Synthesis and application of nanoparticles and biosurfactant for oil-contaminated soil removal

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ABSTRACT
Oil exploration, production and use may cause oil leakage, which can contaminate surrounding soil. Biosurfactants are biologically produced surfactants, which are produced by yeast or bacteria from various substrates like sugars, oils, alkanes, and wastes. Biosurfactants have been used for removal of metals and hydrocarbons from contaminated soils. In addition, some nanoparticles have already shown their effective treatment of petroleum-contaminated soil. This research studies the application of various biosurfactants and nanoparticles for treatment of oil-contaminated soil. The specific objectives of this work include investigation of the removal of oil from contaminated soil by experimental columns containing some selected biosurfactants and nanoparticles in the lab, evaluation of the effect of factors, such as pH, temperature, biosurfactant concentration on the removal efficiency, and determination of the range and sustainability of the developed process. The primary results show that the main composition of contaminated soil was sand and silt, with the moisture content and organic content was 5.45% and 1.44%, respectively. Moreover, the iron/copper bimetallic particles were produced with the average diameter of the particles of 20 nm, whereas the content of iron was higher than copper. The presence of iron oxide and copper oxide was also proven by XRD analysis. In addition, zero valent iron was present in the nanoparticle composition. For testing the oil removal efficiency by biosurfactants and iron/copper particles, a column experiment was designed, and methods of soil extraction and total petroleum hydrocarbon determination were achieved.

RÉSUMÉ
L'exploration, la production et l'utilisation du pétrole peuvent provoquer des fuites de pétrole, qui peuvent contaminer le sol environnant. Les biosurfactants sont des agents tensioactifs biologiques, qui sont produits par des levures ou des bactéries à partir de divers substrats comme les sucres, les huiles, les alkanes et les déchets. Des biosurfactants ont été utilisés dans certaines technologies d'assainissement pour éliminer les métaux et les hydrocarbures des sols contaminés. De plus, certaines nanoparticules ont déjà montré leur efficacité de traitement des sols contaminés par le pétrole. Cette recherche étudiera l'application de divers biosurfactants et nanoparticules pour le traitement des sols contaminés par le pétrole en provenance de la Chine. Les objectifs spécifiques de ce travail comprennent l'étude de l'élimination de l'huile du sol contaminé par des colonnes expérimentales contenant certains biosurfactants et nanoparticules sélectionnées en laboratoire, l'évaluation de l'effet de certains facteurs, tels que le pH, la température, la concentration de biosurfactants sur l'efficacité d'élimination, et détermination de la portée et de la durabilité du processus développé. Les principaux résultats montrent que la composition principale du sol contaminé était du sable et du limon, avec une teneur en humidité et une teneur organique de 5,45% et 1,44%, respectivement. De plus, les particules bimétalliques fer / cuivre ont été avantageusement fabriquées avec un diamètre moyen de particules de fer et de cuivre de 20 nm, alors que la quantité de fer est supérieure à celle du cuivre. La présence d'oxyde de fer et d'oxyde de cuivre a également été prouvée par analyse XRD. De plus, la présence du fer valent zéro a été confirmé dans les nanoparticules. Pour tester l'efficacité de l'élimination du pétrole par les biosurfactants et les particules de fer / cuivre, une expérience sur colonne a été conçue et des méthodes d'extraction du sol et de détermination des hydrocarbures pétroliers totaux ont été obtenues.

1. INTRODUCTION

Crude oil (petroleum) is a yellowish-black liquid found underground pools and reservoirs, or within sedimentary rocks. It consists of a mixture of hydrocarbons formed by the decomposition of dead plants and animals millions of years ago. It has been used as an energy source for thousands of years ago. When released into the environment, it is degraded due to the physical, chemical, and biological changes (or weathering) (Devold et al. 2013). The degradation rates are based on its physical and chemical characteristics.

Petroleum hydrocarbons in oil are mainly composed of two groups: aliphatics and aromatics. Aliphatics include alkanes, alkenes, and cycloalkanes, while aromatics are comprised of at least one benzene ring in their structure (e.g. polycyclic aromatic hydrocarbons – PAHs; benzene, toluene, ethylbenzene, xylenes – BTEX) (Williams et al. 2006). Although the composition of crude oil depends on source, its basic elemental constitution includes carbon (83-87%) and hydrogen (10-14%) (Stauffer et al. 2008).

The fate of petroleum hydrocarbons in the environment includes three main processes: adsorption to soil particles, volatilization, dissolution in water. In addition, petroleum hydrocarbons may be biodegraded by different bacteria and microorganism populations present in soils and sediments, such as *Pseudomonas*. Due to the high-energy electrons in their composition, the petroleum hydrocarbons are considered as the food sources (or electron donors) for the microbial populations. The biodegradation rates for different types of petroleum hydrocarbons are dependent on the occurrence of their terminal electron acceptor processes (TEAP), such as dissolved oxygen (DO), nitrate (NO_3^-), insoluble manganese (Mn^{4+}), ferric iron (Fe^{3+}), sulfate (SO_4^{2-}), and carbon dioxide (CO_2). For high molecular weight hydrocarbons, the biodegradation rates are normally slow, which is due to their biodegradation-resistant properties.

When PAHs enter the soil, they may attach to particles (in the soil) and may remain in the soil for a long period of time, which can contaminate the soils and sediments. Moreover, the transport of PAHs (in fuel oil) in contaminated soil may cause negative effects to the aquatic communities downstream of the contaminated sites (Wang et al. 2009).

In fact, oil is released to the soil by two general pathways: flow infiltration of bulk oil as a result of gravity forces and capillary action, and separation of individual compounds from bulk oil mixture and dissolution in air or water, which contribute significantly to the soil contamination. During normal operation at oil fields, contamination of the soil is caused by the leakage and spillage of crude oil from oil wells, sumps and pits, tank batteries, gathering lines, and pump stations.

Presently, various oil-contaminated remediation methods are available, for example thermal treatment, soil washing, soil vapor extraction, bioremediation, solidification, and stabilization (Dadrasnia et al. 2015). However, they are expensive, and can form hazardous by-products and reduce the nutrient and organic matter contents in soil (Lim et al. 2016). Therefore, it is essential to research other sustainable and cost-effective remediation methods.

Surfactants are the amphiphilic compounds. They are surface active agents. They are composed of both hydrophilic and hydrophobic portions that give surfactants their detergency and solubilization properties. Therefore, they can be used to wash or flush the soil. Moreover, they are also used as household detergents, adhesives, flocculating, wetting and foaming agents. The head of surfactant molecules is hydrophilic (e.g. carbohydrate, amino acid, carboxylic acid, phosphate, alcohol), while the tail is hydrophobic (e.g. fatty acids, hydroxyl fatty acids). Therefore, in aqueous solutions, the combination of these hydrophobic tails may solubilize the hydrophobic organics more easily (Lin et al. 1996, Vu et al. 2015). Surfactants are commonly used to enhance the removal of oil from a specific media by formation of emulsions and foams (Kaczorek et al. 2018, Mulligan et al. 2005, Urum et al. 2004, Yao et al. 2017).

Biosurfactants are surfactants that are produced by yeast, bacteria or fungi from many substrates including sugars, oils, alkanes and wastes. In an aqueous solution, if the concentration of biosurfactants is higher than a certain critical value, which is called critical micelle concentration (CMC), the monomer molecules may aggregate and form micelles. In other words, CMC is the minimum concentration to form micelle. If the concentration of biosurfactants is more than CMC, their molecules will associate to form micelles and bilayers (Kaczorek et al. 2018). The CMC is also used to estimate the surfactant efficiency. The lower CMC, the higher surfactant efficiency. The reason is because a low CMC means that less biosurfactant is required to decrease the surface tension (Lin et al. 1996).

Compared with other chemically produced surfactants, such as synthetic surfactants, biosurfactants are considered more eco-friendly due to their biodegradability. Biosurfactants have been used for removal of heavy metals, organic contaminants, or crude oil from contaminated soils (Mulligan et al. 2001, Mulligan et al. 2005, Urum et al. 2004)

In recent years, nanoparticles have been used as the new adsorbents in the remediation techniques. Compared with other materials, they have many advantages, such as large specific surface area, high adsorption sites, can be transported to difficult target zones of a contaminated site (Bains et al. 2019). Different types of nanoparticles have been effectively studied for remediation techniques over the past few years. One of the most widely used nanoparticles is nanoscale zero valent iron (nZVI), which is due to their low toxicity, high reactivity, low cost, and potential for broader application (Babaee et al. 2017). For example, nZVI was effectively used for removal of total petroleum hydrocarbons (TPHs), polycyclic aromatic hydrocarbons (PAHs), and biodiesel in contaminated soil (Babaee et al. 2017, Chang et al. 2005, Jiang et al. 2018, Murgueitio et al. 2018, Pardo et al. 2015, Pardo et al. 2016, Zhao et al. 2016). Hence, combination of nanoparticles and biosurfactant will be a promising method for removal of oil-contaminated soil.

The main goal of this project is to investigate the synthesis and application of iron/copper (Fe/Cu) nanoparticles and some biosurfactants for removal of oil

from contaminated soil. The specific objectives of this work are to: (i) synthesize Fe/Cu nanoparticles, (ii) investigate the removal of oil from contaminated soil by Fe/Cu nanoparticles and some selected biosurfactants, (iii) evaluate the effect of some factors on the removal efficiency

2. MATERIALS AND METHODS

2.1. Materials

Iron (II) sulfate heptahydrate 99% ($FeSO_4.7H_2O$) and sodium borohydride 98% ($NaBH_4$) powders were purchased from Acros Organics, New Jersey, USA. Copper (II) sulfate pentahydrate 99% ($CuSO_4.5H_2O$) was obtained from Fisher Scientific, Pennsylvania, USA. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) solutions were purchased from Fisher Scientific, Pennsylvania, USA and used without purification. The water used for this research was deionized (DI) water produced from the Barnstead Nanopure water purification system (Thermo Scientific).

2.2. Soil Source and Characterization

Oil-contaminated soil was obtained from a contaminated site, stored at 4_oC in a refrigerator in the laboratory. The characterization of this soil, such as particle size, distribution and percentage of clay, silt, and sand was analyzed by a laser scattering particle size distribution analyzer (Horiba LA-950V2, Japan). The organic content was determined by ASTM D2974-14 method.

$$moisture\ content(\%) = \left(\frac{W_w - W_d}{W_w}\right) * 100\% \qquad [1]$$

$$organic\ content\ (\%)\ = \left(\frac{W_d - W_b}{W_d}\right) * 100\% \qquad [2]$$

W_w: weight of wet soil, g
W_d: weight of dry soil, g
W_b: weight of burned soil, g

2.3. Surface Tension Measurement of Biosurfactants

Two biosurfactants (rhamnolipid and sophorolipid) were obtained from Jeneil Biosurfactant Company, USA. Surface tension of the rhamnolipid biosurfactant solution was measured using a Kruss K10 force tensiometer (Krüss GmbH, Germany) with a platinum plate. Each measurement was repeated five times and average results were reported. The temperature was held constant at 20_oC by circulating thermo-stated water through a jacketed vessel containing the sample. The experimental variability of these surface tension measurements was approximately 0.1 mN/m

2.4. Synthesis of Fe/Cu Nanoparticles

The synthesis of Fe/Cu particles was prepared by the approach of Morales-Luckie et al. (2008). In this method,

5mM $FeSO_4.7H_2O$ and 5mM $CuSO_4.5H_2O$ solutions were prepared separately in two beakers. Then, 500 ml of each solution were mixed and stirred under nitrogen at room temperature for 30 min. The pH of the resulting mixture was adjusted to 7.0 by 0.1M and 1M NaOH solutions. Afterwards, 100 ml of 10mM $NaBH_4$ aqueous solution was poured quickly into the mixture under stirring.
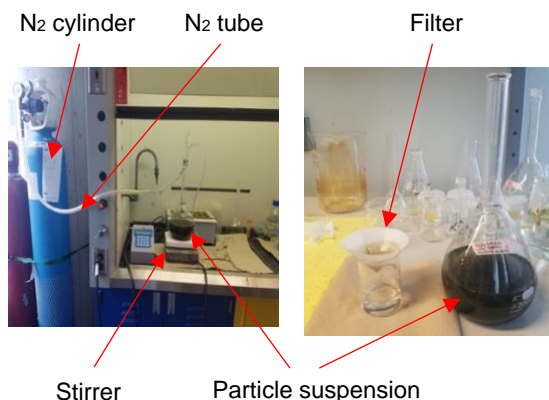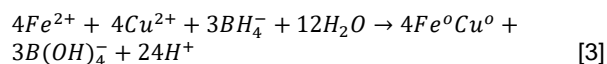

Figure 1. Fe/Cu particle synthesis system

The reaction for this process is represented by the following reaction:

$$4Fe^{2+} + 4Cu^{2+} + 3BH_4^- + 12H_2O \rightarrow 4Fe^oCu^o + 3B(OH)_4^- + 24H^+ \qquad [3]$$

A black precipitate (zero valent, Fe_oCu_o) was obtained, filtered, and washed three times by de-ionized (DI) water. Finally, water was removed by acetone and the Fe-Cu black particles were attained.

2.5. Characterization of Fe/Cu Nanoparticles

The chemical composition and crystallographic structure of the Fe/Cu particles were obtained by X-ray diffractometer (Philips X'Pert PRO Multipurpose, Netherlands) equipped with Cu K-alpha radiation. The air-dried Fe/Cu particles sample was ground and diffracted at 4000 positions over a 2θ range of 10_o to 90_o.

Transmission electron microscope (TEM, Tecnai G2 F20 S/TEM, USA) were used to investigate the morphology of Fe/Cu particles. The high-resolution TEM images show the size and location of synthesized Fe/Cu particles.

2.6. Batch Experiments

The batch experiments were carried out to investigate the effect of Fe/Cu particles and biosurfactants on the removal of total petroleum hydrocarbons from contaminated soils. Two sets of batch tests were conducted in two beakers (500 ml) at room temperature. In the first set, oil-contaminated soil was mixed with nanoparticles in the beaker, and biosurfactant was added to the mixture. In the

second set, oil-contaminated soil was mixed with biosurfactant, and nanoparticles were added to the mixture. The beaker was covered by an aluminum foil and shaken by a shaker at 0.228xg at room temperature for 24 h. After that, the mixture was centrifuged at 900xg for 30 min and filtered through a 25 nm Millipore membrane filter. The final solution was extracted, and oil concentration in the sample will be analyzed by the gas chromatography with flame ionization detector (GC/FID) instrument, following the EPA 8015 method.

The effect of some factors on batch experiments will be determined, such as pH, temperature, particle size and amount, contact time, mixing type, mixing time, other contaminants, ionic strength, additive types, amount and ratio of additives

2.7. Column Experiment

The column experiment will be conducted in a plastic column (L = 25 cm, D = 2.5 cm) (Figure 2). The aqueous biosurfactant and nanoparticles suspension solution will be added at the top of the column and allowed to percolate through the column by a peristaltic pump (Masterflex easy-load II). At the bottom of the column, a filter will be used to keep the soil inside the column during experiment time. Water was leached through the soil column for permeability tests. After that, the effluent solution was centrifuged at 900xg for 30 min and filtered through a 25 nm Millipore membrane filter. The final solution was extracted by soil extraction method, and oil concentration in the sample will be analyzed by the gas chromatography with flame ionization detector (GC/FID) instrument, following the EPA 8015 method.

Biosurfactant   Tube   Column reactor

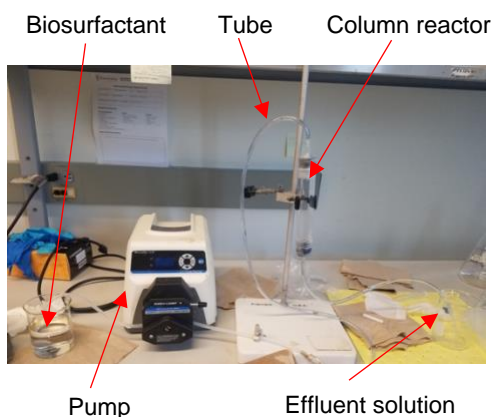Pump   Effluent solution

Figure 2. Column experiment

The effect of some factors on batch experiments will be determined, such as pH, temperature, particle size and amount, contact time, presence of organic matter, additive types, amount and ratio of additives. The control experiments were carried out by adding only nanoparticles, adding only biosurfactants, as well as adding separately the nanoparticles and biosurfactants. All experiments will be conducted in triplicate and with mass balance. The

experiments will continue until the amount of oil detected in the leachate is negligible.

2.8. Soil Extraction Method

The extraction of soil follows the approach of Wang et al. (1994). In this method, contaminated soil was extracted three times by sonication of 1:1 hexane/dichloromethane, dichloromethane, and dichloromethane for 30 min or until the extraction was colorless. The total extracts were collected and filtered by glass fiber filter. The final solution was obtained.

2.9. Total Petroleum Hydrocarbon Measurement

Total petroleum hydrocarbons in contaminated soil were measured by gas chromatography with flame ionization detector (GC/FID, CP-3800 Varian, USA), following the EPA 8015 method. The GC conditions suggested by Thermo Fisher Scientific are shown in Table 1

Table 1. Gas chromatography conditions (Galbiati et al. 2015)

Parameters	Value
Carrier gas	Helium
Flowrate, ml/min	2.0, constant flow
Oven temperature, ^oC	45^oC (1 min), 25^oC/min to 340^oC (hold 2 min)
Injector temperature, ^oC	300
Injector mode	Splitless
Splitless time, min	0.8
Splitflow, mL/min	50
Detector temperature, ^oC	340
Injected volume, µL	2.0

The syringe was rinsed by dichloromethane and n-pentane solvents.

3. RESULTS AND DISCUSSION

3.1. Soil Characterization

The composition of contaminated soil is shown in Table 2

Table 2. Characteristics of tested soil

Characteristics	Oil-contaminated soil
Median size, µm	91.54
Mean size, µm	99.03
D10, µm	23.46
D90, µm	185.31
Sand, %	67.49
Silt, %	30.50
Clay, %	0.00
Colloid, %	2.01
Moisture content, %	5.45
Organic content, %	1.44

In terms of particle size of approximately 100 nm, this soil is classified as the fine sandy soil (US Bureau of Soils 1985).

3.2. Biosurfactant Surface Tension

The surface tensions of some biosurfactants are shown in Table 3. The surface tensions of rhamnolipid biosurfactants are similar. Moreover, sophorolipid has a slightly higher surface tension value. This result has been shown previously (Nguyen et al. 2011).

Table 3. Surface tension of tested biosufactants

Biosurfactant	Surface tension (mN/m)
Rhamnolipid JBR 425	26.99
Rhamnolipid JBR 210	30.74
Rhamnolipid 1.5%	26.98
Sophorolipid 1.5%	34.38

3.3. Scanning Electron Microscopy of Fe/Cu Nanoparticles

The morphology of Fe/Cu particles is introduced by the SEM image (Figure 3). The agglomeration of Fe/Cu bimetallic nanoparticles is clearly shown as a result of magnetic and electrostatic attractions. However, it is hard to see the boundaries between different nanoparticles.
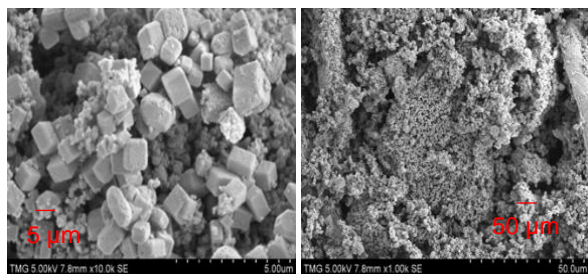

Figure 3. SEM images of Fe/Cu particles with high (left, 10k) and low (right, 1k) magnification

3.4. Transmission Electron Microscopy of Fe/Cu Nanoparticles

The TEM images of Fe/Cu particles are shown in Figure 4. The presence of nanosized Fe and Cu particles is clearly indicated by the TEM images. The average diameter of particles is about 20 nm. Moreover, the nanoparticles are spherical and have similar sizes and shapes. The boundaries between different nanoparticles are clearly observed. In addition, the TEM image under high magnification (right) shows the presence of zero valent iron (ZVI) on the nanoparticle composition. These ZVIs can play a large role for the reduction of contaminants
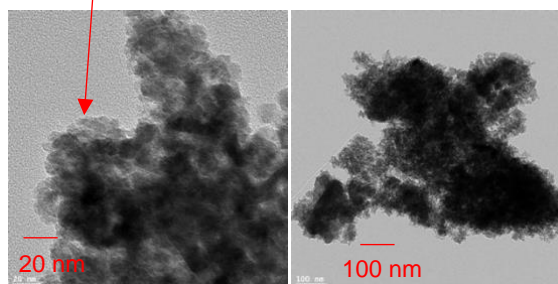
Zero valent

Figure 4. TEM images of Fe/Cu particles with high (left) and low (right) magnification

In addition, the elemental distribution of Fe/Cu nanoparticles (Figure 5) indicates the high amounts of Fe and Cu in the composition of the nanoparticle sample. Moreover, the distribution of Fe is higher than Cu in the nanoparticle composition.
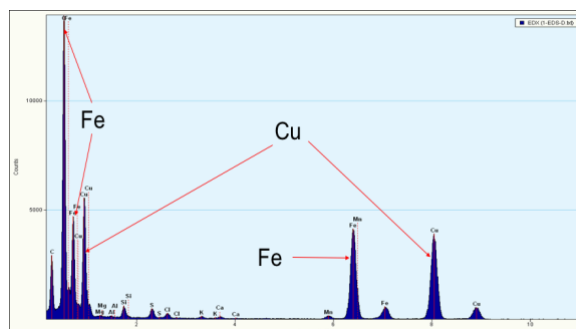

Figure 5. Elemental distribution of Fe/Cu nanoparticles

3.5. X-ray Diffraction of Fe/Cu Nanoparticles

The XRD peaks of synthesized bimetallic Fe/Cu nanoparticles are shown in Figure 6. An observation of diffraction peak at 44.6 is equivalent to the (110) diffraction of iron and (111) diffraction of copper. Moreover, the presence of iron oxide (Fe_3O_4) is confirmed by peaks at 29.2, 35.6, 43.3, 62.9 of the 2θ range. In the meanwhile, copper oxide (CuO) on the grid surface is confirmed by the diffraction peak at 34.4, 39.1, 74.1 of the 2θ range. The presence of Fe_3O_4 and CuO is due to the oxidation of Fe and Cu, respectively.

Furthermore, the amount of Fe_3O_4 in the nanoparticle is higher than CuO, which indicates the thick layer of Fe_3O_4 and the thin layer of CuO. This XRD design suggests a Fe/Cu structure, whereas the Fe atoms are presumably embedded within the Cu matrix.
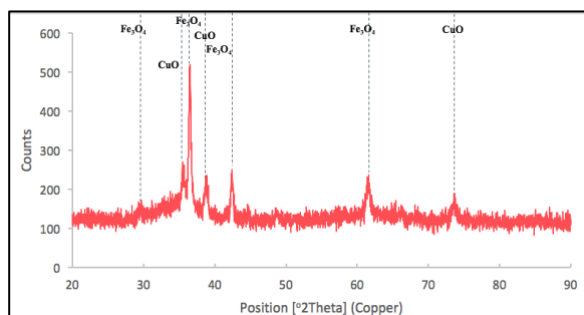
Figure 6. XRD analysis of Fe/Cu nanoparticles

This type of structure is typical of a one-step synthesis of bimetallic nanoparticles. These results are similar to previous articles (Morales-Luckie et al. 2008, Tabrizian et al. 2018)

4. CONCLUSIONS

In conclusion, the characterization of oil-contaminated soils was obtained. In particular, the moisture content and organic content of soil sample was 5.45% and 1.44%, respectively. Moreover, the main composition of contaminated soil was sand and silt. In addition, the surface tensions of two biosurfactants were measured, where rhamnolipid biosurfactant had a lower value than the sophorolipid biosurfactant.

Furthermore, the iron/copper bimetallic particles were successfully synthesized. Their SEM images showed the aggregation of iron/copper bimetallic nanoparticles on the particle surface. In addition, the TEM images indicated the nanosize of the iron and copper particles with the average diameter of particles of 20 nm. The spherical and similar size and shape of different nanoparticles were observed. The presence of zero valent iron on the nanoparticle composition was also detected. Besides, the elemental distribution of particles demonstrated the higher amount of iron than copper in the nanoparticle composition. Moreover, the presence of iron oxide and copper oxide on the grid surface of nanoparticles is confirmed by the XRD analysis of the Fe/Cu nanoparticles. In the meanwhile, a typical structure of Fe/Cu bimetallic nanoparticles, where Fe atoms are presumably embedded within the Cu matrix is also suggested from the XRD analysis. These results are corresponding to previous research.

Finally, the design of a column experiment and methods of soil extraction and total petroleum hydrocarbons measurement were obtained. They will be used to test the oil removal efficiency by biosurfactants and Fe/Cu nanoparticles, as well as determine the total petroleum hydrocarbons from contaminated soil.

In the future, the batch and column experiments will be conducted. Gas chromatography with flame ionization detector (GC/FID) and inductively coupled plasma mass spectrometry (ICP-MS) instruments will be used to measure the total petroleum hydrocarbons and leached metal ions in effluent solution, respectively. Moreover, the addition of biosurfactant as a solution and as a foam will be conducted and compared with regards to the oil treatment efficiency.

5. ACKNOWLEDGEMENTS

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