Purging of Oil Contaminants in Soil Using Combination of Fenton Advanced Oxidation and Sulfate Radical (A Case Study: Masjed Soleiman, Iran)

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Oil exploration and production zones are very frequently contaminated with petroleum hydrocarbons or its derivatives. The most important exploration and production zones are located in South-west and South of the country, in Iran. Masjed Soleiman city is located on an oil field. The soil of this region has been affected by the petroleum composition. Mach petroleum seepages and springs (asphalt, oil and gas) with active oil and gas wells in Masjed soleiman caused this contamination. Restoration of soil contaminated with hydrocarbons at the sites has become a very interesting scientific challenge, mainly because of the actual complexity of the matrix. A large number of studies have been reported for the treatment of oil contaminated soil. One of the technologies is advanced oxidation. Advanced oxidation processes has the potential for rapidly treating or pretreating of pollution by TPHs. Applying the advanced oxidation processes have proven to be effective in treating and recovering the soil, mainly because they are faster than the other processes and are able to degrade toxic recalcitrant matter. The aim of this study is to evaluate effectiveness of the advanced oxidation process of oil contaminated soil by combination of Fenton and sulfate radical.
Materials and methods: The study area is located in the Zagros fold belt, and considered as a part of the Dezful embayment. Masjed Soleiman is located on Aghajari, Mishan, and Gachsaran formations. The Gachsaran formation is located inside the Asmari Formation as one of the largest oil reservoirs in southern Iran. Joint and Fractures systems caused oil spills to the surface. The lithology of these formations is composed of gray marl, limestone, brown to gray sand lime stone and carbonate. Due to the weather conditions, the climate of the region is known as the cold and dry. In this study, soil samples contain two types of soil, Petroleum-contaminated soil and clean soil. Sampling locations are shown in Figure 1. Soil characteristics were determined based on clean soil test. Clean soil passed from a 40 mesh sieve. Physical – chemical properties of the samples were, pH (7.3), organic matter (2.59%), Calcium carbonate ($CaCO_3$) (18.75%), clay (5.4%), sand (10.2%), silt (84%), and soil texture (silt loam).
In this study, advanced oxidation process was used for cleaning up the contaminated soil in the Masjed Soleiman. Materials used in the experiment are including: Hydrogen peroxide (Merck, 35%), potassium per sulfate (pxtra, 98, India), Optical Spectrometer (GCB model UV/VIS199), sulfuric acid (98%) and potassium dichromate.
Although hydrogen peroxide is highly reactive and capable to oxidize a wide range of pollutants, but the limitations of the peroxide is unstable and rapidly decomposes in the soil texture. Recently, increasing attention has been paid to the sulfate radical due to its high efficiency of mineralization of organic pollutants. On the other hand, one of the systems that contain hydrogen peroxide and per sulfate with H_2O_2 oxidation and stability is resulted from the higher degradation rate of soil. The removal efficiency of contaminants by iron oxide catalyzed by Fenton-like reaction is influenced by parameters such as types and concentrations of iron oxides, H_2O_2 concentration, and the presence of other oxidant-consuming compounds and pH. Initially, experiments were carried out to determine the optimal concentrations of hydrogen peroxide and potassium per sulfate. To obtain optimal concentrations, different amounts of hydrogen peroxide and potassium per sulfate were added to soil samples. Then, samples were added to the dichromate and sulfuric acid to measure the amount of organic matter remaining in the soil. It is used analyzing samples of the spectrometer. The spectrometer was adjusted on 620 wavelengths. This spectrum is based on the use of dichromate. The results are shown in Table 1 and Figure 2.
Concentrations selected for this experiment, 0.15 gr of potassium per sulfate, hydrogen peroxide and 4 cc. Other effective factors are the test: pH, temperature and the amount of catalyst. This experiment was done in neutral pH and temperature of 50°C. The iron oxides were used in the soil as a catalyst potential. We used the experimental stage to increase the removal rate. Hydrogen peroxide and potassium persulfate were added in three steps over three days.
The results of this study have indicated that an advanced oxidation process can be used as a powerful method in this study. This method was able to remove a significant percentage of contamination of soil during three days. The first step was to remove 19 percent of contamination. The next steps were to

remove the 45 and 48 percent, respectively. The result is shown in Table 2. Although hydrogen peroxide-based oxidation is more powerful for the removal of contaminants, its oxidative strength cannot exist in a remedial system for a long time due to ease of decomposition of hydrogen peroxide and rapid disappearance of hydroxyl radicals. These experiments indicated that both hydrogen peroxide and potassium persulfate have a positive impact on oxidation of petroleum compounds in soil. According to the most appropriate optimization of hydrogen peroxide and potassium persulfate removal rate, the ratio of 1:0.05 is obtained. It should be noted that although hydrogen peroxide can be activated by ferrous ion and persulfate, ferrous ion is also a scavenger of sulfate and hydroxyl free radicals. Thus, ferrous ion concentrations should be controlled to minimize the adverse effects of ferrous ion on sulfate radical production. In addition, ferrous ion can also decompose persulfate anion according to reaction. Thus, excess addition of ferrous ion may reduce the efficiency of contaminant removal.

Keywords: advanced oxidation process, Masjed Soleiman, oil contamination, soil