Microbial Electrochemical-based Biofuel Cell System for Remediation of Oil Contaminated Soil

Haozhe Zheng*

College of Quality and Safety engineering, China Jiliang University, Hangzhou, 310018, China

*Corresponding author: 1900604102@cjlu.edu.cn

Abstract. With the growing problem of oil seepage from gas stations around the world, remediation of oil-contaminated soils is receiving increased attention. Microbial electrochemical techniques have been shown to remove hydrocarbons from soil. Microbial fuel cells (MFC) show a strong potential to immobilize and dissipate contaminants using microorganisms. In this context, this review briefly introduces the conventional methods for remediation of petroleum soil contamination, focusing on the effects of different factors and configurations on the effectiveness of MFC remediation. Compared to traditional remediation methods, applying MFC to petroleum leaks in gas stations has better environmental and economic benefits. It does not require the application of chemicals or ex situ remediation of the soil, which largely reduces the cost and does not cause secondary pollution to the surrounding environment such as soil or atmosphere. In the long term, this technology has a good potential to enhance the remediation effect by changing the applied electric field, soil texture, and petroleum degrading bacteria. In addition, making soil MFC simultaneously achieve combined remediation of petroleum hydrocarbons and other contaminants remains to be studied. Finally, this paper emphasizes that there are few practical applications about MFC site remediation and there is a need to conduct site tests with large scale. If the pilot-scale tests are similar to the laboratory-scale treatment results, the technology will gain more popularity.

Keywords: Microbial Electrochemical Technology, Microbial Fuel Cell, Oil Contaminated Soil, Gas Station Leakage Problems

1. Introduction

In recent years, the construction and operation of gas stations has increased worldwide as the automotive industry and vehicle ownership continue to grow. There are over 119,000 gas stations across China by 2020, studies show that 70% of underground storage tanks that are more than 15 years old would have leakage problems. Similarly, in the United States, for example, which has more than 115,000 gas stations, more than 50% of them already have storage tank leakage problems. The oil that seeps out will not only cause great damage to the soil environment, but will also contaminate the groundwater, which is the main source of drinking water in cities. The Chinese Academy of Sciences once did a survey on some gas stations in Tianjin. Total petroleum hydrocarbons were detected in 85% of the groundwater samples and 79% of the polycyclic aromatic hydrocarbons, which can affect the human body and even cause cancer. Therefore, the treatment of oil-contaminated land and groundwater in gas stations and surrounding areas is urgent.

In recent years, microbial electrochemical techniques have been shown to remove hydrocarbons from soil. Microbial fuel cells (MFC) show a strong potential to immobilize and dissipate contaminants using microorganisms and have a low cost without the addition of various chemicals. There has been a lot of research on MFC for treating soil petroleum contamination, and they have improved the conventional MFC to increase their effectiveness. Some scholars proposed to use with pre-cultured anodes to enhance contaminant remediation and simultaneously generate electricity. Li et al. [1] developed a sand amendment method to increase soil porosity to enhance petroleum hydrocarbon degradation. It has also been shown that by enhancing the electric field of the external circuit, the electronic exchange efficiency can be improved thus enabling the entire microbial fuel cell to enhance its ability to exchange substances and degrade pollutants.

This paper briefly introduces conventional technologies for remediation of petroleum-contaminated soil, focusing on principles, key factors and utilization of soil remediation using bioelectrochemical technology, and points out the research directions for MFC remediation technology.

2. Traditional remediation technologies

The underground storage tanks at gas stations generally store only gasoline and diesel oil. Among them, the main components of gasoline include C4-C12 hydrocarbons, and diesel is less volatile than gasoline which mainly is hydrocarbons of C10-C22. The hydrocarbons in petroleum often exist in liquid form, insoluble or even insoluble in water, with a density smaller than that of water, so it is made into a Light Non-aqueous Phase Liquids (LNAPLs). LNAPLs would seep out of the fissure of the storage tank, penetrate into the soil by gravity and undergoes vertical and horizontal diffusion, eventually extend to the groundwater surface. Volatile organic (VOCs) compounds in LNAPLS would rise during infiltration and remain in the soil crevices, becoming a part of the soil gas. Therefore, the soil and groundwater need to be remediated synergistically, and the actual remediation methods used in soil/groundwater at home and abroad are mainly including physical, chemical and biological remediation methods.

2.1. Physical method

Physical remediation technology used physical methods to separate petroleum contaminants from the soil. Common physical remediation techniques include soil vapor extraction, incineration pyrolysis, scrubbing, etc. Soil gas phase extraction uses a gas pump and other devices to force the directional flow of soil air and entrain VOCs to migrate to the ground for treatment. This method achieves contaminant removal without soil transfer, which is low cost, high efficiency and suitable for sandy soils in unsaturated areas with high VOCs content. The incineration pyrolysis method takes advantage of the easy combustion of hydrocarbons and other components in petroleum and their volatility at high temperatures to remove pollutants from the soil. The degradation rate of petroleum and PAHs in soil can theoretically up to more than 99% [2]. However, the cost of this method is high and it also produces massive harmful gases, as well as destroying other organic materials in the soil. The soil washing method makes use of chemical reagents such as surfactants to wash the soil in situ, as shown in Fig. 1. Saeld Gitipour et al. [3] find that large particle size soil eluted better, with 92.39% oil removal when the surfactant SDS (sodium dodecyl sulfate) was used to wash the petroleum-contaminated soil.

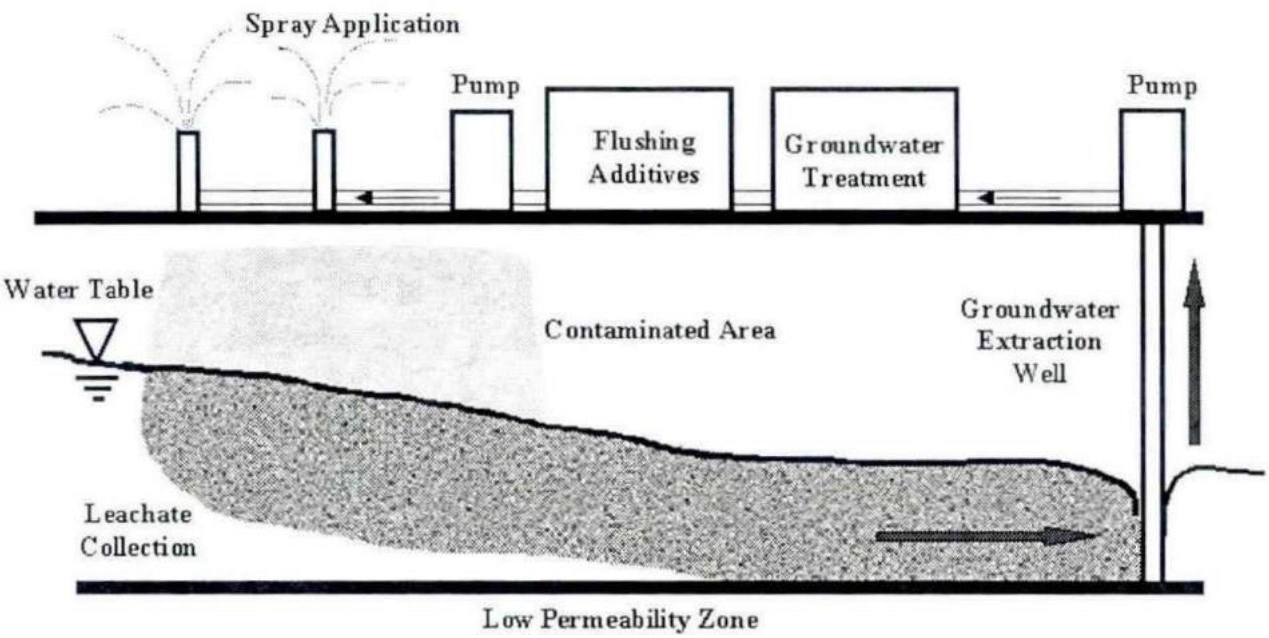

Figure 1. In-situ soil washing method [4]

2.2. Chemical method

Chemical remediation techniques are a relatively common means of remediating oil-contaminated land. The current classification of this technology includes chemical oxidation, chemical scrubbing, solvent extraction and photocatalysis.

2.1.1 Chemical oxidation

The chemical oxidation can be divided into ordinary and advanced oxidation methods. Ordinary oxidation method reduces the toxicity and diffusivity of pollutants by spraying or injecting chemical oxidants into the soil. These oxidants include $KMnO_4$, H_2O_2, CaO_2, $Na_2S_2O_8$, etc. Kailun Chen et al found that the petroleum removal rate for these oxidant systems at a soil pH of 7.8 was $KMnO_4 > CaO_2 \geq H_2O_2 > K_2S_2O_8$. In the range of 0-48 h, the petroleum removal rate of each oxidant system increased rapidly with the increase of reaction time, but in the range of 48-240 h, the petroleum removal rate increased slowly. However, some studies have shown that $KMnO_4$ is not very effective in treating diesel, gasoline and BTEX type pollutants.

The advanced oxidation method is Fenton oxidation, in which H_2O_2 is coupled with soluble iron compounds to produce OH·, which can react with unsaturated organic pollutants to form free radicals and eventually further oxidize to produce CO_2 and H_2O. This method does not cause secondary pollution, but the utilization rate of H_2O_2 is low.

2.2.2 Solvent extraction

The solvent extraction method is to isolate or purify liquid mixtures by using the difference in partitioning properties of solutes between two mutually incompatible or partially mutually soluble solvents. Common extractants include organic solvents, surfactants, cyclodextrins and supercritical fluids. Soil properties, contaminant properties affect the effectiveness of these extractants. Some studies have shown that sandy soils have stronger diffusivity of extractants due to larger soil porosity compared to soils with higher content of chalk and clay. The latter has a larger specific surface area which could strongly absorb the contaminants, and extractive solubilization becomes difficult. The oil drag rate decreases as the water content of the soil increases, because a water film forms between the extractant and the soil and the migration efficiency of the contaminant would decrease.

2.3. Biological method

Microbial remediation technology uses both the metabolism of intrinsic microorganisms in contaminated soil and the degradation ability of exogenous microorganisms to eliminate contaminants from the soil. Microorganisms mainly use the catalytic action of intracellular enzymes to achieve the dissipation of contaminants such as gasoline and diesel fuel. More than 200 species of bacteria, fungi, actinomycetes, yeasts, and molds in more than 100 genera have been proven in studies to successfully digest pollutants such as gasoline and diesel fuel in soil [5]. Traditional microbial remediation techniques include situ bioremediation and ex situ remediation. The former applies nutrients and other additives to contaminated sites to degrade oil by using indigenous microorganisms or add some exogenous degrading bacteria and create a certain environment to accelerate the elimination of pollutants. Ex situ remediation technology involves excavating and sending contaminated soil to a designated site to remove contaminants using a reactor or landfill site. Finally, it is sent back to the original site. This method is more expensive to treat and consumes more energy.

3. Bioelectrochemical remediation technology

Microbial electrochemical techniques are increasingly used in the field of environmental remediation because of their environmentally sustainable properties and the use of microbial degradation, such as no need to add chemicals, no secondary pollution and little or no energy consumption.

3.1. Principle and mechanism

MET is mainly based on electrocatalytic oxidation or reduction reactions of electroactive microorganisms, where the anode in the soil environment and the air cathode formed a closed circuit through the connection of an external circuit. The electroactive microorganisms are located at the anode to degrade the pollutants and produce electrons and protons, which flow through the external circuit (wire or conductive material) to the cathode. In the meanwhile, cathode becomes the migration direction of the protons, where they participate in the reduction reaction initiated by the consumption of electrons at the cathode (Fig. 2). The above two electrodes can usually be considered as inexhaustible electron donors and acceptors, where microorganisms convert chemical energy into electrical energy [6]. The directed movement of electrons can generate electric currents, in principle, can be used to supply electricity like the microbial fuel cells. However, in some cases, such as soil environments with high ohmic internal resistance, this can lead to increased mass transfer resistance of the electron flow and require an external power source to drive the redox reaction.

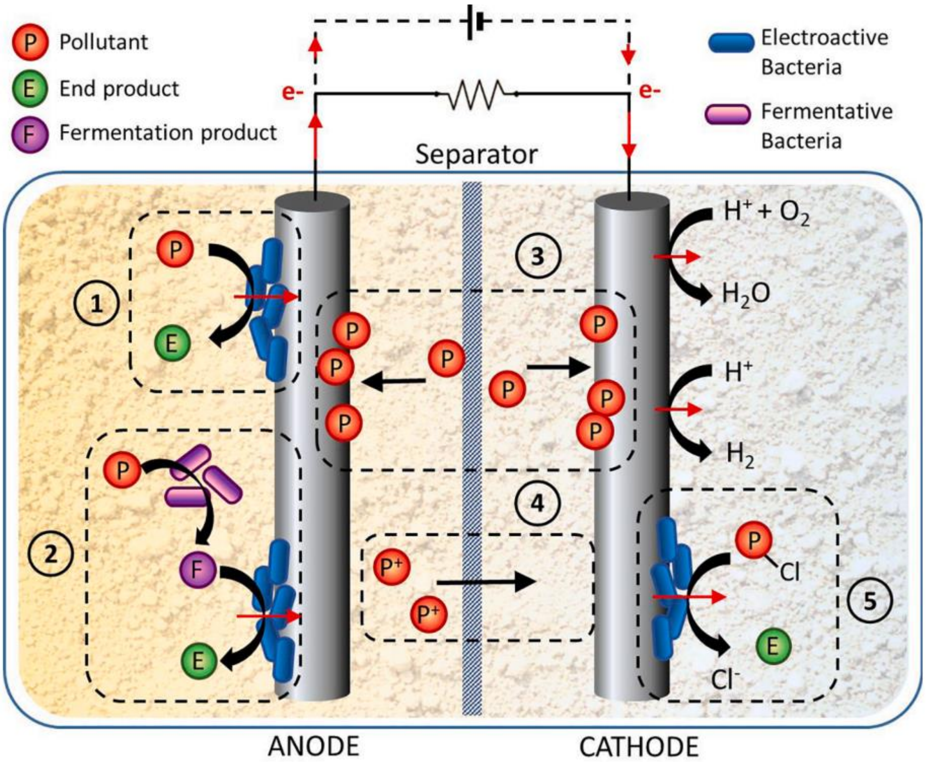

Figure 2. Schematic diagram of the basic principles and components of the MET system [7]

3.2. Influencing factors

When a MET system is constructed for remediation of petroleum contaminated soil, its remediation efficacy is influenced by many factors. They can usually be divided into soil properties, MET-based bioremediation device configurations, and oil and water properties.

3.2.1 Soil properties

Soil properties are the determining factors in the bioelectrochemical remediation process. The common influencing characteristics are soil moisture content, electrical conductivity, pH, salinity, temperature, etc. Conductivity is closely related to soil texture, water content and soil salinity. At low conductivity, electrons and ions move slowly and thus lead to rapid decay of microbial electrochemical activity, which greatly reduces the remediation radius and efficiency of microorganisms. Xiaojing Li et al. reported a new method of sand amendment. This method is used to change the texture of the soil by mixing sand with clay soil. Although sandy soils are less capable of retaining moisture and harboring fertilizers, they have better permeability. As a result, the porosity of the soil can be increased from 44.5% to 51.3% and the electrical conductivity enhanced by 46% to increase charge migration (from 2.5C to 3.5C/g soil). [1]. Water content affects microbial replenishment and reaction activity by influencing the hydraulic conductivity in the soil. Xin Wang et al. created a U-tube microbial fuel cell in which the initial water content of the soil reduced from 33% to 28% and 23% in the experiment [7], resulting in a decrease in charge output and hydrocarbon breakdown rate due to an increase in electrical resistance. This suggests that a decrease in water content in soil can cause a decrease in electrical conductivity. Salinity in soil can affect the rate of nutrient transfer and soil conductivity during microbial growth. Minai-Tehrani et al. [8] demonstrated that when the concentration of NaCl in the soil increased from 1% to 5%, the degradation rate of PAHs and other substances decreased significantly.

3.2.2 Additives and oil types

The biodegradation efficiency of pollutants can be enhanced by altering or adding micro- or macroscopic nutrients and electron acceptors. This is due to the fact that the water solubility and mobility of petroleum hydrocarbons affects the mass transfer efficiency and microorganisms need a larger contact area to perform better. Several studies have shown that the efficiency of material transfer is related to the water solubility and mobility of petroleum hydrocarbons. Thus, artificially manufactured or naturally derived surfactants can be added to enhance these two factors, thus achieving an increased rate of pollutant degradation. Interestingly, however, the current research on surfactants is still controversial. Alcantara et al. showed that the removal of PAHs from soil could be increased with the amount of surfactant (Tween 80) added. The effect of rhamnolipids on enhancing electrochemical remediation of diesel-contaminated soils was demonstrated by Gonzini et al [9]. They discovered that increasing the certain dosage of rhamnolipids boosted the efficacy of diesel cleanup by 86.7%. In contrast, Lu et al. demonstrated that surfactant (Triton x-100) addition to soil MFCs with anodes loaded with carbon cloth resulted in a decrease in PAH removal. Therefore, as far as the current study is concerned, the actual effect of surfactants and the application environment need to be experimented in many aspects.

There is a general convergence of research on conductive additives that can increase the power production of MET systems by adding conductive materials such as carbon fibers and biochar. Carbon fiber is by far the most common modifier, and it can enhance the electron transfer efficiency of microorganisms by reducing resistance. When carbon fiber is combined with virgin contaminated soil, the maximum current density, maximum power density, and cumulative charge output of MFC are 10, 22, and 16 times greater, respectively, than those of closed-circuit control (no additives) [1]. The type of oil also has an effect on the remediation performance of MFC, the degradability of diesel is higher than that of aged oil. In general, PAHs that have been aged for a long time are difficult to be degraded, and the scarcity of metabolic electrons in these soils has limited bioavailability of contaminants.

3.3. Application of configuration

Currently, there are six main types of microbial soil remediation system configurations as follows, and the application of 5 different configurations of devices : insertion-type, tubular or column-type, U-type, multi-anode, and graphite rod in petroleum-contaminated soil is shown in Table 1.

Table 1. Soil MFC configuration

Configuration	Reaction time/d	Degradation rate	Contaminant type	References
Insertion-type	10	90.1%	Phenol	[10]
Tubular or column-type	120	82.1-89.7%	TPH	[11]
U-type	--	18%&36%	TPH&PAHs	[12]
Multi-anode (horizontally arranged)	135	12.5%	TPH	[13]
Multi-anode (vertically arranged)	135	8.3%	TPH	[13]

For petroleum spills at gas stations, the column-type configuration degrades diesel and gasoline best. The main structure of the system is a perforated PVC tube. From the outside to the inside is the anode, the separator and the cathode are attached to the wall of the tube. The cathode layer faces the wall of the tube and comes into contact with the air through holes in the body of the tube. The anode layer is then wrapped around the outermost side which exposed to the soil (Fig. 3). The anode is made of carbon cloth or biochar, and the air cathode consists of activated carbon cloth and four PTFE diffusion layers. The cathode and anode are connected by an external resistor of 100 Ω. The device is also equipped with a separator to prevent short circuits.

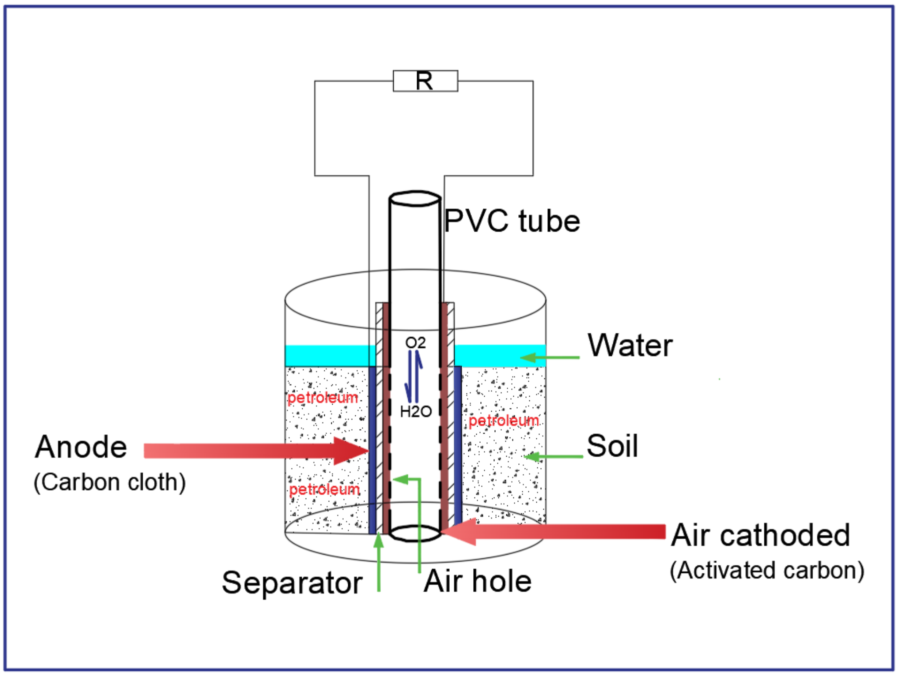

Figure 3. Tubular or column-type MFC

3.4. Suggestion

Bioelectrochemical systems have clear advantages over physical and chemical methods of remediation, which are usually relatively expensive and have long-term side effects on the soil. Air cathode MFC has the potential to be sustainable in the long term and has a good cost effectiveness. For gas stations, the column system fits well into the site requirements of the station and can be easily installed around facilities such as storage tanks.

4. Conclusion

Microbial electrochemistry has been extensively studied for the treatment of petroleum contamination in soils, and MFC is a representative and mature technology for this method, which allows the remediation of contaminated soils with little or no chemical addition. Moreover, this technology does not require any kind of movement of the soil to be treated, allowing for long term remediation with minimal maintenance. The traditional methods may have limitations in use on the one hand, and have secondary contamination or higher costs on the other. Soil gas phase extraction technology for sandy soils in unsaturated areas with high VOCs content. The incineration pyrolysis method has a high removal rate but causes secondary pollution. Chemical oxidation and solvent extraction techniques both require the addition of chemicals, and traditional biotechnologies are often accompanied by the same high costs and energy wastage. Therefore, MFC has a lower cost than traditional remediation methods and does not produce secondary pollution, which has a better economic benefit. Among the MFC configurations, tubular or columnar type are more effective in remediating site contamination, have lower electrical power losses, and are more easily placed in gas stations. There are fewer more specific studies on the use of MFC to remediate oil leakage problems in gas stations. Most of these MFCs are still in the laboratory stage, and larger scale site experiments are needed next to measure the economics and practicality. The influence of different soil environments on the radius of MFC remediation still needs to be explored. Soil MFC combines petroleum hydrocarbons with other soil contaminants, such as microplastics, heavy metals, etc., for joint remediation can be the future development direction of MFC.

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