a beaker set in a thermostat water bath. In the leaching process, Nitric acid solution was mixed with a steel slag sample and leached at a certain temperature for a specific time. Subsequently, the residue was removed by filtration. The amount of Mn in the leaching filtrate was analyzed by atomic absorption spectroscopy. The leaching efficiency of the Mn element was determined as a function of leaching time, nitric acid concentration, liquid-solid ratio (L/g), and stirring speed. The leaching efficiency % was calculated by the following equations **(Marouane et al., 2019):**

$$L\% = (C1 \times V)\ (Co \times W) \times 100$$

Where:

L%: percent of leaching efficiency.

$C1$: concentration of a metal in solution in g/l.

Co: concentration of a metal in solid in wt%.

V: volume of leaching solution in l.

W: weight of solid sample in gm.

The solvent extraction technique was employed to separate the element transferred from the aqueous to the organic phase. The extraction percentage (E%) reflects elements' separation and extraction degrees. An organic phase of the mixture (Octylpyro phosphoric acid /OPPA) was used as an extraction agent dissolved in the diluent. The present compound was diluted using kerosene, benzene, and toluene. The course of the extraction experiment and the effect of parameters, like types of the diluted agents, concentrations of extraction agent, contact time, and organic/aqueous phase ratio, were studied. The extraction percentage (E) was calculated by the following equations **(Chang et al., 2016):**

$$E\% = \frac{[Me]org - [Me]ag}{[Me]ag}$$

[Me]aq and [Me]org are the metal ions concentrations in the aqueous and organic phases. E is the extraction percentage.

3. RESULTS AND DISCUSSION

This work consists of two parts: the first is an extensive study of the effect of variables that can affect the leaching process rate for Mn element from steel slag (reaction time, nitric acid concentration, solid to liquid ratio, and stirring speed), and the second is the evaluation of the extraction of Mn element from leached solution.

3.1 Influence of the Type of Acid upon the Leaching

The influence of the type of acid (HNO_3, H_2SO_4, and CH_3COOH) with a concentration of (1 M) on the Mn element leaching was studied with a contact time of 30 min, the temperature of 25°C, solid/liquid (S/L) ratio (1/3 g/ml) and stirring speed of 300 rpm. The obtained results are presented graphically as a relation between total leached percentage (L%) and acid type in **Fig.2.** HNO_3 has a more significant effect than other acids, and this is probably because the nitric acid is strong and has a relatively small molecular weight, and this might be anticipated for having a fast diffusion rate in comparison to other acids in the process of leaching **(Muna et al., 2020).** Thus, nitric acid has been chosen for the upcoming experiments.

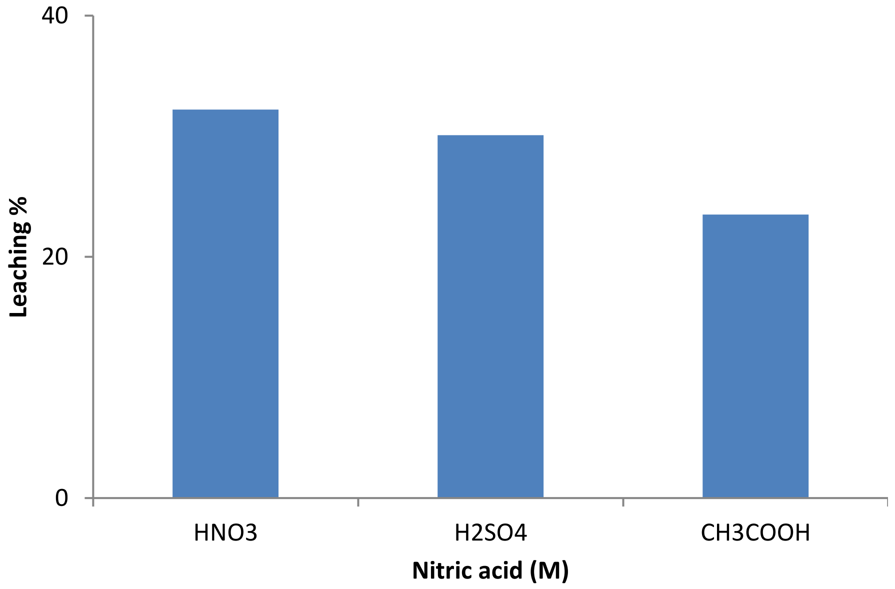

Figure 2. Effect of acids concentration on the leaching of Mn element.

3.2 Effect of nitric acid concentration on leaching

Under the experimental condition of reaction temperature 25±1°C, liquid/solid ratio 3:1, reaction time 30 min, and ore particle size 150-63 µm, the effect of nitric acid concentration on the element leaching result was investigated. The acid concentrations used in the experiments ranged from 1 to 2M. Experimental results are shown in **Fig.3.** It can be seen that the leaching of Mn element increased from 32.2 to 40.4 with the increase in acid concentration from 0.2 to 2M. This behaviour may be attributed to the acid being a strong acid and has a relatively small molecular weight; this might be anticipated for having a fast diffusion rate.

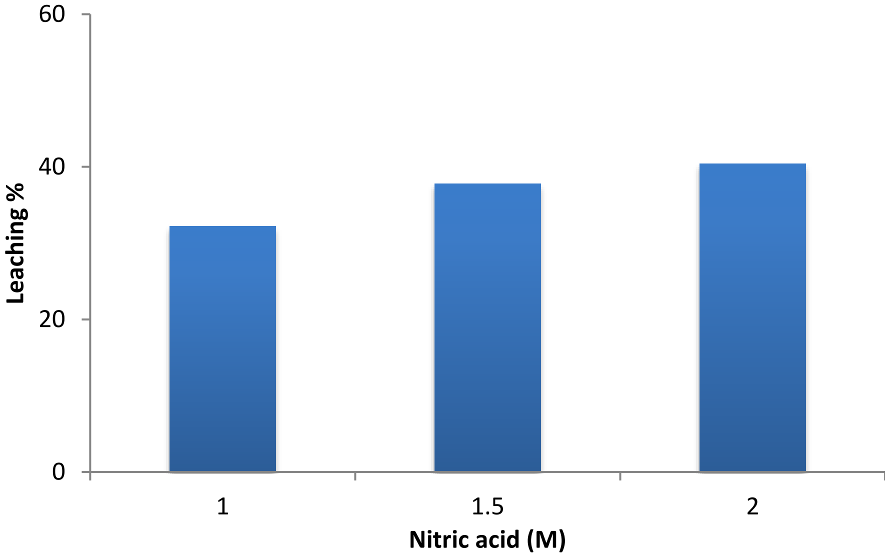

Figure 3. Effect of nitric acid concentration on the leaching of Mn element.

3.3 Effect of contact time on leaching

Within the conditions of ore particle size 63-150µm, reaction temperature 25ºC, solid to liquid ratio (1/3 g/L), and nitric acid 2 M, a series of experiments were implemented to examine the impact of reaction time on the efficiency of leaching the element. **Fig.4** provides the results of the effect of contact time on Mn element leaching efficiency. The increase in contact time is leading to a higher leaching efficiency. Leaching efficiency increases sharply at the reaction time of 30 min up to 90 min. However, the increase in leaching efficiency indicated in the period (from 90 to 120 min) only minor augments in leaching recovery, showing that the leaching reaction reached the equilibration at 90 min. Thus, considering the leaching economy, the major required leaching time should be close to 90 min.

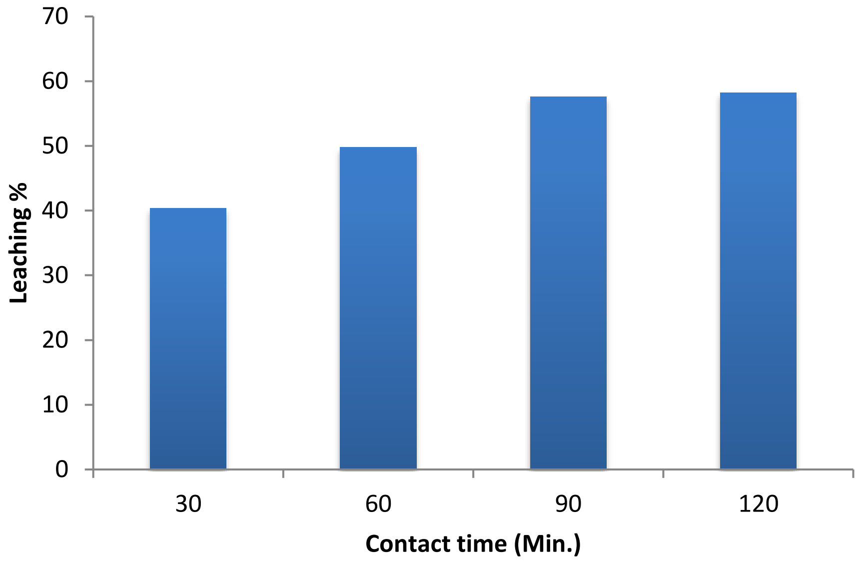

Figure 4. Effect of contact time on the leaching of Mn element.

3.4 Effect of stirring speed on leaching

The effect of agitation speed on percentage leaching is studied under constant temperature at 25°C, and 3:1 ratio of liquid to the solid phase, reaction time 90 min, ore particle size 150-63 µm, nitric acid concentration 2M. The result is presented in **Fig.5**. Results are provided in **Fig. 5**; the leaching of the Mn element increases gradually at speeds between 300 to 700 rpm. However, when increasing the speed to more than 900 rpm, the leaching efficiency decreases. During the leaching process, the heterogeneous reaction occurs at the interface between the phases of solid and liquid, at the boundary between two phases, and the diffusion layer is created. When considering the solid in the aqueous phase, such a layer includes a stationary aqueous layer. The diffusion layer might be thinned through excessive stirring, yet not totally removed, in which the leaching effectively elevated with the increase in stirring speed for 900 rpm. Increasing the stirring speed causes an increase in leaching efficiency because of the suspension of mineral particles and a decrease in the thickness of the mass transfer boundary layer on the particle's surface. While the noted lower efficiency of leaching with a higher stirring rate of more than 900 rpm might be ascribed to the aggregation of the granules as a result of the collision that has resulted from the high speed, this reduced the dispersion of the granules in the solution **(Yuhong, et al., 2017).**

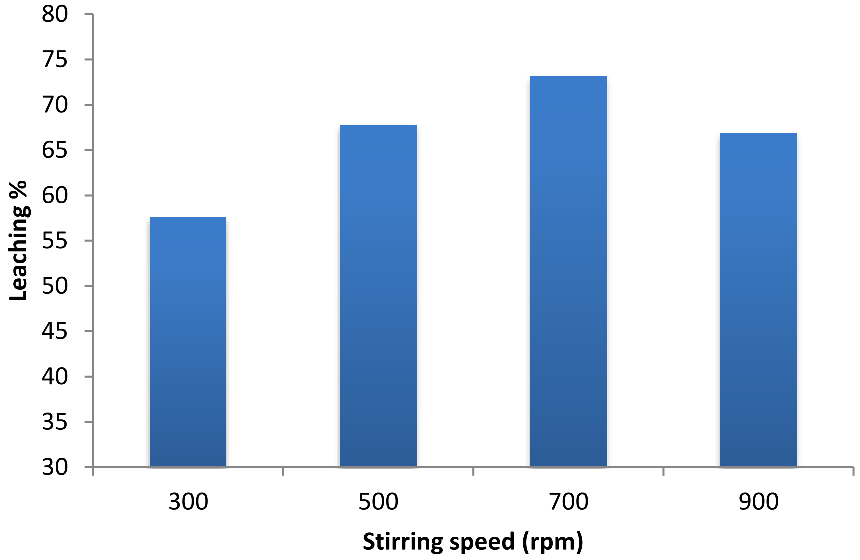

Figure 5. Effect of stirring speed on the leaching of Mn element.

3.5 Effect of solid/liquid ratio on leaching

The results of these experiments are illustrated in Fig.6. The following liquid to solid ratios was used: (1:1, 2:1, 4:1, 8:1, and 15:1 L/g), with the constant conditions: stirring speed 700 rpm, temperature 25°C, and 90 min reaction time**.** It can be concluded that the (L %) increases as the liquid to solid ratio increases, where the highest percentage of leaching obtained is at 15:1, reaching 83.5%, while the lowest leaching reached 66.6 % at 1:1 L/g. The increase in (L%) is due to the diffusion of ore particles within the solution when the liquid to solid ratio increases **(Marouane et al., 2021).** This process helps prevent aggregations and ease mixing the solution with the slag particles, thus increasing the reaction rate. This behavior is in agreement with that recorded by **(Meshram et al., 2014).**

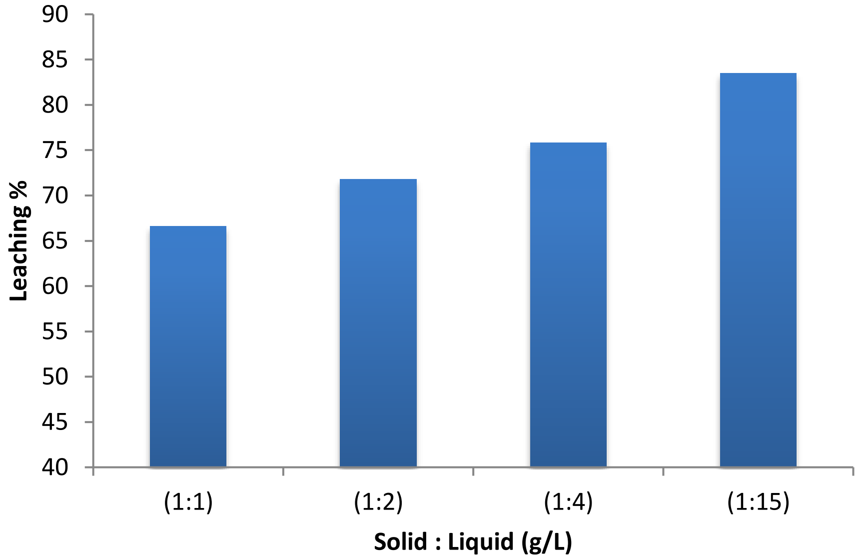

Figure 6. Effect of Solid to liquid on the leaching of Mn element.

3.6 Effect of diluents types on extraction element by OPPA

The extractant of OPPA was prepared by diluting 40 % with the appropriate diluent to a final volume of 100 ml. Three diluents were selected, i.e., toluene, benzene, and kerosene. The extraction experiment was performed at a contact time 10 min, (O/A) ratio of (1/1), and 400 rpm stirring speed, in addition to the concentrations of OPPA of 30%. The findings obtained are shown in **Fig.7.** It is found that the distribution ratio using kerosene as diluent has higher values than the other diluents in the case of using OPPA as extractant. Regardless of the utilized extractant, the total ion extraction tends to be high in the kerosene compared to toluene and benzene. The separation process used aliphatic diluents was the best comparison with aromatic diluents. The extraction of elements was high with kerosene as diluent compared with benzene and toluene, which give lower extraction due to lower solubility of the extracted species in such diluents. The aliphatic diluents come with a low dielectric constant compared to aromatic diluents (the dielectric constant for benzene was 2.28, for toluene 2.38, while for kerosene was 1.8) **(Dongchan et al., 2014).** Diluents are having less dielectric constant exhibit greater efficiency of extraction **(Chunlei et al., 2014).**

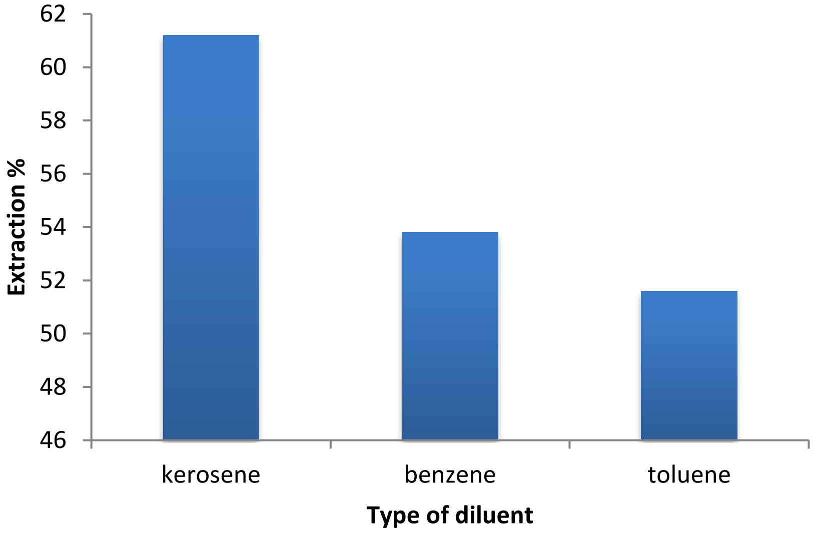

Figure 7. Effect of the diluents on the extraction of Mn.

3.7 Effect of OPPA concentration on extraction

Mn element has been extracted from the aqueous phase to the organic one, which involves 30-60 % OPPA concentrations tested on the elements' extraction efficiency. The mixture was subjected to agitation for 10 minutes at a temperature of 25°C, aqueous: organic ratio (A: O = 1:1), and a 400 rpm stirring rate. The results are displayed in **Fig.8.** The OPPA concentration values in kerosene are considered an influencing factor in the extraction of the element. There was an increase in the extraction effectiveness of elements with concentration to reach a maximum value of 50%. Also, there was a decrease in extraction effectiveness after such value. The increase in concentration after 50% decreased the dilution related to OPPA in kerosene that decreased its capability for extraction elements **(El-Didamony et al., 2012).**

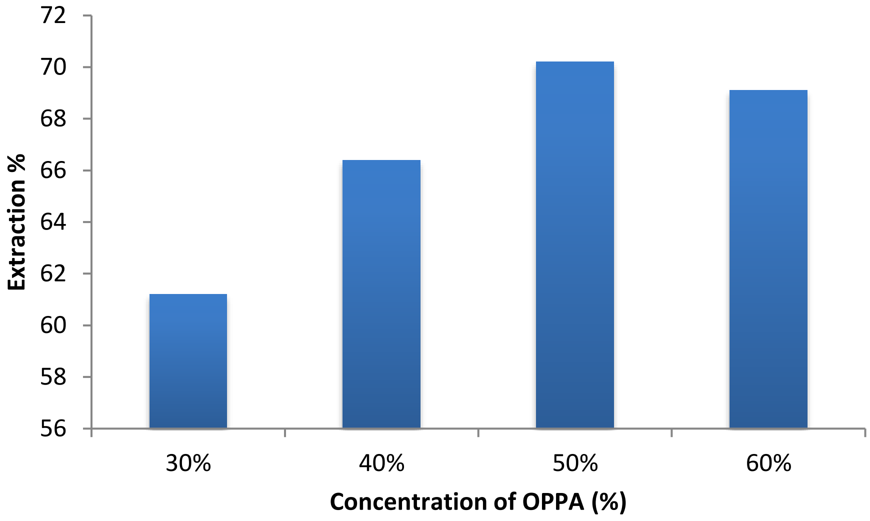

Figure 8. Effect of the concentration of OPPA on the extraction of Mn.

3.8 Effect of contact time on extraction

The highest time conducted in extracting Mn element 74.5% by OPPA was 15 min, from many other studies of changing time (8, 10, 12, and 15) min. **Fig. 9** shows the time effect on the extraction of the Mn element by OPPA. The O/A ratio was constant at 1/1and OPPA concentration at 50%, the temperature of 25°C, and the stirring speed was 400 rpm. **Fig. 9** shows that the contact times have a small effect, reflecting that Mn quickly reached equilibrium within 12 minutes. Therefore, a contact time of 12 minutes was selected for the latter experiments.

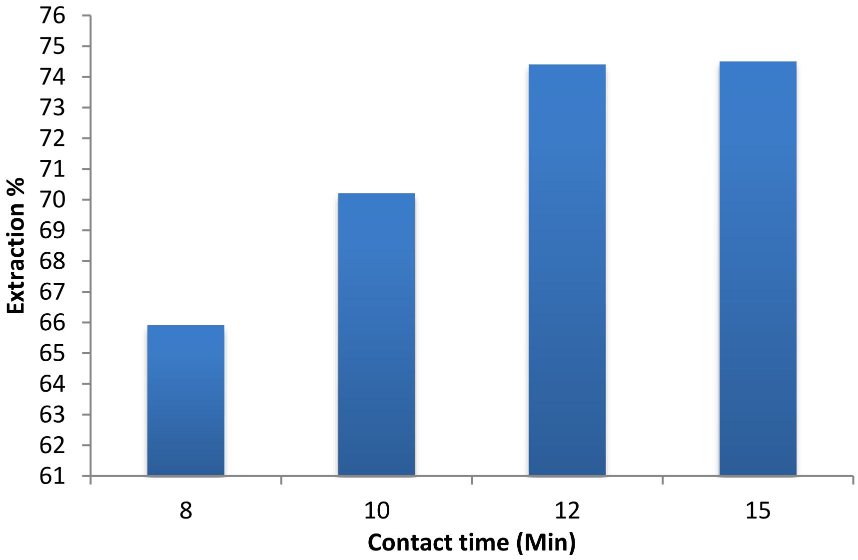

Figure 9. Effect of the contact time on the extraction of Mn.

3.9 Effect of organic/aqueous phase ratio on extraction

The highest extraction percent of Mn element is 87.8% at O/A (4/1); from other different parameters of O\A = 4/1, 3/1, 2/1, 1/1, 1/4, 1/3, 1/2, OPPA concentration is 50% and 12 min., the temperature of 25°C and stirring speed 400 rpm. **Table 2** shows the correlation between E % to O/A ratio. The maximum extraction was observed at a ratio of 4:1 O/A (87.8%) and decreased to 84.3% at 2:1, as shown in **Table 2.** The lowest extraction rate was observed at 1:1 O/A. The ratio of 4:1 yielded a high percentage of Mn element extraction probably because the concentration of kerosene in the organic phase is higher when the aqueous to organic phase ratio is lower. This behavior agrees well with that observed by **(El-Ashtoukhy and Fouad, 2015).**

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Table 2. Effect of O/A on the extraction.

No.	O/A	Extraction %
1	1/1	74.5
2	2/1	77.3
3	3/1	82.4
4	4/1	87.8
5	1/2	84.3
6	1/3	84.1
7	1/4	82.9

3.10 Effect of stirring rate on extraction

To study the impact of stirring rate (500-900 rpm) on the extraction efficiency of Mn element, experiments were implemented with 4/1 (O:A) ratio, 50% OPPA-Kerosene, temperature of 25°C, and contact time of 12 minutes. **Fig. 10** shows that the agitation speed at the lowest value has less effect on the extraction efficiency of the Mn element. However, when the agitation speed was increased the extraction efficiency increased. It has been demonstrated that by raising the speed of stirring between 500 and 900 rpm, the extraction rate would increase. These results explained the fact that the increase in stirring speed enhanced the diffusion of ions into the organic phase; in addition to that, the increase in the values of stirring rate would decrease the interfacial area and increase the mass transfer coefficient in the aqueous feed phase **(Mohd et al., 2019).**

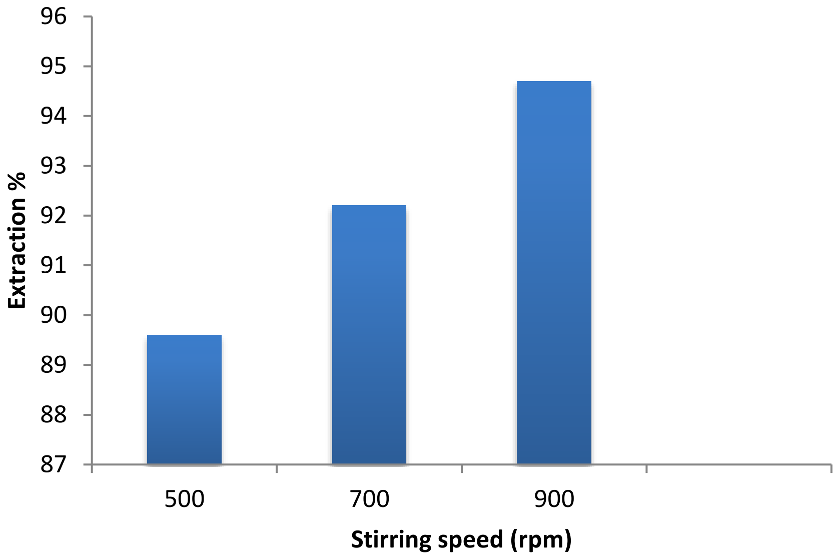

Figure 10. Effect the stirring speed on the extraction of Mn.

CONCLUSIONS

1. The best leaching process of the Mn element from the bauxite ore was obtained with nitric acid (HNO_3) compared with other leaching agents (H_2SO_4 and CH_3COOH).
2. The best leaching process of Mn element from slag with nitric acid is under the conditions of temperature 25°C, nitric acid concentration 2 M, time 90 min, S/L ratio 1/100, and stirring rate 700 rpm.
3. OPPA is efficient as an agent extraction. It is found that the distribution ratio using kerosene as diluent has higher values than the other diluents, such as benzene and toluene.
4. The highest extraction percentage of Mn element is when using 50% OPPA-kerosene at a temperature of 25°C, contact time of 12 min, organic/aqueous ratio 4/1, and stirring speed of 900 rpm.

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