



# Performance evaluation of a novel multi-metal catalyst solution obtained from electronic waste bioleaching on upgrading and enhancing oil recovery

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## ABSTRACT

Due to the high costs and associated high CO<sub>2</sub> emissions of thermal methods, this study focuses on upgrading heavy oil and enhancing oil recovery within reservoir temperature ranges. In this research, a novel, low-cost, and environmentally friendly multi-metal catalyst has been used, which is actually extracted from electronic waste (E-waste). At optimal conditions, which include 80 °C, 12 h of retention time, and 0.2 % v/v of the multi-metal catalyst, this catalyst effectively reduced the viscosity of heavy oil from 687 to 580 mPa.s. To analyze heavy oil before and after the process, Fourier transform infrared spectroscopy (FTIR) was conducted. FTIR spectra indicates that the multi-metal catalyst has reduced the amount of aromatic compounds, shortened hydrocarbon chains, and decreased double and triple bonds. Micromodel tests were conducted by multi-metal catalyst flooding at optimal temperature and retention time obtained from static experiments. Heavy oil recovery through multi-metal catalyst flooding reached 38 %, which is a 10.5 % increase compared to deionized water flooding. The contact angle of the rock was measured after contact with the multi-metal catalyst. The multi-metal catalyst reduced the contact angle by 55 °, changing the wettability of carbonate rock from oil-wet to water-wet. The absorption test indicates that the multi-metal catalyst dissolves certain metals in the rock, most likely due to the high pH of the catalyst. As a result, the permeability of the rock may increase due to the dissolution of the rock metals.

## 1. Introduction

The quick depletion of conventional oil resources has led global attention towards unconventional reservoirs, such as bitumen, heavy and extra heavy oil. Heavy and extra heavy oil reservoirs comprise 70 % of the world's total oil reservoirs, and exploration and production from these reservoirs are essential [1]. A variety of enhanced oil recovery (EOR) techniques have been developed, which are classified into chemical, gas injection, and thermal. Chemical EOR methods are based on the injection of chemical compounds [2]. Chemical EOR methods are categorized into the injection of surfactants, polymers, and alkaline/surfactant/polymer (ASP) [3–5]. Chemical injection is mostly used for heavy oil EOR but is not very suitable for immobile bitumen or oil sands. Lowering the interfacial

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tension (IFT), mobility control, and wettability alteration are the solutions in chemical-based recovery technologies [6,7]. Surfactant flooding reduces interfacial tension (IFT) between water and oil, enabling the displacement of trapped oil [8]. In polymer flooding, a polymer with high molecular weight and high viscosity is added to the injection fluid to decrease the mobility of water and thus improve the displacement efficiency [9]. The concept of mobility control is the base of the polymer flooding method [10]. Alkaline surfactant polymer (ASP) flooding comprises two sources of surfactants and a polymer. One surfactant is in-situ produced by the injected alkaline chemicals. Alkaline chemicals react with the surface-active components that originate from oil. The injected surfactant reduces the IFT between oil and water. The polymer increases the viscosity of the aqueous solution to minimize channeling and enhance mobility control [11]. Gas injection is one of the oldest EOR techniques used for light oils. An available gas, like natural gas, CO<sub>2</sub>, or nitrogen which is miscible with oil, is injected into the reservoir to maintain the pressure and then gas saturation increases at the interface zone. This high gas saturation can significantly reduce the IFT between two interacting fluids, cause oil swelling, and then improve oil displacement efficiency [12]. Among these methods, thermal injection is recognized as an effective method for heavy and extra-heavy oil reservoirs. Due to the properties of heavy oil such as high viscosity, high H/C ratio and high amount of heteroatoms, production of heavy oil reservoirs has faced many challenges [13]. It is important to note that the viscosity of oil is directly associated with temperature. As temperature increases, oil viscosity decreases. Therefore, thermal sources can be utilized to reduce viscosity, commonly known as steam-based thermal injection. So, the first method to reduce viscosity is heat injection [14]. Cyclic Steam Stimulation (CSS), steam flooding, Steam-Assisted Gravity Drainage (SAGD) and In-Situ Combustion (ISC) are effective thermal methods. The most common applied method of all these techniques is steam injection. Steam production is associated with high production of CO<sub>2</sub>, which is not environmentally friendly. On the other hand, the high cost of production and injection of steam as a heat source reduces the profits in such processes [15]. In-situ upgrading of heavy oil using catalyst is a promising technology that reduces the environmental foot print of thermal methods and cost-effectively enhances the quality of the produced oil. In the catalytic process, long chain hydrocarbons decompose to lighter fractions with smaller molecular weights, resulting in reduced viscosity and improved mobility for heavy oil production [16–24]. Consequently, we sought a method to eliminate the need for an external heat source by using a catalyst for oil upgrading, thus, enhancing the process of enhanced oil recovery. Researches are focusing on exploring of cost-effective, highly efficient, stable and environmentally friendly catalysts at laboratory and field scales. The catalysts for EOR purposes can be roughly categorized as (1) water-soluble catalysts [25–28], (2) oil-soluble catalysts [29–32], (3) amphiphilic catalysts [33–37], (4) minerals and zeolites [38–40], (5) dispersed NPs [24,41–48]. Metals have been used as catalysts in most researches in the catalytic upgrading heavy oil. Rivas et al. found Ni (II) and Co (II) salts useful in aquathermolysis [49]. Clark et al. studied the impact of Al(III), first row transition metal including Sr(III), VO(II), Cr(III), Ni(II) and Cu(II), and Group VIII B metal including Fe(II), Co(II), Ni (II), Rh (III), Os(III), Ir(III), Ru(III), Pt(II) and Pt(IV) salts on aquathermolysis of thiophene and tetrahydrothiophene as an organosulfur molecular in heavy oils [27,28]. They found out that Al (III) and first row metal species and Pt (IV) in Group VIII B have impact on sulfur content reduction by breaking the C–S bond and thus reducing molecular weight. Experimental results show that various oil-soluble forms of Ni (II), Co (II), Fe (II) and Fe (III) catalysts, along with various hydrogen donors such as tetralin, formamide, and formic acid have also performed significantly efficient in viscosity reduction of heavy oil [50–52]. Nanoparticles are made of metals in nanoscale. Hashemi et al. studied micro-emulsions including trimetallic (W, Ni, and Mo) nanoparticles as a catalyst in oil upgrading [43]. Based on research findings, most of catalysts which are used in the oil upgrading process are heavy metals. Therefore, it is valuable to consider metals extraction from wastes, and evaluate their performance as environmentally friendly catalysts.

Due to the unprecedented growth of the electrical and electronics industries in recent decades, the generation of electrical and electronic waste is an inevitable reality. There are over 69 elements of Mendeleev table in e-waste such as gold, silver, copper, platinum, palladium, ruthenium, rhodium, iridium, osmium, cobalt, palladium, indium, germanium, bismuth, antimony and noncritical metals such as aluminum and iron. Countries could reduce their material requirement in a safe and stable way by recycling e-waste [53]. The presence of precious metals such as gold, silver and nickel in E-waste make their recycling more economically and logically viable. These are called artificial or secondary ores because they are richer than natural ores [54]. It is worthy to note that the metals extracted from E-waste can be applied as catalyst, and till now there has been no research about the performance of environmentally friendly catalyst on in-situ heavy oil upgrading and EOR.

There are several technologies for extracting metals from industrial wastes, including pyrometallurgy, hydrometallurgy and biohydrometallurgy. The active participation of micro-organisms in geochemical processes has developed technological processes called biohydrometallurgy. These processes are based on chemical or physical interactions between the micro-organisms, side product and their substance. One of these processes is bioleaching which metals are dissolved by micro-organisms from inorganic sources (such as minerals) [55]. In general, bioleaching is a process in which metals are dissolved from a source by certain micro-organisms, or micro-organisms are used to extract elements from a material [56]. In other words, the conversion of solid metals to their soluble form by micro-organisms is called bioleaching. The use of this method has been considered in recent decades. The bioleaching method has many advantages including easy to use, high safety, lack of environmental side effects and low costs [57,58]. To use a catalyst in EOR, the catalyst must be in a soluble form for injection. This means that catalytic metals should be initially dissolved in water, oil, or an amphiphilic solution. In this study, it is possible to directly use the bioleaching solution as a multi-metal catalyst before the need for separating, purifying and redissolving them for injection. Consequently, the direct use of bioleaching solution as a multi-metal catalyst reduces the cost of separating and purifying the extracted metals from this method. Therefore, not only does the use of this type of multi-metal catalyst have environmental benefits, but it also leads to a reduction in costs for the utilization of these extracted metals. As such, this study has found an effective way for the use of metals obtained by bioleaching solution method. As mentioned earlier, most of the catalysts used in the in-situ heavy oils upgrading are metals. Therefore in this study catalytic role of metals from electronic waste in in-situ upgrading of heavy oil and enhancing oil recovery at reservoir temperature has been investigated. In addition, multi-metal catalyst displacement in the porous medium, effect of the multi-metal catalyst on wettability and adsorption on the rock

has been investigated.

## 2. Materials and methods

The heavy oil feedstock used in this study was collected from Iranian carbonate fields. The density and viscosity at 25 °C are 0.9 g/cm<sup>3</sup> and 687 mPa.s, respectively. Viscosity reduction is calculated by  $\Delta\mu = \mu - \mu_0$  where  $\mu_0$  (mPa.s) is initial oil viscosity and  $\mu$  (mPa.s) is oil viscosity after the reaction. The relative viscosity reduction is calculated by  $\Delta\eta = ((\mu - \mu_0)/\mu_0) \times 100$ .

### 2.1. Catalyst preparation

First, the spent telecommunication printed circuit boards (STPCBs) were collected and cut into small pieces of approximately 1 or 2 cm. A micronizer (Hertzog; Germany) shredder was utilized for 30 s to achieve a powdered form. Subsequently, the powder was sieved using a mesh #200, ensuring a particle size of less than 75  $\mu\text{m}$  for a consistent powder. Any particles larger than 75  $\mu\text{m}$  were reintroduced into the micronizer, and the crushing and sieving process was repeated until the entire sample passed through mesh #200. The resulting powder called STPCBs powder, was retained for future research purposes [59]. Previously published data indicates that the inclusion of glycine and methionine in the culture medium could significantly enhance cyanide production by cyanogenic bacteria [60]. When glycine is present in the culture medium, micro-organisms can directly convert glycine into HCN, resulting in an increased cyanide yield within the culture medium, which aids in the dissolution of metals [61]. Then extracting metals through the bioleaching experiment was conducted using *Pseudomonas atacamensis* with the accession number SSB01000008, STPCBs powder, and nutrient broth (NB) culture medium that is enriched with glycine and methionine.

The study utilized a one-step bioleaching method to recover metals from STPCBs powder. This method involved using flasks containing 100 mL of NB medium with optimized glycine concentration and methionine, incubated at 30 °C and 160 rpm for 7 days. A control flask without bacterial inoculation was used to assess the impact of bacteria on metals recovery. Daily water evaporation was accounted for and added to the flasks, and samples were collected on designated days. The samples were processed through centrifugation at 6000 rpm, separating solid particles from the bioleaching solution. Also, the bioleaching solution was passed through a 0.22  $\mu\text{m}$  filter. ICP-OES (Vista-pro; Varian; Australia) was used to measure the concentration of metals in the bioleaching solution. As such, this solution contains culture medium, bacterial metabolites, remained bacteria and extracted metals which is used as multi-metal catalyst. Therefore, to prevent the growth of fungi and bacteria, the multi-metal catalyst is kept in the refrigerator for further experiments. More details can be found in Ref. [62].

## 3. Experimental procedure

### 3.1. Heavy oil upgrading experiments

All the experiments were conducted by adding catalyst in designed mass concentration to 40 mL oil in reusable bottles and cap (Made of Duran borosilicate glass, type 3.3, for maximum chemical and thermal shock resistance). The sealed bottles were heated in the oven. At the conclusion of the designated time, the heating was halted. Next, the mixture was cooled to be analyzed. The viscosity measurement of the oil samples before and after reaction was conducted on Aton Paar Rheometer at 25 °C, and the changes of crude oil before and after reaction were characterized by FTIR spectra. All the experiments were carried out within the average reservoir temperature range. The typical range for reservoir temperatures in the world is 60–100 °C [63] which has been considered for the conducted experiments. Preliminary studies have been conducted for choosing the amount of multi-metal catalyst. According to the results, 0.2 to 1 vol percent was selected. Such research has been conducted within the time frame of 24–36 h. For more detailed observations, retention times from 6 to 72 h were considered [19,34,35,37]. Design of Experiment (DOE) was used to design experiment conditions. Design of experiments is defined as a branch of applied statistics that deals with planning, conducting, analyzing, and interpreting controlled tests to evaluate the factors that control the value of a parameter or group of parameters. DOE is a powerful data collection and analysis tool that can be used in a variety of experimental situations. It saves cost by minimizing process variation and reducing rework and balances uncontrollable condition affect, decreases the systematic errors and increases possibility of getting impartial and repeatable results by randomization. In addition, it also prepares optimal conditions for considered responses [64]. In this research, experimental design was performed by Central Composite Design method (CCD). Table 1 shows experiment conditions and the independent variables.

A series of tests presented in Table 3 are designed by the Central Composite Design method (CCD) to investigate the effect of these factors on heavy oil viscosity.

**Table 1**

Design of experiments: factors and levels for CCD designs.

Factors	Unit	Low axial	Low fractional	Central	High fractional	High axial
Amount of catalyst	%v/v	0.2	0.4	0.6	0.8	1.0
Temperature	°C	60	70	80	90	100
Retention time	h	6	22	39	55	72

### 3.2. Oil displacement by catalyst injection

Micromodels are two-dimensional simplified porous medium as replacement for cores using fluid flow studies in porous medium. Micromodel experiments are performed to observe the direction of fluid flow in a porous medium. In fact, the advantage of this model in comparison with cores obtained from drilling, is the ability to observe the fluids displacement, leading to the preparation of improved models for fluid flow in porous medium. Many researchers conducted studies using micromodels [65–67]. In this study, a micromodel has been used to investigate the performance of multi-metal catalyst in enhanced oil recovery.

A heterogeneous five-spot glass micromodel has been used to study catalyst effect on oil displacement and calculate the oil recovery [68]. The micromodel is designed according to one of the Iranian carbonate reservoirs. The micromodel's properties are 38 % porosity, 890 mD permeability,  $6 \times 6 \times 0.006 \text{ cm}^3$  bulk volume.

Because the glasses are strongly water-wet, it's necessary to make them oil-wet. So before each flooding test the following steps are conducted [69]:

1. Micromodel is saturated by sodium hydroxide solution for 1 h.
2. The micromodel is washed by distilled water and put it to an oven at 200 °C for 30 min
3. The micromodel is saturated by the mixture of trichloro (methyl) silane (2 %) and toluene (98 %) for 3-5 min.
4. For washing micromodel, methanol is injected. Next, in order to evaporate methanol, it is placed into the oven at 100 °C.

After making the micromodel oil-wet, it was saturated by heavy oil with a constant flow rate 3 mL/h. Then multi-metal catalyst was injected into the micromodel at rate of 0.05 mL/h. During the injection, photos were taken every 60 s with a digital microscopic lens camera and amount of oil recovery was calculated by computer image processing.

### 3.3. Catalyst-rock interaction

Optimal temperature and retention time conditions are used to investigate the adsorption of multi-metal catalyst on the rock. 1 g of powdered rock in size of 200–300  $\mu\text{m}$  is mixed with 10 mL of multi-metal catalyst solution and is placed at the optimal temperature and retention time in the oven. At the end, the multi-metal catalyst has been separated from powdered rock by using a filter paper and has been subjected to ICP-OES analysis.

### 3.4. Wettability measurement

In this study in order to measure the wettability of the rock, the contact angle method has been used. The system for implementation of this process has been shown Fig. 1. One of the usual methods of contact angle measurement is sessile-drop technique that is used to calculate the contact angle in this study. In order to measure the contact angle the prepared sample is placed in a measuring chamber containing deionized water. In this system the contact between rock surface and liquid environment is downwards. According to Fig. 1 the drop oil is injected slowly and sticks to the rock surface, and microscopic images are captured with a high-resolution camera. The left and right angles of the drop are measured by Image J software and the average angles are reported.

First, oil contact angle on the rock is measured in the environment of deionized water. Then rock thin section is placed in 20 mL of multi-metal catalyst at the optimal retention time and temperature. Next, rock thin section is separated from the multi-metal catalyst and oil. Then contact angle is measured in the environment of deionized water. In order to interpret the results coming from the micromodels, the glass type using to build the micromodel is made oil-wet and this process were repeated for oil-wet glass thin section.

**Table 2**  
Metals concentration of bioleaching solution extracted E-waste.

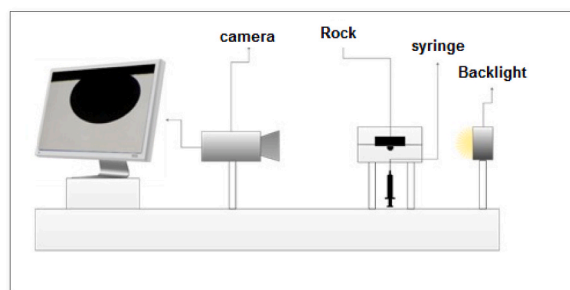
Metal	/mg/l	Metal	mg/l	Metal	mg/l
Cu	916.90	Si	0.73	Dy	0.28
K	395.70	Pr	0.61	Au	0.22
P	107.05	Ag	0.60	Fe	0.20
Na	54.40	Sn	0.48	Pd	0.19
Zn	30.01	Mn	0.10	Ba	0.19
Ni	5.95	Co	0.05	Ga	<0.01
Mg	3.27	Al	0.46	In	<0.01
Ca	3.26	Bi	0.43	Cr	<0.01
Ce	0.85	Nd	0.42	Sr	<0.01

According to Fig. 2, the rock mainly contains calcium carbonate so it is carbonate rock. Very small peaks are seen in Fig. 2 represent the rare metals within the calcium carbonate rock.

**Table 3**  
Results of designed experiments.

Run	Catalyst (%v/v)	Temperature (°C)	Retention time (h)	Relative viscosity reduction $\Delta\eta$ (%)
1	0.2	80	39	2.56
2	0.4	90	55	2.08
3	0.4	90	22	4.53
4	0.4	70	22	10.20
5	0.4	70	55	-35.35 <sup>a</sup>
6	0.6	80	6	3.47
7	0.6	100	39	-31.24 <sup>a</sup>
8	0.6	80	39	9.10
9	0.6	80	39	8.22
10	0.6	80	72	4.10
11	0.6	80	39	10.13
12	0.6	80	39	9.27
13	0.6	60	39	4.66
14	0.8	70	22	9.05
15	0.8	70	55	4.66
16	0.8	90	22	10.52
17	0.8	90	55	1.62
18	1.0	80	39	8.05

<sup>a</sup> Negative numbers indicate an increase of viscosity.



**Fig. 1.** Schematic of the system for measuring the contact angle.

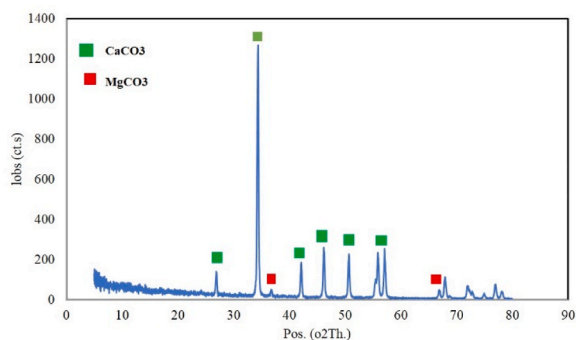
## 4. Results and discussion

### 4.1. Characterization of multi-metal catalyst and rock

Metals concentration of bioleaching solution is shown in Table 2. The highest metal concentration in bioleaching solution is copper..

### 4.2. Analysis of viscosity

One of the most important signs of oil upgrading is viscosity reduction. So the oil viscosity is measured after all the designed



**Fig. 2.** XRD patterns of rock sample.

experiments (Table 3).

Also, Fig. 3 shows the oil viscosity changes according to each parameter separately. Each parameter alone especially affects the viscosity. For example, as shown in Fig. 3(a) there is an optimal value for temperature. After that, the viscosity starts to increase. Also, Fig. 3(b) shows an optimal value for the amount of multi-metal catalyst. After this optimal value, the viscosity starts to decrease. But for the time there is not an optimal value. It means when time increases, oil viscosity increases (Fig. 3(c)).

Optimal conditions have been defined by the highest viscosity reduction. These conditions have been achieved with a confidence level 95 % by CCD method with Design Expert software (version 11). The other analyses for upgrading have been conducted at the optimal conditions. Confirmation test was also conducted at optimal conditions.  $\Delta\mu$  is viscosity reduction after confirmation test and  $\Delta\eta$  (%) is relative viscosity reduction (Table 4).

#### 4.3. Characterization of oil composition

FTIR spectra analysis of oil samples were conducted before and after test in optimal conditions. The purpose of FTIR spectra analysis is investigation of the change in bonds and compounds in crude oil due to the upgrading. FTIR spectra shows that the multi-

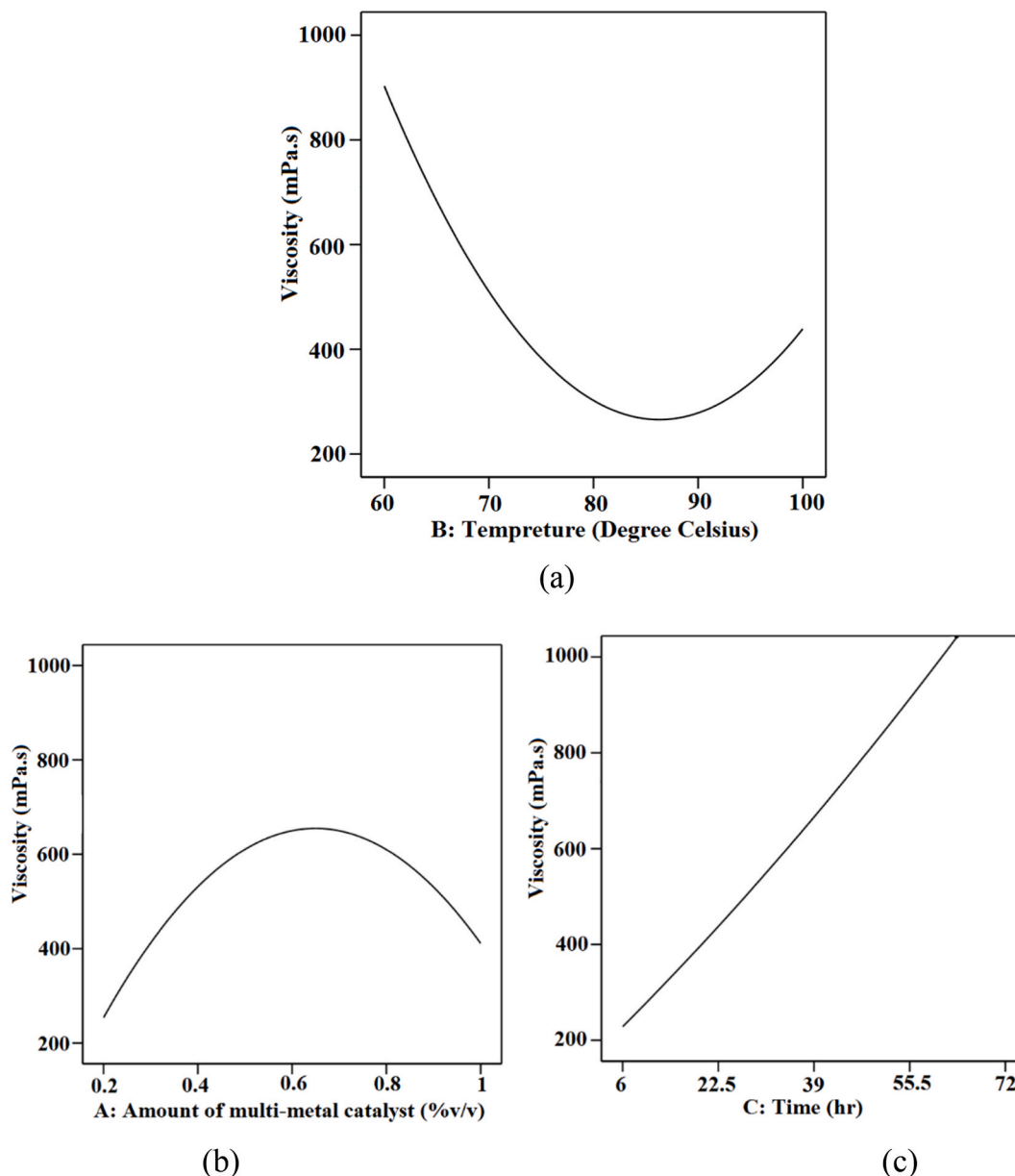


Fig. 3. The effect of each parameter on oil viscosity. a) Temperature. b) Amount of multi-metal catalyst. c) Retention time.

**Table 4**  
The optimal conditions obtained by experiments.

Catalyst (%v/v)	Temperature (°C)	Retention time (h)	Original viscosity (mPa.s)	Predicted viscosity (mPa.s)	Viscosity at optimal conditions (mPa.s)	$\Delta\mu$ (mPa.s)	$\Delta\eta$ (%)
0.2	80.0	12.0	687.0	564.0	580.0	107.0	15.6

metal catalyst has reformed some of the bonds.

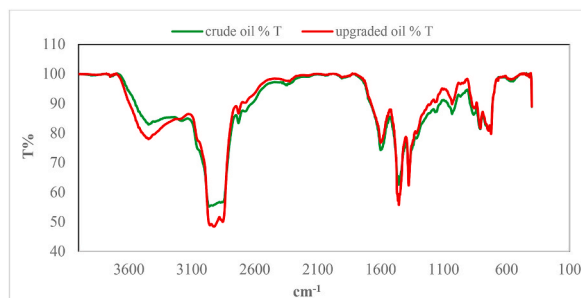
In the FTIR spectra graph 2500–3700  $\text{cm}^{-1}$  interval is called the Hydrogen Stretching Zone because the vibration frequencies of  $N-H$ ,  $N-H$  and  $O-H$  appear in this region. The 2000–2300  $\text{cm}^{-1}$  range refer to the Triple Bond Stretching Region because  $C\equiv C$  and  $C\equiv N$  bonds appear in this area. The 1600–2000  $\text{cm}^{-1}$  interval is known as the Double Bond Stretching Region, because the bonds  $C=C$ ,  $C=N$  and  $C=O$  are existed in this region. The 1000–1600  $\text{cm}^{-1}$  range is called the Fingerprint Region because various bonds such as  $C-C$ ,  $C-N$ ,  $C-O$  (single bonds),  $C-H$  bending bond and some benzene ring bonds determining functional groups are located in this area. The last range, 400–1000  $\text{cm}^{-1}$  refers to aromatic region [70–72]. The peak frequencies of  $2926 \pm 10 \text{ cm}^{-1}$  and  $2850 \pm 10 \text{ cm}^{-1}$  refer to the  $\text{CH}_2$  asymmetric bond and the  $\text{CH}_2$  symmetric bond, respectively. The  $\text{CH}_3$  asymmetric bond and  $\text{CH}_3$  symmetric bond exist at  $2962 \pm 10 \text{ cm}^{-1}$  and  $2872 \pm 10 \text{ cm}^{-1}$ , respectively. In the fingerprint area, a couple peak of  $\text{CH}_2$  scissor bond is placed at  $1455 \pm 10 \text{ cm}^{-1}$ ,  $\text{CH}_3$  umbrella bond exist at  $1375 \pm 10 \text{ cm}^{-1}$ ,  $\text{CH}_2$  rock bond exist at a frequency of  $720 \pm 10 \text{ cm}^{-1}$ . An increase in intensity of the  $\text{CH}_2$  symmetric band,  $\text{CH}_3$  symmetric band,  $\text{CH}_2$  scissors mode,  $\text{CH}_3$  umbrella bond, and  $\text{CH}_2$  rock mode means an increase in alkane chain concentration in the sample. The alkane hydrocarbons contain only single carbon-carbon bonds [73]. According to Fig. 4, due to the performance of the multi-metal catalyst, the intensities of the  $\text{CH}_2$  symmetric,  $\text{CH}_3$  symmetric peaks have increased, which means an increase in the alkane chain in the oil. In other words, triple or double bonds have been reduced to single bonds, which is one of the aspects of oil upgrading. An increase of  $\text{CH}_3$  peak intensity more than  $\text{CH}_2$  peak indicates that the oil sample is lighter [74]. As mentioned earlier, the 400–1000  $\text{cm}^{-1}$  range indicates aromatic compounds. According to the FTIR spectra analysis, the intensity of these peaks in the upgraded oil decreases which means a reduction in aromatic compounds. Because asphaltene contains aromatic compounds, reducing the intensity of these peaks in the upgraded oil means reducing the amount of asphaltene. Peak intensity of  $\text{CH}_3$  is more than  $\text{CH}_2$  in Fig. 4 which indicate the oil sample is lighter too [74]. Table 5 shows the ratio of  $\text{CH}_2$  scissor to  $\text{CH}_3$  umbrella and the ratio  $\text{CH}_2$  asymmetric to  $\text{CH}_3$  asymmetric. These two ratios represent the average size of molecules and the number of carbons in their molecular chain. Reducing these ratios indicates a reduction in the number of carbons and a shorter carbon chain [75]. According to the figures and Table 5 after the optimal experiment both ratios is decreased indicating carbon chain is shorter. It means an increase in light compounds due to the breaking and upgrading of crude oil.

Therefore, the performances of multi-metal catalyst are reducing the amount of aromatic compounds, making hydrocarbon chains shorter and reducing double and triple bonds.

#### 4.4. Analysis of micromodel flooding

Micromodel tests were conducted at optimal temperature and retention time obtained from static experiments. In the first scenario, the multi-metal catalyst was injected until breakthrough time in the first step (Fig. 5(a)); after staying the micromodel at optimal temperature and time. Next, the multi-metal catalyst was injected again to remove the upgraded oil. In the second scenario the initial injection is carried out with deionized water until breakthrough time (Fig. 5(b)). After that the multi-metal catalyst is injected. Then, micromodel is kept at optimal retention time and temperature. After the retention time, the catalyst is injected again. As shown in Fig. 5(a), the injection of the multi-metal catalyst caused the flow to be more steadily and make breakthrough longer. So the injected fluid improves sweep efficiency. As a result, the fluid moves more piston-like. By contrast, water flooding let a greater volume of oil remain in the porous medium and fingering phenomenon becomes more obvious and also lateral diffusion is decreased. As a result, the breakthrough of multi-metal catalyst injection happens later than that of water injection. Leading to a higher oil recovery for multi-metal catalyst (33.27 %) in comparison with the water injection (22.3 %). The results have been shown in Fig. 6 and Table 6.

The observed phenomena in the microscopic images at Fig. 5 contain wettability alteration, emulsion formation (water-in-oil) and



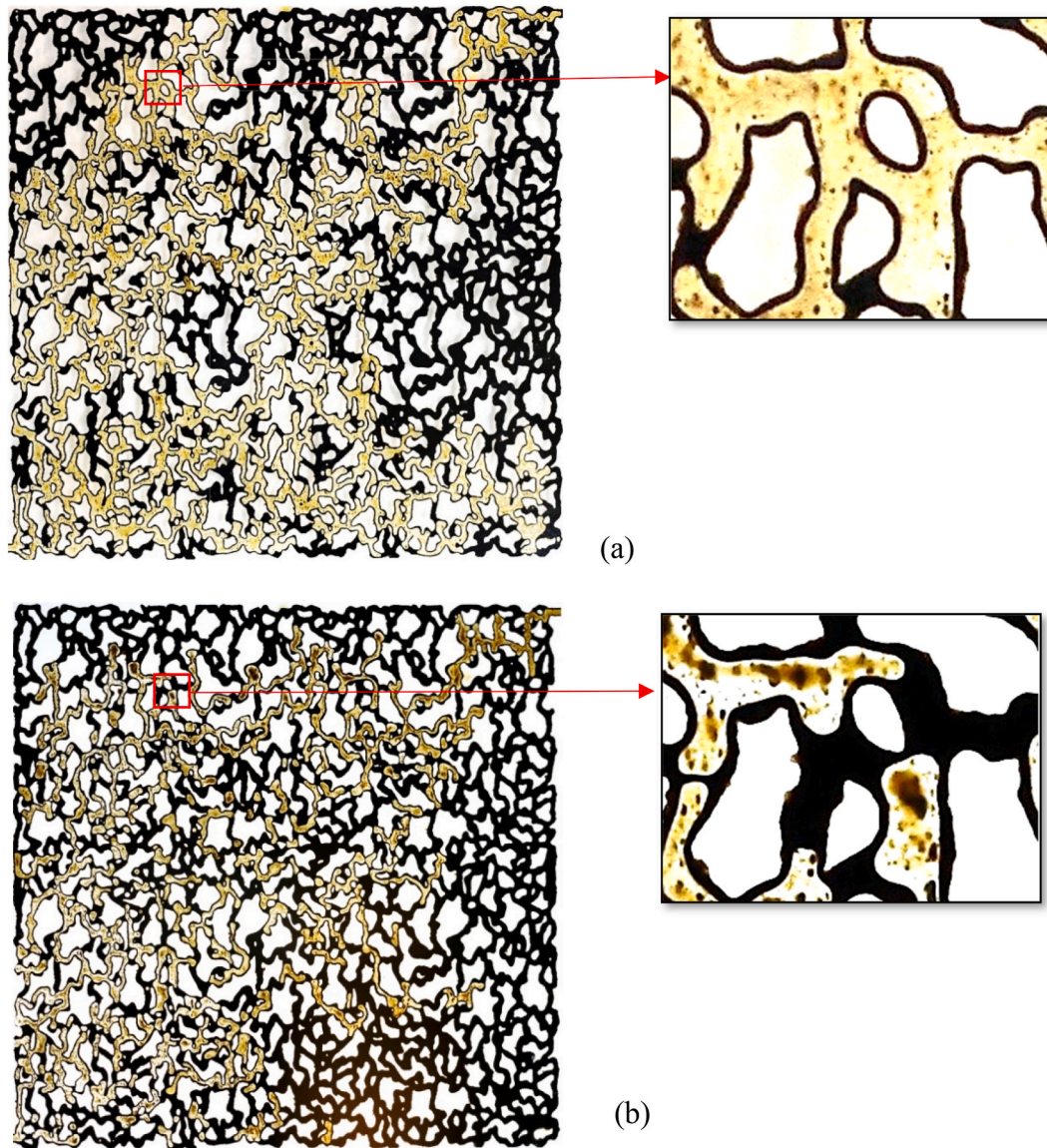
**Fig. 4.** The FTIR spectra of the heavy oil before and after upgrading.



**Table 5**

The ratio of CH2 scissor to CH3 umbrella and the ratio CH2 asymmetric to CH3 asymmetric for crude oil and upgraded oil.

Oil sample	CH2 asymmetric/CH3 asymmetric	CH2 scissor/CH3 umbrella
Crude oil	1.00	0.94
Upgraded oil	0.98	0.87

**Fig. 5.** Macroscopic and microscopic oil displacement at breakthrough time: (a) multi-metal catalyst flooding (b) deionized water flooding.

large emulsion drops. As shown in the microscopic image in Fig. 5(b) in deionized water flooding, the oil layer's thickness on the wall of pores is more than the oil layer's thickness in the multi-metal catalyst flooding. This difference is referred to wettability alteration. In other words, according to the microscopic image in Fig. 5(a), the multi-metal catalyst flooding can reduce the oil layer's thickness on the wall of pores causing wettability alteration from oil-wet to water-wet condition.

#### 4.5. Effect of multi-metal catalyst on wettability alteration

In general, the pressure decreases after the breakthrough so the displacement mechanism occurs due to capillary forces, and this changes water and oil saturation. When heavy oil is at static state, asphaltene molecules produce viscous structures by self-aggregation



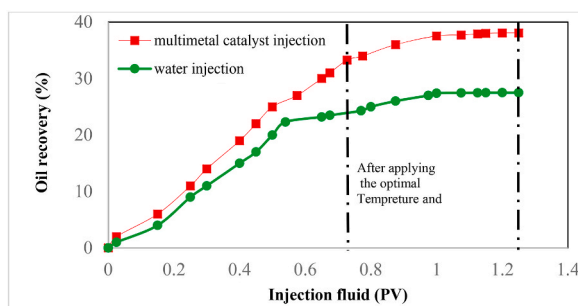


Fig. 6. Oil recovery versus pore volume of injected fluid.

Table 6

Micromodel flooding results.

Factor	Multi-metal catalyst flooding	Water flooding
Breakthrough time (PV)	0.72	0.54
Breakthrough time (minute)	249.00	185.00
Oil recovery at breakthrough time (%)	33.27	22.30
Oil recovery after applying the optimal temperature and retention time (%)	38.07	27.50

and physical interaction with the porous medium. To break these viscous structures and move thought heavy oil some force is required. However, the motive force at both ends of the micromodel or reservoir is insignificant and oil displacement cannot break these structures alone. While the main mechanism is capillary force, if the system is water-wet, it can provide the energy needed to break down viscous structures [76]. Therefore, one of the factors to increase recovery is making rock water-wet. The contact angle is a quantity to express the wettability of a solid surface by a liquid. Depending on whether the angle is smaller or larger than  $90^\circ$ , the solid surface is water-wet or oil-wet respectively [77]. Then, to investigate the wettability alteration of the rock by the multi-metal catalyst, oil-wet rock thin section was placed in the multi-metal catalyst at the optimal temperature and retention time condition obtaining in static testing so that the surface of the rock thin section is completely covered by the catalyst. Fig. 7(a) shows the average contact angle of the oil-wet rock before contact with the multi-metal catalyst and the measured contact angle of that was  $138.7^\circ$ . Also, Fig. 7(b) shows oil-wet rock after covering by multi-metal catalyst and the average contact angle decreased to  $83.6^\circ$ . The measurement of the contact angle of the rock after contact with a multi-metal catalyst shows that this multi-metal solution reduces the contact angle and changes the wettability of carbonate rock from oil-wet to water-wet.

The dynamic tests were conducted by injecting into an oil-wet micromodel. In order to examine the mechanisms within the micromodel accurately, the wettability test was conducted by using oil-wet glass. For this purpose the oil-wet glass is placed in a multi-metal catalyst under optimal temperature and retention time condition. After that contact angle is measured. Fig. 8(a) shows oil-wet glass before contact with the multi-metal catalyst and the measured contact angle of that was  $153.5^\circ$ . Also, Fig. 8(b) shows oil-wet glass after being covered by the multi-metal catalyst and the measured contact angle decreased to  $129.5^\circ$ . Covering the glass by catalyst slightly alters wettability to water-wet. This little wettability alteration can effect on enhanced oil recovery.

Wettability depends on the electrical charges of carbonate rock surface [78]. Carbonate rock surfaces absorb negative charges from oil components such as carboxylic acid, asphaltene and naphthenic acid compounds due to positive charges on carbonate rock surfaces. Absorption of these compounds is one of the main factors for making carbonate rocks oil-wet. So reducing the amount of these compounds in oil causes the wettability to become water-wet. As mentioned, according to Fig. 4, the asphaltene compounds of upgraded are reduced. Therefore, one of the factors to reduce the contact angle in the presence of multi-metal catalyst is to reduce the amount of asphaltene compounds in crude oil. Also, the multi-metal catalyst can reduce asphaltene on the rock surface contains oil which lead the rock to become water-wet. Therefore, both the asphaltene reduction on the rock surface and oil change the wettability of the rock.

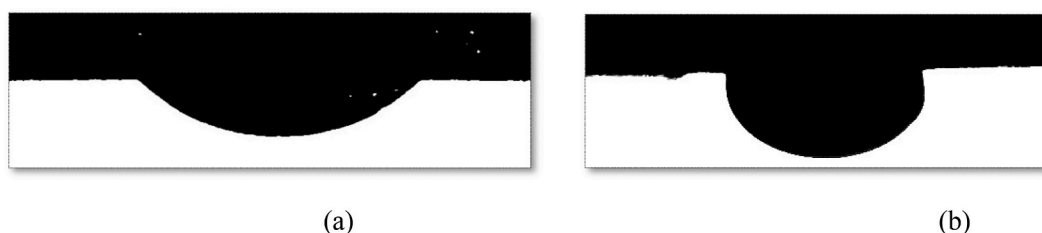


Fig. 7. Measurement of contact angle of rock. (a) Oil-wet rock before test. (b) After contact with multi-metal catalyst at optimal conditions.



**Fig. 8.** Measurement of contact angle of glass. (a) Oil-wet glass before the test. (b) Glass after contact with multi-metal in optimal condition.

As mentioned, wettability depends on electrical surface charges of carbonate rock so by changing these electrical charges, wettability can change. The following chemical process occurs between the fluid and the rock [79].



The acidic and alkaline properties of the environment depend on the presence of  $OH^-$  and  $H^+$  ions, and the high level of hydroxide ions indicates the alkaline environment. The pH of the multi-metal catalyst is equal 9 ( $pH = 9$ ) and adding it to rock and oil increases the amount of hydroxide ions in the environment. According to Le Chatelier's principle in thermodynamic concepts, adding a substance to a reaction causes the reaction to proceed in order to reduce that substance [80]. According to this principle, an increase in the pH of the reaction environment which means an increase of  $OH^-$  causes equation (1) to go backwards and the amount of  $Ca^{2+}$  on the rock surface decreases meaning a decrease positive charges on the surface of the carbonate rock. Therefore, the absorption of negative charges of oil components should be reduced and consequently the carbonate rock should become water-wet.

Another reason for the change of the contact angle can be the alteration of the capillary pressure. In the water injection cases, interfacial tension between water and oil is high. High interfacial tension between oil and water means high capillary forces which cause oil to remain as continuous phases. In order to increase the oil recovery capillary pressure must be reduced. The capillary number indicates the ratio of viscous forces to capillary forces. Therefore, reducing capillary pressure increases capillary number. The oil emulsion formation in water often causes interfacial tension between two phases to decrease which increases the capillary number and the trapped oil produces in this way. In fact, emulsion formation increases microscopic displacement. On the other hand, as described in Section 3.3 multi-metal catalyst converts long hydrocarbon chains into shorter chains. Since the vapor pressure of the lighter hydrocarbons is higher, according to equation (2), an increase the amount of lighter hydrocarbons rise the vapor pressure and consequently rise partial pressure and finally increases the total pressure [81].

$$P_i = X_i P_{vi} \quad (2)$$

Where  $P_i$  is partial pressure of component i,  $X_i$  is mole fraction of component i,  $P_{vi}$  is vapor pressure of component i. According to equation (3), an increase in the oil pressure reduces the pressure difference between wet (oil) and non-wet (water) and thus reduces the capillary pressure between the two fluids [82].

$$P_c = P_{nw} - P_w = P_w - P_o \quad (3)$$

where  $P_c$  is capillary pressure,  $P_{nw}$  is pressure in nonwetting phase,  $P_w$  is pressure in wetting phase, second  $P_w$  is pressure in the water phase,  $P_o$  is pressure in the oil phase [83].

$$N_c = \frac{F_v}{F_c} \quad (4)$$

Where  $N_c$  is capillary number,  $F_v$  is viscous forces and  $F_c$  is capillary forces. According to equation (4), the reduction of capillary pressure increases the capillary number and consequently produces more oil. So one of the main reasons for the reduction in capillary forces is actually the increase in vapor pressure through the upgrading process. The reduction of capillary pressure causes the wettability to improve.

#### 4.6. Absorption of multi-metal catalyst on rock

One of the important objects about chemical flooding is reservoir damage. Researchers try to use chemical materials that do not block the pore throats [84]. Measurement of metal concentrations after contacting powdered rock with multi-metal catalyst shows that the concentration of most metals has increased after the absorption test. As is observed in Fig. 9, silicon, iron, calcium, magnesium and sodium had the highest increase compare to other metals. The increase in concentration of the predominant metals shows that multi-metal catalyst can dissolve the rock partially due to the high pH, and it may increase the permeability of the rock due to the dissolution of the rock metals.

The low cost and low damage of using metals extracted from E-waste through the bioleaching method as a multi-metal catalyst make it an efficient method for oil upgrading and EOR, especially for reservoirs that cannot use thermal methods extensively.

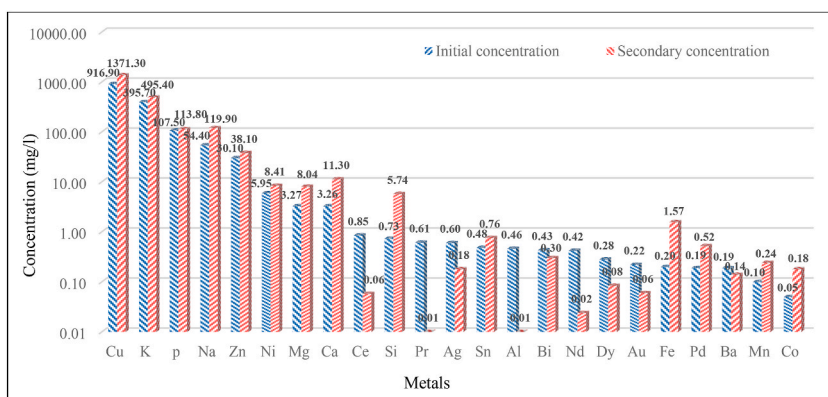


Fig. 9. The change in the metals concentration (mg/l) of multi-metal catalyst before and after contact with rock powder.

## 5. Future works and perspective

Metals from the bioleaching method as a multi-metal catalyst are considered novel materials for in-situ oil upgrading. To gain a better understanding of the challenges posed by this multi-metal catalyst on other parameters, further investigation of certain issues such as the interactions of the multi-metal catalyst with the rock and fluid, including changes in interfacial tension between two fluids. The effect of this multi-metal catalyst on reservoir damage, including the plugging of porous medium needs to be studied. This method has been performed without additional heat and only under reservoir temperature conditions, but it can be combined with electromagnetic waves, the presence of nanoparticles, and high temperatures to achieve better results. The performance of multi-metal catalyst under different conditions and different types of oil should be analyzed. Providing a method for the refining catalyst for subsequent uses and its separation from oil should be investigated. Toxicity and remediation tests should be conducted to assess the environmental and health effects of chemicals, pollutants, drugs, chemical products, and other substances on living organisms. As mentioned, the bioleaching solution containing metals is the multi-metal catalyst used in this research. Since the bioleaching solution contains culture medium, bacterial metabolites, remaining bacteria, and extracted metals, there may even be specific interactions between these substances and the oil that require further investigation, particularly regarding the reactions that lead to oil upgrading and enhanced oil recovery. Identifying the involved chemical reactions can better describe the performance of other catalysts, including the catalyst used in this study.

## 6. Conclusions

In this study, the use of a multi-metal catalyst obtained from E-waste in heavy oil in-situ upgrading and consequently enhancing oil recovery within reservoir temperature ranges has investigated. As such, the environmental and economic advantage of this research is using recycled metals extracted E-waste instead of paying too much for catalytic metals. This multi-metal catalyst has shown good catalytic effects in heavy oil upgrading process.

- At optimal conditions including 80 °C, 12 h, and 0.2 %v/v of multi-metal catalyst, the viscosity of heavy oil was reduced (from 687 to 580 mPa.s). Consequently, this novel multi-metal catalyst can upgrade oil in low temperature (reservoir temperature).
- The FTIR spectra of heavy oil before and after the upgrading process indicates that the multi-metal catalyst has reduced the amount of aromatic compounds, shortened hydrocarbon chains, and decreased double and triple bonds.
- Micromodel tests were conducted by multi-metal catalyst flooding at optimal conditions obtained from static experiments. Heavy oil recovery is 38 % by multi-metal flooding and applying optimal conditions. Oil recovery is increased by 10.5 % compared to the deionized water injection.
- The Contact angle of rock after contact with the multi-metal catalyst has been measured. The multi-metal catalyst reduced the contact angle by 55° and changed the wettability of carbonate rock from oil-wet to water-wet.
- The absorption test indicates that the multi-metal catalyst dissolves some metals in the rock partially due to the high pH of the multi-metal catalyst. As a result, the permeability of the rock may increase due to the dissolution of the rock metals.

## CRedit authorship contribution statement

**Kimia Faryadi:** Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Arezou Jafari:** Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition, Conceptualization. **Seyyed Mohammad Mousavi:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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