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Application of lightweight expanded clay aggregate as sorbent for crude oil cleanup

Mohammad Pouramini[a,*], Ali Torabian[a], Fariborz Mohammadi Tehrani[b]

[a]*Faculty of Environment, University of Tehran, No. 25, Ghods St., Enghelab Ave., Tehran 14155-6135, Iran, Tel. +98 9352845506, Fax +98 2166407719, email: m.pouramini@ut.ac.ir (M. Pouramini), Tel. +98 912125 7996, Fax +98 2166407719, email: atorabi@ut.ac.ir (A. Torabian)*

[b]*Department of Civil and Geomatics Engineering, California State University, Fresno, California, United States, Tel. +1(559) 278-1762, Fax +1(559) 278-7002, email: ftehrani@csufresno.edu (F.M. Tehrani)*

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ABSTRACT

This paper presents studies on the effect and capacity of lightweight expanded clay aggregates (LECA) as adsorbents for cleaning up crude oil from aquatic environment. These studies incorporate the effect of adsorbent particle size, surface modification, API (American Petroleum Institute) degree, and the contact time. Sorbent characterization has been determined using SEM, XRD, XRF, and BET. Optimum sorption was reached during the first 10 min, followed by a steady state of crude oil sorption. Furthermore, results indicated that fine LECA particles have higher adsorption efficiency due to the increase of specific surface area. Decreasing the API degree had a significant influence on the rise of the adsorption rate. The results indicated that the LECA performs better in heavier oil than lighter oil. Overall, LECA was found to be a proper adsorbent for cleanup oil spill from an aquatic environment, which could also be collected from the water surface rapidly.

Keywords: Crude oil; LECA; Cleanup; Bentonite; Sealant; Adsorption; Oil spills; Particle size

1. Introduction:

Serving energy demands is a growing issue worldwide [1]. Indeed, it has been projected by the International Energy Agency (IEA) that by the year of 2030, nearly 60% of the total worldwide energy growth will be fulfilled by fossil fuel sources, like heavy oil, coal, and natural gas [2]. Oil is radically stored and transported in large quantities via tankers, which requires cost-effective solutions to transport oil. Whether in storage or in transport, oils are at times spilled onto land or within water bodies, which happens to be a growing issue worldwide. Disasters, such as the Deep Water Horizon oil spill and the Exxon Valdez oil spill, serve as evidences that coastal oil spills present risk to the economy and natural resources, and could directly influence public's health [3]. In 1989, in Exxon Valdez in Alaska on the coastal reef of the Prince William Sound (PWS), an enormous amount of 11 million gallons of crude oil - nearly 260 thousand barrels of crude oil, spilled into the ocean, one mile off the shore [4]. This spill had a huge impact on wildlife, such as sea otters, sea birds, bald eagles, killer whales, and harbor seals [5]. The largest marine oil spillage in the history of the petroleum industry, the Deepwater Horizon oil spill, took place in the Gulf of Mexico on April 20, 2010 [6]. The overall oil spillage was assessed at around 210 million gallons of oil equivalent to 4.9 million barrels of oil [7]. As indicated in these evidences, crude oil discharge can do serious harm to oceans and coastal areas. Such damage might remain on coastlines for years and leave adverse effects on the marine environment. Some fractions of oil can result in chronic sub-acute toxicological effects, including reduced growth and reproduction, poor health, low recruitment rates. These effects can change population dynamics and spoil tropic interactions and the structure of natural communities within ecosystems [8]. The estimation is that over two million tons of oil enters marine environments

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*Corresponding author.

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from ships and other sea-based activities on an annual basis. Table 1 summarizes the total hydrocarbon pollution of marine environments worldwide [9].

It is worth noting that physical/mechanical methods are the primary response options for oil spill cleanup, but the crude oil recovery is just about 10–15% [10]. Physical strategies consist of the use of booms, skimmers, washing, cutting vegetation and burning [11]. All oil discharged into the ocean will begin physically changing in a process called weathering. Weathering alters the way in which oil behaves and can transpire at various levels. There are vigorous variables affecting this process, such as temperature, sunlight on the spill site, behavior of the environment and the number of microbes available to deplete the crude oil [12]. Spill experts must distinguish how spilled crude oil would weather, in order to adopt the best response plan and technology for the cleanup. Other factors like the API (American Petroleum Institute) gravity (or the petroleum product weight) and the physical states of the environment at the time of the oil spill, would affect the chosen technique. Examples of oil weathering include evaporation, dissolution, dispersions, absorption, emulsification, and photo oxidation. Since heavy and light crude oils behave differently, specifying the type of spilled petroleum oil is very important. The light crude oil has a lower density, viscosity, and boiling point compared to the heavy crude oil [13–15]. The existing hydrocarbons in the aquatic environment can derive from natural oil seepage and human activities, including extraction, transportation, refining, storage, and employment of crude oil [16,17]. Ongoing investigations and developments focus on enhancing techniques by decreasing the number of experiments, presenting data on the direct additive effects of variables, as well as data on the influence of interactions between variables using experimental strategies. Such statistical strategy has been effectively used in numerous fields [18–21]. The strategy considers influences of materials, equipment, and process conditions to obtain the right parameters and their ranges for further research. Most currently employed techniques have high maintenance costs and require relatively expensive mineral adsorbents. Such high cost require adjustment in the expected effectiveness of the employed techniques to balance the economy of the project. Thus, cost is a significant parameter for comparing the sorbent materials. In general, a sorbent may be considered as "low cost", if requiring little processing, is ample in nature, or is a by-product or waste material of industry [22]. LECA (Light Expanded Clay Aggregate) is made from the expansion of a specific type of clay in rotary kilns with an approximate temperature of 1200°C and resemble morph state of materials. These particles tend to preserve a neutral pH, which makes them harmless to plants. Further, LECA has no tendency to reach chemically to other substances, hence, it is not degradable. Thus, they are geo-chemically perceived as manufactured volcanic rocks, which are not biodegradable, and yet do not pose a toxic threat toward the environment. Physical crushing and grinding of LECA will ultimately result in mineral fine particles similar to clay. The non-toxicity and neutral pH of LECA particles are essential reasons for their environment-friendly characteristics. The LECA has nearly round-shaped particles with rough surfaces [23,24]. The LECA is lightweight, incompressible against constant pressure, non-toxic, sound and temperature insulator, with a natural pH. The LECA in this study is produced in Saveh, Iran, and is cheaper than other industrial absorbents, and therefore, it can be applied as a convenient, inexpensive, and environmentally friendly adsorbent for the cleanup of crude oil from aquatic environment [24,25]. The high porosity of LECA makes it applicable in horticulture that requires retain of moisture in the growing media. Further, LECA has applications in construction, as lightweight aggregates, as well as in water treatment amenities for the desalination of civic wastewater and fresh water [26–30]. The focal point is that there are no known disadvantages of LECA as a material for water treatment. LECA has also been successfully used for the removal of heavy metals in water [31].The miniature pores of LECA, which resemble separated air pockets, allows these aggregates to retain moisture and still remain floating on water [32]. Due to its porous structure, it can readily absorb and retain environmental pollutants. The focus of this study is to evaluate and to compare normal adsorbents of LECA in cleaning up crude oil from aquatic environments. Efficiency of experimental adsorbents was studied after changing adsorbent particle sizes, surface modification with Bentonite and Sealant (Maleki GmbH solution), different types of crude oil, and the contact time (10, 60, 120, and 240 min).

Table 1
Annual hydrocarbon contamination of marine environments worldwide [9]

Source	Amount (1000 tons/year)	Percent
Land-based	1200	45.45
Oil transportation and shipping	457	17.31
Offshore production discharge	20	0.76
Small craft activity	53	2.01
Atmospheric fallout	300	11.36
Natural seeps	600	22.73
Other	10	0.38
Total	2640	100.00

2. Materials and methods

2.1. Seawater sampling

Seawater was collected from Bandar Abbas in Hormozgan Province, adjacent to the Persian Gulf in Iran (Latitude: 27.1832 N, Longitude: 56.2666 E). Table 2 presents water characteristics at the sampling station, measured

Table 2
Water characteristics at sampling station

Property	Amount
Seawater pH	7.96
Ec (mS/cm)	61.27
TDS (mg/lit)	59400
Salinity (ppt) or (g/Kg)	40
T (C)	26.5

with Conductivity benchtop meter inoLab® Cond 7110 (WTW Company, Germany). The pH was measured with pH meter (Metrohm, Swiss made).

2.2. Adsorbent

The adsorbents LECA (with grain size 0–4, 4–10, 10–25 crushed, and 10–25 mm) was provided from LECA Plant in Saveh, Iran. Bentonite was provided by the LECA Company in Tehran, Iran. In the coating process, 500 g of sieved LECA was soaked in water, coated with Bentonite Powder, and dried out in room temperature. Sealant product was provided from exclusive agent of Maleki GmbH (German Company) from Tehran, Iran. For the coating process, 500 g of sieved LECA was soaked twice in the Maleki sealant solution, and then dried in room temperature. To prepare crushed granules of studied adsorbents, samples were first crushed manually. Then, they were washed with ion free water to remove dust, and were placed in the oven for 12 h in 105°C to remove the excess water and humidity [33]. Following the stage of drying, they were kept in containers in the laboratory.

2.3. Characterization of adsorbent

To characterize the physicochemical properties of LECA, scanning electron microscopy (SEM) and X-ray fluorescence spectroscopy (XRF) techniques were applied. The SEM analysis was implemented using a VEGA3 TESCAN, Czech Republic and French Multi-National Company. The extent to which the major and trace elements in the resultant ash samples were concentrated was determined using a wavelength XRF spectrometer (Magix-pro Philips, Netherland). In assessing the chemical structure and determining the types of phases forming adsorbents qualitatively, XRD (Bruker D4 Siemens, Germany) test were used (Table 3). In this table, sample numbers S1, S2, and S3 refer to samples which their physicochemical characterizations were measured by XRF and XRD in different periods of time for LECA. All samples S1, S2, and S3 are LECA particles, but they were not measured at the same time. Characterizations of samples no. 1 (S1) and no. 2 (S2) were measured by the XRF method; and those of no. 3 (S3) were measured by the XRD method. The microscope is equipped with the EDX system, so Energy Dispersive X-ray microAnalysis (EDXA) has been used (VEGA3 TESCAN, Czech Republic and French Multi-National Company) during the test to determine the characterization of samples (Table 4).

Table 5 shows the chemical composition of the LECA. The ratio of SiO_2/ Al_2O_3 (62/18) is 3.44, indicating that the LECA is known as a silicate component [34]. The N_2 adsorption/desorption analyses were performed(Micromeritics' TriStar II PLUS, USA) at –196°C in laboratory of science faculty at the University of Tehran, Iran. Sorbents were degassed at 300°C for 6 h. Specific surface area (S_{BET}), total pore volume (V_p), and pore diameter (D) of samples were obtained by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods using Micromeritics analysis software (Table 6). All tests were done in accordance with relevant ASTM standards, unless reported otherwise [35].

2.4. Preparation of crude oil

The crude oils used in this research were provided from Research Institute of Petroleum Industry in Tehran, Iran. Table 7 presents properties of crude oils used in this research.

The discharged oil on water surface is subject to physical change in a process called weathering. Thus, it is of utmost importance to simulate this phenomenon in the laboratory environment. In this study, the simulation was facilitated by

Table 3
XRF and XRD analysis

Analysis	Sample no.	Formula (%)											
		SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)	SO_3 (%)	P_2O_5 (%)	TiO_2 (%)	SrO (%)	L.O.I * (%)
XRF	S1	58.50	16.50	9.20	4.60	3.50	1.40	4.60	0.30	0.20	0.90	0.10	0.10
XRF	S2	58.90	17.20	8.80	3.70	3.20	1.30	4.50	0.40	0.20	0.80	0.10	0.70
XRD	S3	60.30	18.00	7.29	4.44	3.20	1.83	3.72	0.40	–	–	–	0.00

XRD Result: Feldspar + Quartz + Dolomite + Clay Mineral

* L.O.I = Loss On Ignition

Table 4
EDS charts – Chemical characterization of a sample

Quantitative results	C (%)	O (%)	Na (%)	Mg (%)	Al (%)	Si (%)	S (%)	K (%)	Ca (%)	Fe (%)
LECA	11.38	54.40	1.54	0.10	4.86	23.10	0.00	3.63	0.44	0.59
LECA CRUSHED	7.53	51.37	1.32	2.39	7.96	19.82	0.23	2.68	1.75	5.01
LECA CRUSHED + MALEKI	27.44	44.23	0.99	1.51	4.32	15.61	0.00	1.73	1.02	3.20
LECA + MALEKI	25.82	32.97	0.99	1.73	4.89	21.96	0.00	1.13	6.57	3.96
LECA + BENTONIE	6.27	55.65	1.80	1.66	5.59	18.05	3.06	0.47	4.62	2.88

Table 5
Sorbent characterization

Constituent (Parameters)	Value
Surface area (0.5–2.5 mm) (m^2/m^3)	2200
Surface area (2–4 mm) (m^2/m^3)	1000
Surface area (4–10 mm) (m^2/m^3)	550
Surface area (10–20 mm) (m^2/m^3)	300
Specific surface area (1.5–2.5 mm) (m^2/g)	2.93
Fire resistance	High
Thermal conductivity coefficient (W/mK)	0.07–0.10
Resistance to acids	High
Resistance to alkali	High
pH resistance	High
SiO_2 (%)	62
Al_2O_3 (%)	18
Fe_2O_3 (%)	7
CaO (%)	3
MgO (%)	3
K_2O (%)	4
Na_2O (%)	5
C (total) (%)	0.02
Loss on ignition	1.36
(SiO_2/Al_2O_3)	3.44

Source: Saint-Gobain Weber Company, Filtralite Department in Oslo, Norway and Dansk LECA A/S, Randers, 8900-Denmark [34].

Table 6
Specific surface area (S_{BET}), total pore volume (V_p), and pore diameter (D) for sorbents taken by BET and BJH methods

Materials	S_{BET} (m^2/g)	V_p (cm^3/g)	D (nm)
Pure LECA	2.1816	0.0044	6.2651
LECA + Bentonite	16.1959	0.0425	11.9860
LECA + Sealant	1.3080	0.0077	5.9116

Table 7
Crude oil characteristics

Type	API gravity	Viscosity @ 20°C (mm^2/sec)
Type I (Lg)	33.53	13.55
Type II (Wg)	30.92	21.77
Type III (Se)	19.20	–

pumping crude oil into a glass container and keeping the oil for two days inside the container. This resulted in nearly 20–30% decrease in the oil volume.

2.5. Extraction and analyses of crude oil

Total petroleum hydrocarbons (TPH) were measured with the help of the US-EPA Method-1664 Revision B called n-Hexane Extractable Material [36]. To increase the accuracy, all experiments were done in a triplicate basis. The effect of various parameters, such as adsorbent particle sizes, surface modifications, different types of crude oil (API gravity), and contact time (10, 60, 120, and 240 min) were all investigated on the adsorption efficiency by LECA. Further, the effect of coating LECA surface with Bentonite and Maleki GmbH sealants were examined.

2.6. Effect of adsorbent size

In this step optimum adsorbent size was determined as a function of the LECA's grain sizes.

2.7. Effect of surface modification

In order to determine the influence of surface modification on the adsorption efficiency, LECA with and without surface modifiers were tested.

2.8. Effect of API

To determine the effect of API gravity in this article, three kinds of crude oil with different API gravity were tested.

2.9. Effect of contact time

To evaluate the effect of contact time on adsorption process, different contact time in four periods (10, 60, 120, and 120 min) were investigated.

2.10. Sorption requisites

In general, an adsorbent for adsorption of crude oil should assemble several requirements: (1) granular type; (2) efficiency for the removal of pollutant (3) high capacity, selectivity, and rate of adsorption; (4) high physical strength (not disintegrating) in water; (5) ability to be regenerated if required; (6) environmentally friendly; and (7) low cost [37,38].

2.11. Quality assurance and quality control (QA/QC)

It is noteworthy that QA/QC were performed to ensure quality of analysis. Verification of calibration was accomplished with each set of test. In addition, the experiments were conducted at a constant temperature (25±3°C) with constant pH in laboratory. Glassware is cleaned out by being washed in hot water containing detergent, rinsing with tap and distilled water, and rinsing with solvent or baking. Boiling flasks that contain the extracted residue are dried out in an oven at 105–115°C and are then stored in a desiccator.

2.12. Experimental design

The amount of cleanup was selected as a response to investigate the optimum conditions of crude oil cleaning up. The crude oil cleanup depends on various parameters, such as adsorbent particle sizes, surface modification, different types of crude oil (or API gravity), and the contact time (10, 60, 120, and 240 min). Linear Model (LM) in RStudio Program Version 1.0.153 as one of the experimental design methods was used in this work for optimization of oil adsorption. Four significant factors were also specified for evaluating the effect of operation parameters on the efficiency of adsorption. In this study, all 288 experiments (96 tests for each one of the three types of oil) are optimized and modeled several times to obtain desired results at the conclusion of the experiment.

2.13. Data analysis

The data analysis was based on development of a fitting model to the response variable (Y) in the form of an equation. Regression analyses of data were performed with the statistical software package STAT 3.4.1. Furthermore, to investigate the significance of each term in the regression equation, analysis of variance (ANOVA) was utilized for the Linear Model in RStudio program, Version 1.0.153. The small Value of Probability (P-Value), lesser than 0.05, denotes that the model is of significance.

2.14. Water contact angle measurement

The contact angle of water droplet was measured (G10-Kruss, Germany) as a measure of the hydrophobicity of the sorbents by recording the value of water contact angle on sorbents at laboratory temperature.

2.15. Cell viability and proliferation

The study of cell viability was conducted according to ISO10993 part 5 standard. To prevent cell death due to any microbial contamination, sorbents were exposed by ultraviolet (UV) rays and sterilized for 20 min. Sorbents were placed in direct contact with cells, after the process of sterilization. At the end, sorbents were probed by Biotek Instrument (ELx808, USA) at 540 nm and cell images were recorded by an optical microscope for the assessment of their non-toxicity. Furthermore, sorbents were compared with their control group.

3. Results and discussion

3.1. Adsorbent characterization

Characterization of LECA reveals SEM images of the support surfaces with and without immobilized Maleki sealant and also the surface of LECA with and without modification with Bentonite (Fig. 1 with magnitude of 90×). The SEM micrographs demonstrate that LECA is rather porous. From Fig. 1, it can be seen that LECA pellets contain numerous pores with a wide array of sizes, and exterior and interior surfaces that are not smooth. Hence, this structure cause loading more particles on LECA granules. Fig. 1b is related to LECA granules after immobilization of Maleki sealant over them. Also, Fig. 1(b) shows Maleki sealant with high resolution. Since there are no reports about Maleki immobilized onto LECA, the results cannot be compared with the literature. Fig. 1c is related to LECA granules after immobilization of Bentonite particles over them. This image (Fig. 1c) clearly indicates that the surface of LECA granules was covered and agglomerated efficiently with Bentonite. Fig. 1 reports the morphology of granular LECA adsorbent. It can be observed that the material was formed by numerous accumulated small particles, producing a rough surface with a porous structure. The surface of LECA changes after modification as shown in Fig. 2 with more resolution and precision (with magnitude of 5 kx). The X-ray fluorescence analysis (Table 3) affirmed the existence of quartz (SiO_2) as a major mineral. Al_2O_3 and Fe_2O_3 are here as minor minerals, while other metal oxides exist as a trace mineral in the natural sorbent. Moreover, LECA composition was characterized using XRF analysis and the data were reported in Table 3. As shown in Table 3., the core components of LECA are silicon oxide and aluminum oxide, which are much the same as constituents in clinoptilolite zeolites found in nearly all parts of Iran. Likewise, the LECA was mainly comprised of SiO_2 (62%), Al_2O_3 (18%) and Fe_2O_3 (7%) [35].

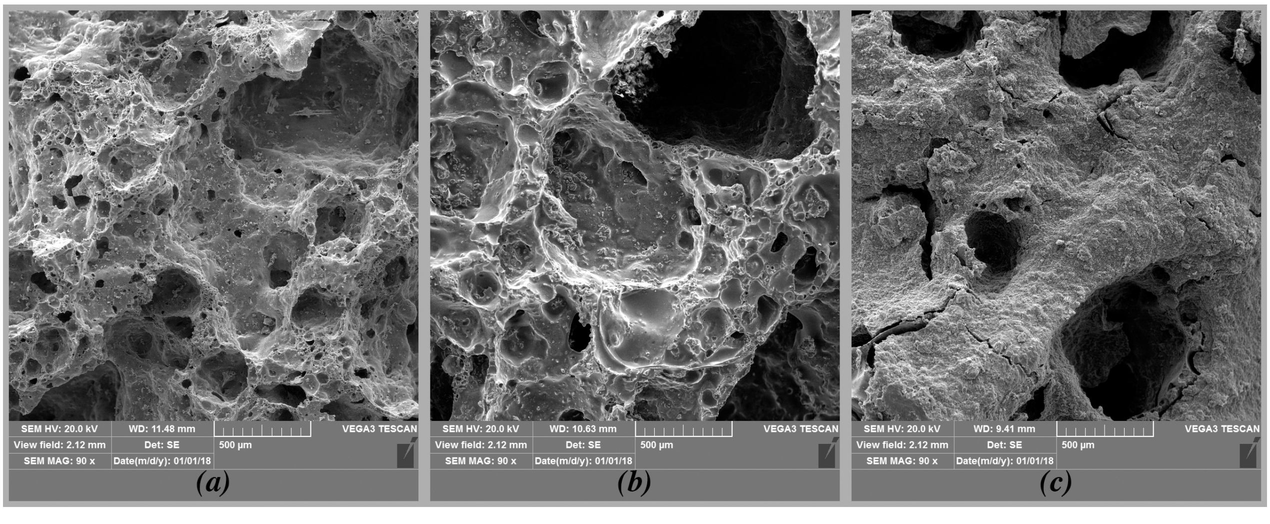


Fig. 1. Scanning electron microscopy (SEM, with magnitude of 90×) of (a) granular LECA (b) Maleki GmbH sealant solution coated on LECA (c) bentonite coated on LECA.

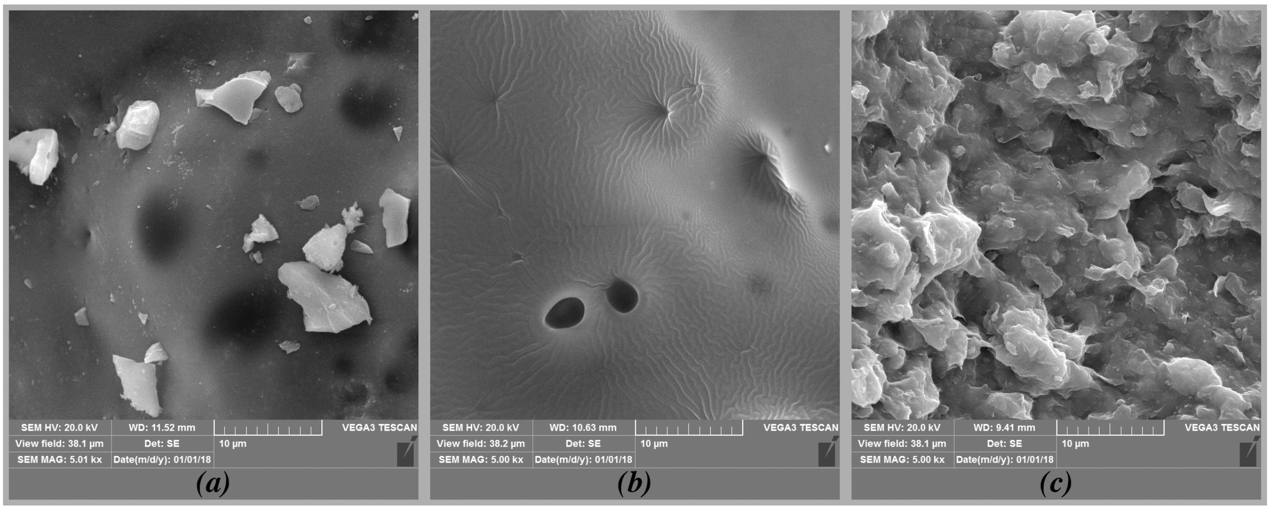


Fig. 2. Scanning electron microscopy (SEM, with magnitude of 5 kx) of (a) granular LECA (b) Maleki GmbH sealant solution coated on LECA (c) bentonite coated on LECA.

Energy dispersive X-ray microAnalysis (EDXA) used (VEGA3 TESCAN, Czech Republic and French Multi-National Company) showed the presence of C, O, Na, Mg, Al, Si, S, K, Ca, and Fe in Table 4.

3.2. The effect of adsorbents particles size

In the initial stage of the experiment, the effect of adsorbents particles size was studied. Based on previous studies [39,40], particle size of the adsorbent is a factor affecting the degree to which the adsorption process is efficient. Therefore, this study aims to investigate the effect of the particle size on the removal efficiency in four different sizes of LECA granules. Results of these experiments are shown in Fig. 3. According to these results, as adsorbent size decreases, the crude oil removal efficiency increases due to the increase of specific surface area (SSA); That is, as particle size decreases from 10–25 mm to 0–4 mm, the adsorption efficiency of crude oil increases from 25% to 115% (gram adsorbed crude oil/gram adsorbent) for LECA granules. The interesting factor to take notice of is that increased efficiency can take place as a result of the increased adsorbent physical surface. Moreover, small-size adsorbent particles revolve more promptly than bigger particles [39]. Statistical analysis shows that there is a significant difference between changes in adsorbent size and crude oil removal efficiency by LECA adsorbent (p-value < 0.05). Moreover, it is evident that the adsorption capacity for crushed LECA particles does not follow the same trend based on the particle size. The surface of crushed LECA practically shares the same texture as of the interior texture of LECA aggregates. Thus, the porous surface of crushed LECA causes a slight increase in the adsorption rate despite their larger size of particles.

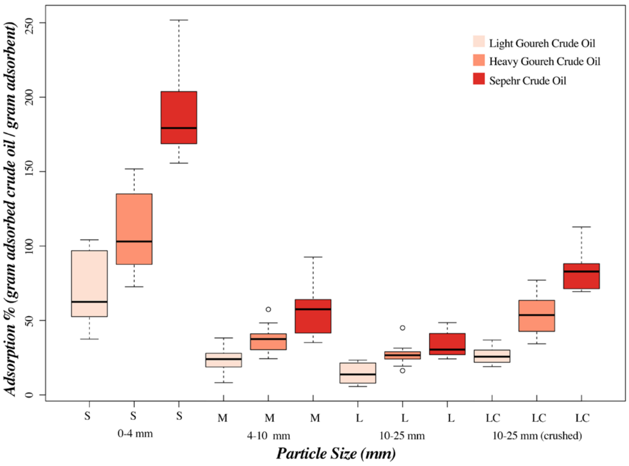


Fig. 3. Effect of particle size.

3.3. The effect of surface modification

In order to modify the LECA surface, a fixed amount of LECA was put in contact with bentonite and Maleki GmbH sealant solution and dried out in room temperature. Afterwards, the tests were carried out for each crude oil (with different API gravity ratio) at 10, 60, 120, and 240 min as shown in Table 7. In order to determine the effect of surface modification on the adsorption efficiency, LECA with and without surface modifiers were tested. Studies show that adding bentonite on the surface of LECA has no positive results and in some cases even lowers the amount of adsorption (Fig. 4). In these tests, pre-wetted LECA grains were in contact with bentonite particles for 2 d. However, observations revealed that bentonite particles were separated from LECA grains after exposure to oil, and thus, they were not efficient to enhance the oil absorption of the LECA.

On the other hand, however, adding Maleki on LECA's surface, improves and increases the amount of adsorption to some extent. This phenomenon appears due to the hydrophobicity of crude oil and Maleki. Different cheap sorbents, such as rice husk, coconut husk, kapok fiber, and bagasse are applied to collect spilled oil due to the pres-

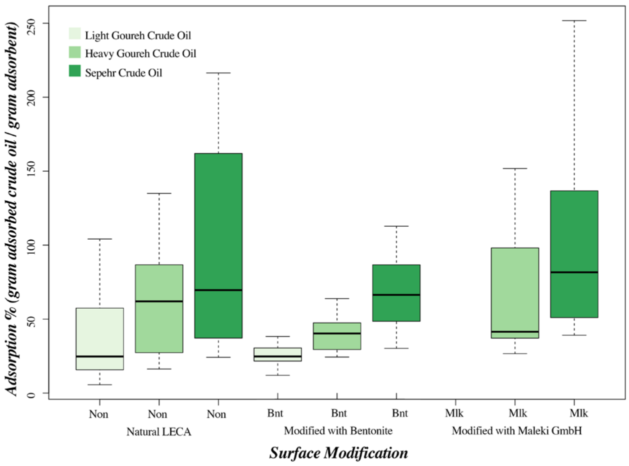


Fig. 4. Effect of surface modification.

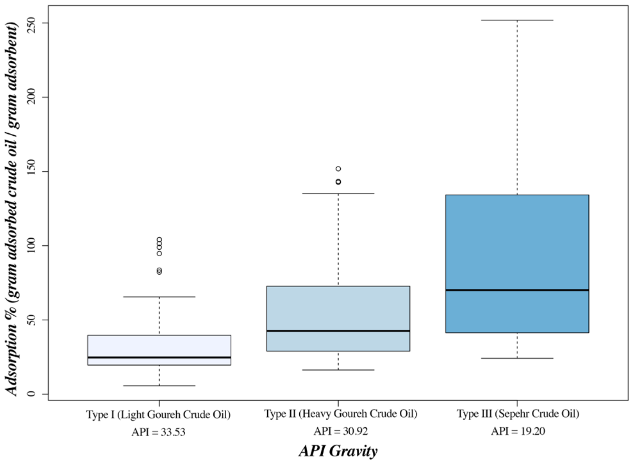


Fig. 5. Effect of API gravity.

ence of ample void spaces in their loose fiber structures and hydrophobicity [37]. Similar trends for sorption mechanisms upon hydrophobicity of PAHs have been disclosed in a case where leonardite (immature coal) was utilized as sorbent [41] and likewise when lignin-based sorbents were employed [42].

3.4. The effect of crude oil with different API gravity

To determine the consequence of API gravity in this article, three kinds of crude oil with different API gravity as shown in Table 7 were tested. This parameter would be one of the most dominant factors and would play one of the greatest roles in this research. As shown in Fig. 5, by increasing the specific weight of crude oil (or decreasing API degree), the adsorption would significantly increase due to the viscosity phenomenon.

3.5. The effect of contact time

According to the fiscals, P-value, and the amount of akaike information criterion (AIC), RStudio Program optimizes and changes four different contact times into two short and long-term time. The effect of contact time on the adsorption process was studied (Fig. 6). According to these results, the adsorption efficiency slightly increased with the increasing contact time. The maximum removal efficiency was achieved at the first 10 min of contact time or specifically in short-term time. As the contact time exceeds, crude oil sorption increases due to the increment in collisions between the adsorbent and the adsorbed. These results also indicate that the adsorption process of crude oil in the first 10 min is higher than later times. This phenomenon is related to the large number of vacant surface sites on the surface of the absorbent in the early stage. These outcomes are harmonious with results from former studies [39]. The major sorption procedure appears to be based upon a fast attraction of the crude oil with high hydrophobicity or low polarity towards the hydrophobic sides of the LECA surface on prompt exposure. This procedure was improved with contact time [26].

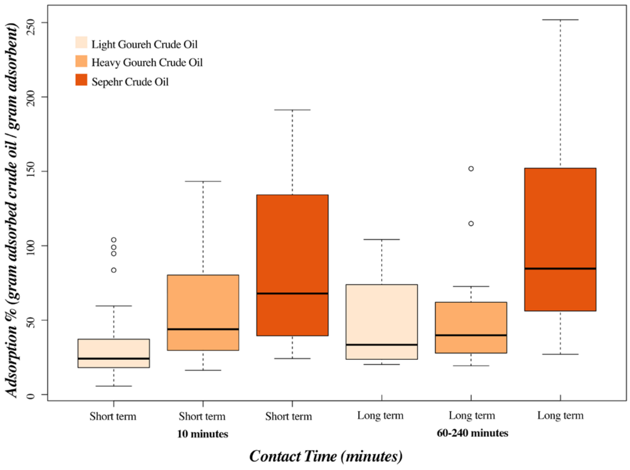


Fig. 6. Effect of contact time.

3.6. Comparison of the performance of LECA with other sorbents

As shown in Table 8, the adsorption efficiency of walnut shell is lower, while that of rice husk is higher when compared to that of LECA. Though it may not be reasonable to compare these two different sorbents, it is obvious that each sorbent has its own benefits. LECA is both economic and allows the use of numerous folds of the particles to boost the sorption of crude oil in field applications. In comparison with chemical materials that require high level technology for their production, LECA is a low cost construction materials that can be produced with minimum input energy. Further, application of LECA as a fire-resistant material (up to 4 h at 1100°C) reduces application costs of oil spill cleaning. The high absorption rate of LECA, nearly 1.02–1.4 tons of oil per m^3 of fine LECA is another economic benefit of LECA. In addition, it is also easy to collect LECA from aquatic environments as soon as crude oil is absorbed. LECA particles have applications in other water-related infrastructure and therefore, there

Table 8
Maximum adsorption capacity of some adsorbents for oil clean up

Adsorbent	Oil	Sorption capacity/ removal (g/g)	Reference
Rice husk	Marine diesel	19	[43]
Banana skins	Crude oil	5–7	[44]
Rice husk	Crude oil	2.98–6.22	[45]
Wool fibers	Oil	5.56	[46]
Rice husk	Gasoline	3.7	[47]
Modified oil palm leaves	Crude oil	1.2	[48]
Walnut shell	Mineral/ Vegetable oil	0.56–0.74	[49]
Coconut husk	Used engine oil	0.249	[50]
Chitosan	Bio-diesel	0.14	[51]
Natural LECA	Crude oil	1–2.1	Present work
LECA modified with Bentonite	Crude oil	1–2.2	Present work
LECA modified with Maleki GmbH sealant	Crude oil	2.1–2.5	Present work

are established methods of deployment and collection. A conventional method of collection is the application of skimmers and hydrophobic meshes. Collected LECA can be re-used after washing or burning the oil, or, it can be recycled to the rotary kiln to reproduce LECA. LECA particles can be easily pumped, as it is common as a low-cost deployment method in construction sites. Moreover, LECA is heat resistant and thus can be restored by incineration at high temperatures. Table 8 lists maximum sorption capacities for adsorbents recently used for oil adsorption. As can be seen, maximum sorption capacity for natural LECA was higher than other materials, except Rice husk, Banana skins, and Wool fibers that showed higher maximum adsorption capacity.

3.7. Optimization and verification

Statistical optimization resting upon desirability function was conducted. A set of attempts were implemented to assert the optimal discharge when the process factors were put at favorable levels. Standard deviation and error were considered for justification of experiments. Errors between predicted and actual characters were calculated in accordance with Eq. (1).

$$\text{Error} = (\text{Actual value} - \text{Predicted value}) / \text{Actual value} \times 100 \quad (1)$$

3.8. Optimization of removal conditions using linear model in RStudio program

The analysis of variance (ANOVA) for the models was carried out and the importance of model was examined by analyzing the crucial differences among sources of variation in experimental results, i.e. the value of probability (P-value), and the coefficient of multiple determination (R^2). Furthermore, the model was remarkably noteworthy, since it was obvious from the very low probability (P-value < 2.2e-16). As shown by Eq. (2), an experimental relationship was attained between the response and independent variables:

$$Y = 8.15985 + (0.57932)\,X_1 + (-4.22612)\,X_2 + (-5.21269)\,X_3 + (-3.11364)\,X_4 + (-0.03969)\,X_5 + (1.45376)\,X_6 + (1.76576)\,X_7 + (4.98327)\,X_8 + (1.36319)\,X_2{\times}X_5 + (1.14606)\,X_3{\times}X_5 + (-0.48127)\,X_2{\times}X_6 + (-0.22589)\,X_3{\times}X_6 + (-1.69235)\,X_4{\times}X_6 + (-0.38404)\,X_2{\times}X_7 + (-0.43949)\,X_3{\times}X_7 + (0.34747)\,X_4{\times}X_7 + (-2.12729)\,X_2{\times}X_8 + (-2.83346)\,X_3{\times}X_8 + (-1.03740)\,X_4{\times}X_8 \quad (2)$$

where all variables are defined in Table 9.

As demonstrated before, the anticipated adsorption efficiencies by Eq. (2) are in accordance with the experimental values. The correlation coefficient (R^2) is a quantitative criterion for assessing the interaction between the empirical figures and the anticipated values. By analyzing empirical outcomes and the predicted data, it was discovered that there was a logical correlation between the predicted values and the experimental data with $R^2 = 0.9358$. Additionally, adjusted R^2(Adj-R^2) representing a measure of fit goodness and more suitable for analyzing models with different numbers of independent variables, was found to be 0.9278 which is close to the reciprocal value of R^2. R-square analysis was employed for assessing the certainty of the predicted model. The regression factors in the form of analysis of variance (ANOVA) for the recommended response surface Linear Model of crude oil adsorption process are determined. Thus, it can be confirmed that the Linear Model justifies properly most of the variations in the response, and a high value of determination coefficient ($R^2 = 0.9358$, Adj-$R^2 = 0.9278$) of the predicted model obtained by the ANOVA outcomes illustrates a good agreement between the calculated and observed results within the studied range of experiment. The P-values presented in Table 9 play a considerable role in the correlations between the experiment parameters and the significance of each coefficient. If the enormity of P-value is smaller and the factor effect is larger, the corresponding coefficient is of more importance [52–54].

Table 9
Data's final outputs and P-Value in RStudio Program

Coefficients	Parameters	Estimate	Pr(>|t|)
Intercept		8.15985	< 2e-16
X_1	timeLong	0.57932	3.01e-05
X_2	sizeM	–4.22612	< 2e-16
X_3	sizeL	–5.21269	< 2e-16
X_4	sizeLC	–3.11364	< 2e-16
X_5	coatBnt	–0.03969	0.877981
X_6	coatMlk	1.45376	5.82E-05
X_7	oilWg	1.76576	1.44E-08
X_8	oilSe	4.98327	< 2e-16
$X_2 \times X_5$	sizeM:coatBnt	1.36319	0.000275
$X_3 \times X_5$	sizeL:coatBnt	1.14606	0.001991
$X_2 \times X_6$	sizeM:coatMlk	–0.48127	0.341358
$X_3 \times X_6$	sizeL:coatMlk	–0.22589	0.654809
$X_4 \times X_6$	sizeLC:coatMlk	–1.69235	0.000998
$X_2 \times X_7$	sizeM:oilWg	–0.38404	0.359327
$X_3 \times X_7$	sizeL:oilWg	–0.43949	0.291922
$X_4 \times X_7$	sizeLC:oilWg	0.34747	0.404381
$X_2 \times X_8$	sizeM:oilSe	–2.12729	6.88e-07
$X_3 \times X_8$	sizeL:oilSe	–2.83346	2.84e-10
$X_4 \times X_8$	sizeLC:oilSe	–1.0374	0.014478

Multiple R-squared: 0.9358, Adjusted R-squared: 0.9278,
P-value: < 2.2e-16

As mentioned before, the data and P-values in Table 9 illuminated the impact of adsorbent particle sizes, different types of crude oil (or API gravity) , surface modification, the contact time, and interaction between variables on cleaning up of crude oil. The experiments showed that LECA and modified LECA with Maleki GmbH sealant solution have the potential to adsorb crude oil from the aquatic environment. As shown in Eq. (2), the most effective variables on the adsorption efficiency were found to be adsorbent particle size, weight of crude oil (or API gravity) of the reaction, interaction of the adsorbent particle size and API gravity, and interaction of the adsorbent particle size and surface modification. Modification with Bentonite had negative effects on the adsorption efficiency. On the other hand, however, the modification with Maleki had positive effects on the adsorption efficiency. Positive interaction between adsorbent's particle size and API gravity had an important effect on adsorption efficiency, meaning that simultaneous lessening of both of these factors led to an upsurge in efficiency. As a graphical expression of variables and responses in Table 9, Fig. 7 displays the interaction between particle size and the type of the crude oil that produces the oil adsorption capacity as the response. Crude oil types include Light Goureh Crude Oil (Lg), Heavy Goureh Crude Oil (Wg), and Sepehr Crude Oil (Se), as provided in the legend.

3.9. Water contact angle

The results of contact angle (CA) test indicated that modifying the LECA surface with Maleki sealant led to increase contact angle from 26°to 57° (Fig. 8). The amount of CA on a flat surface less than 90°, between 90° and 150°, and over 150°are considered hydrophilic, hydrophobic, and super hydrophobic, respectively. More hydrophobic sorbents have more potentials to prevent water sorption. This will result in further enhancement of oil sorption due to the lack of competition between molecules of water and oil [37]. As shown in Fig. 8, the amounts of CA for LECA and Sealant coated on LECA surface are both lower than 90°, meaning that either of which are hydrophilic; however, adding sealant on the LECA's surface improves its hydrophobicity to some extent.

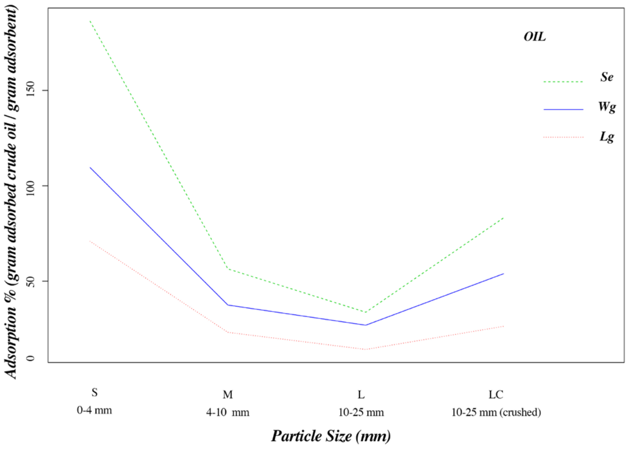


Fig. 7. Interaction plot for adsorption using RStudio program.

3.10. Cell viability and proliferation

After 24 h, cell viability for LECA, sealant coated on LECA surface, and control group were 89.39%, 93.23%, and 94.47%, respectively (Fig. 9). The results of cell viability test on L-929 cells showed no toxicity after 24 h, in as much as cell viabilities' of samples are above 70% considering as a standard of non-toxicity [55].

4. Conclusion

The presented research in this paper studied the LECA adsorption capacity obtained an empirical relationship between the cleanup efficiency (the response) and adsorbent particle sizes, surface modification, different types of crude oil, i.e. API gravity, and the contact time (independent variables) based on experimental results, which was expressed by a curve-fitting equation. The optimum adsorbents particles size was determined to be in the 0–4 mm range. Also, the results showed that the adsorption efficiency of LECA increased with the decrease in the adsorbents particles size. In general, the findings indicated that the performance of LECA with modified surface with Maleki GmbH sealant solution was better in adsorption of crude oil than that of LECA granular modified with Bentonite under similar conditions. According to the results, the adsorption efficiency increased with the increase of the contact time. The maximum removal efficiency was

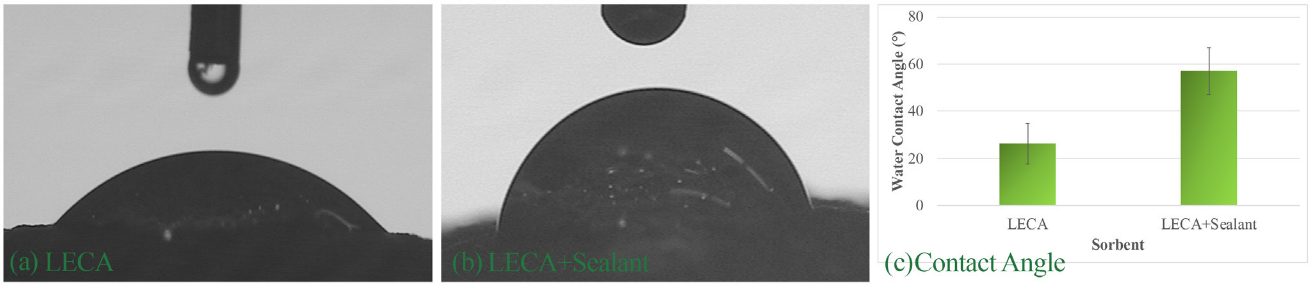
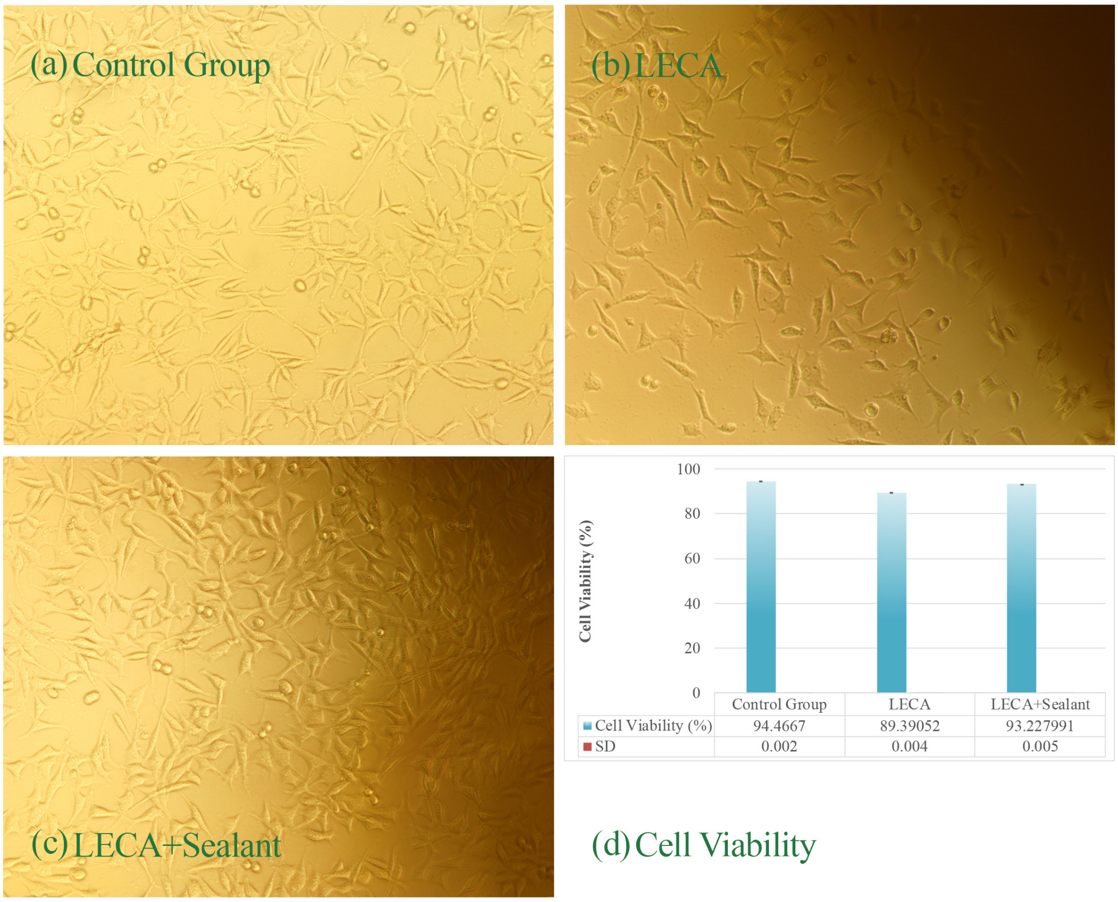


Fig . 8. Water contact angle measurement of (a) LECA and (b) LECA+sealant.



	Control Group	LECA	LECA+Sealant
🟦 Cell Viability (%)	94.4667	89.39052	93.227991
🟥 SD	0.002	0.004	0.005

Fig. 9. Cell viability of (a) control group, (b) LECA, and (c) LECA+sealant after 24 h.

achieved at the first 10 min of contact time. A relatively high determination coefficient ($R^2 = 0.9358$, Adjusted-$R^2 = 0.9278$) obtained by analysis of variance (ANOVA) showed a satisfactory agreement of the prediction model with the experimental values as it was evident from the very low probability value (P-Value < 0.05) using Linear Model in RStudio Program. Moreover, the most effective variables on the crude oil adsorption efficiency were found to be adsorbent particle size, weight of crude oil (or API gravity) of the reaction, interaction between the adsorbent particle size and API gravity, and interaction between adsorbent particle size and surface modification. The price of LECA compares favorably with that of other natural sorbents. LECA therefore can be employed as an applicable alternative material for cleaning up the contaminated water by crude oil. Results of this study showed that LECA can be used as environment-friendly adsorbents for cleaning up crude oil from aquatic environments compared to other expensive adsorbents. These findings suggested that the granular LECA acts as a suitable adsorbent for collecting crude oil pollutants from aquatic environment. Nevertheless, it is evident that further research is needed to amend process variables for larger scales.

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