

Article



Use of a Novel Biopellet to Treat Total Petroleum Hydrocarbon Contaminated Groundwater

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Abstract: Conventional pump-and-treat strategies for dealing with groundwater contamination are both energy- and time-consuming. Potential passive biological techniques are of interest to remedy the massive volume of total petroleum hydrocarbon (TPH)-contaminated groundwater worldwide. In this study, novel biopellets made of TPH-acclimated microbes, fermented fruit peel materials, and CaO₂ recycled from eggshells were manufactured to treat TPH-contaminated groundwater. The biopellets provided 56 mg of oxygen and achieved a C:N:P ratio by weight of 10:4:1. Moreover, each biopellet was capped with alginate to prolong its floating time in water to 25 days. The mimicked groundwater spiked with 500 mg/L diesel TPHs (TPHd) was treated using our novelly manufactured biopellets. After 8 days of treatment, results showed a 98.8% removal of spiked TPHd at a rate of 64.1 mg/L per day, with a microbial count that increased from nearly zero to 1.0×10^7 CFU/mL. The residual TPHd constituents were mainly C13–C18. Furthermore, microbial consumption of N, P, and oxygen was noted during the 8-day period of TPHd removal. As the TPHd level increased to 1500 mg/L, the removal rate reached 45 mg/L per day, and all TPHd had been removed after 22 days.

Keywords: groundwater contamination; total petroleum hydrocarbon (TPH); pump and treat; biopellet; microbial acclimation; diesel TPH removal

1. Introduction

Oil products are numerous and often complex; some float and some sink. These products are commonly named total petroleum hydrocarbons (TPHs). Oil products such as gasoline, diesel, and heavy oil are commonplace and are stored in various oil storage tanks, such as those at gas stations and oil contamination sites, which are common worldwide. In Taiwan, TPH-contaminated sites are featured in the National Priorities List [1], accounting for approximately 38% of the total listed cases. The scope and extent of such sites make an environmentally friendly and cost-saving treatment alternative highly desirable.

Up to 77% of TPH-contaminated groundwater cases are treated using pump-and-treat (P&T) methods [2]. However, the active and prolonged operation of such methods can lead to high energy consumption and secondary pollution. In addition to pump-and-treat, alternative means such as chemical oxidation [3,4], natural attenuation [5], activated carbon adsorption [6], and microwave irradiation [7] have limitations, such as huge volumes of chemical additives, time-consuming processes, secondary pollution, and high energy costs, which have resulted in a global adoption of various biological treatment methods [8–11]. An in situ, biological alternative is desirable because it would be environmentally friendly and passive (i.e., energy-saving).

As Yang et al. indicated in [12], several difficulties must be overcome before bioremediation can be effective. This includes obtaining seed microbes, oxygen, and nutrients and applying them to groundwater. Yet, most of the time, those necessary elements are often added one after another, which may have two disadvantages: (1) all the required elements need to be mixed thoroughly, and (2) the spread elements could be depleted rather quickly and need to be re-injected often. Both are not easy tasks, especially when working with groundwater contamination. Thus, we propose using biopellets combined with embedded TPH-acclimated degraders, oxygen supplied by recycled substances, and abundant microbial nutrients to stimulate the growth of TPH degraders. To achieve this, we used fermented fruit peels to provide microbial nutrients. Although Lee et al. [13], Lin et al. [14], and Lin et al. [15] have suggested using reagent-grade CaO_2 for the oxygen supply, we used recycled eggshells to generate CaO₂. TPH degraders were incubated using aged, TPH-contaminated soil. Each packed pellet was coated with alginate to increase its floating time so the pellet would stay closer to the lighter oil like diesel in the groundwater for a longer period of time. The pellets were used as designed to assess their treatment efficacy in water columns filled with diesel TPH (TPHd) to mimic TPH-contaminated groundwater. Over a period of 30 days with various spikes in TPHd levels, the removal of TPHd, oxygen levels, consumption of nutrients, and number of microbes were recorded. The pellets assessed in this study can applied by simply throwing the required number of pellets into a treatment well or wall or an underground water reservoir, allowing great savings in mechanical energy and avoiding secondary pollution.

2. Material and Methods

2.1. The Reactor

A custom-made glass column (Figure 1) with a diameter of 4.5 cm and a height of 75 cm was filled with TPH-contaminated water and served as the reactor to mimic a groundwater contamination environment. The total and working volumes of the column were 1190 and 1000 cm³, respectively. Diesel purchased from the Chinese Petroleum Corporation in Taiwan was mixed with distilled and deionized water at designated concentrations and poured into the column before the treatment started. The dominant TPH constituents of the diesel were analyzed and are given in Table 1. Their carbon numbers ranged from C6 to C36, and their elution times ranged from 13.35 to 42.33 min. Because most of the compounds were less dense than water, TPHs at depths of 10, 30, and 50 cm were monitored over time to trace their existence and to evaluate the reaction performance.



Figure 1. Setup of the water column reactor mimicking a groundwater system.

No. of Peaks	Compounds	Carbon Number	Density (g/cm ³)	Eluted Time (min)
1	Naphthalene	C ₁₀	1.14	13.350
2	Dodecane	C ₁₂	0.75	13.522
3	Tridecane	C ₁₃	0.756	15.137
4	Naphthalene, 2-methyl-	C ₁₁	NA	15.204
5	Naphthalene, 1-methyl-	C ₁₁	NA	15.452
6	Tetradecane	C ₁₄	0.764	16.613
7	2,6,10-Trimethyltridecane	C ₁₆	NA	17.446
8	Heptadecane	C ₁₇	0.777	17.985
9	Butane, 2,2-dimethyl-	C ₆	NA	19.455
10	Hexadecane	C ₁₆	0.770	19.457
11	Eicosane	C ₂₀	NA	28.921
12	Phenanthrene, 2,3-dimethyl-	C ₁₆	NA	29.784
13	1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	C ₂₄	0.946	41.426
14	Hexatriacontane	C ₃₆	NA	42.331

Table 1. Constituents of target diesel total petroleum hydrocarbon (TPHd) in this study.

2.2. Novel Biopellets

Biopellets were formed from fermented fruit peels, microbial support materials, acclimated microbes as TPH degraders, recycled CaO₂ for an oxygen supply, and soil if needed for density adjustment. The fermented materials were purchased from Shengyuan Bio-Resource Tech Company in Kaohsiung City, Taiwan. TPH-aged soil obtained from a TPH-contaminated site in Taiwan was used to derive seed microbes that were enriched in the column reactor at increasing designated TPH concentrations over 60 days. During the acclimation process, four runs labeled as Runs I–IV were designed and operated: seed microbes only, diesel only, diesel with seeds at the final spike of 1600 mg/L TPHd, and a repeat of Run III with a higher final spike of 4000 mg/L. In Runs III and IV, TPHd was spiked at concentrations of 200, 400, 800, and 1600 or 4000 mg/L on Days 0, 9, 22, and 35, respectively. The rate of TPHd removal from the water during the acclimation period was monitored, and the daily removal rate after each spike was recorded.

For the oxygen supply, eggshells were first ashed by heating at 900 °C. Then, hydrogen peroxide was added to the ash, and it was dried at 105 °C to obtain CaO₂. Reagent-grade CaO₂ was purchased from the Alfa Aesar Company, and its oxygen release over time in 600 mL of water was compared with that of the eggshell recycled CaO₂ in the same amount of water. To isolate the moisture from CaO₂ within the pellets, encapsulation of the eggshell-derived CaO₂ was performed and tested. Oxygen concentration and total organic carbon (TOC) in the water were determined using a dissolved oxygen (DO) meter (DO600 EXTECH) and a TOC analyzer (TOC 5000a SHIMADZU), respectively. Other parameters such as total nitrogen, total phosphates, and pH were determined following the Standard Methods for the Examination of Water and Wastewater [16].

The pellets were manufactured with a pellet-making machine made by Shengyuan Bio-Resource Tech. Co. using variable pressure ranges (i.e., $0-1000 \text{ kg/cm}^2$). For each pellet, 5.3 g of the fermented material, 1 mL of microbes at cell content of $6.9 \times 10^8 \text{ CFU/mL}$, 0.25 g of CaO₂, and various amounts of ashed soil (depending on desired pellet density) were placed in a cell and compressed. Theoretically, through the CaO₂ + H₂O $\rightarrow 1/2O_2$ + Ca(OH)₂ reaction, 0.25 g of CaO₂ should release 56 mg of oxygen into the water. Since only floating pellets were needed in this study, no ashed soil was added. After the pellets were formed, 10 wt% alginate with 10 wt% CaCl₂ was used to cap the pellets several times, and the pellets' floating time was tested. Each pellet was compressed by a cylindrical die with an inner diameter of 2.2 cm and a height of 2.0 cm.

The artificial TPH-contaminated water was treated in the column reactor with pulse inputs of TPH over time. The TPH concentration started at 500 mg/L and was later raised to 1500 mg/L. Blank (biopellet only) and control (diesel only) runs were also conducted. The TPH concentrations at 10, 30, and 50 cm below the water's surface were sampled and quantified to determine the change in TPH levels over time. Changes in N, P, O, and microbial numbers were also monitored. To determine the TPHd level in the water, a 2-mL water sample was extracted using hexane and subsequent centrifugation (company, model) at 10,000 rpm; the centrate was collected and prepared using the internal standard (i.e., 2,4,6-tribromophenol) to qualify its TPH content in a gas chromatography (GC)–mass spectrometry (OP2020 Shimadzu) machine equipped with a Shimadzu Rtx-5MS column. For details of the GC analysis procedure, please refer to Shen et al. [17].

2.4. Data Quality

For quality assurance, all measurements were performed in triplicate. Percentage error (% error) was calculated as the standard deviation divided by the mean of the measurement outcomes, and a 5% limit was adopted to ensure data consistency. Each experimental run was assessed at least twice, with some assessed in quadruplicate, and the results were summarized and are presented as mean values.

3. Results and Discussion

3.1. Microbial Acclimation

Native microbial consortia from the aged soil of a TPH-contaminated site were acclimated to gradually increasing TPH spikes for 60 days. Figure 2 (I–IV) shows the TPHd remaining after each of the four designed runs: seed microbes only, diesel only, diesel with seeds at the final spike of 1600 mg/L TPHd, and a repeat of Run III with a final spike of 4000 mg/L TPHd. The results showed no residual TPHd in Run I because no TPHd was added. In Run II, in which only diesel was added, spikes of 800 and 1600 mg/L TPHd resulted in daily TPHd removal rates of 6.1 and 12.9 mg/L per day, respectively, which might be caused by vaporization or minimal microbial degradation. The results also demonstrated that no TPHd was detected below 50 cm of depth, and most diesels stayed on the top layer of the water. We used the TPH concentration at the 10-cm depth—where the TPH concentration was roughly equal to the mean spiked initial concentration of TPHd—to test TPHd degradation over time. Run III was spiked with the same amount of TPHs as used in Run II, and the daily removal rates in Runs II and III were 34.1 and 46.2 mg/L, respectively. The higher removal rates in Run III were caused by the microbial degradation of TPHd caused by the addition of the seed microbes. However, the results of Run IV showed that the addition of a spike of 4000 mg/L resulted in a lower TPHd removal rate of 12.5 mg/L per day, only approximately 1/4 that of Run III. Thus, the Run III operation was considered appropriate for microbial acclimation to TPHd; thereafter, the microbes in Run III, deemed as acclimated microbes, were used to manufacture biopellets.

3.2. Biopellet Manufacturing and Performances

By using the substances mentioned in Section 2, the detailed biopellet manufacturing process and some of the parameters were finalized (given in Figure 3). Each biopellet was obtained by being compressed at 100 kg/cm² to form one prototype pellet. Although higher pressures of up to 1000 kg/cm² were also tested, the structure of the pellet changed only a little. After compression, each prototype pellet was then soaked and dried three times in 10% alginate and 10% CaCl₂ solutions in series, which increased its floating time to 11, 19, and 25 days after each respective series. Thus, each biopellet underwent three coatings before being used in the pilot reactor test. The final biopellets were about 2.4 and 2.2 cm in diameter and height, respectively.



Figure 2. Acclimation of the seed microbes over 60 days with stepwise TPHd spiking strategies. *R* is the average daily TPHd removal rate in mg/L per day.



Figure 3. The biopellet manufacturing process.

The manufactured biopellets were tested to demonstrate their release of nutrients (i.e., C, N, and P) in a 500-mL flask. The results in Figure 4 demonstrate that approximately 23.8 and 5.7 mg of N and P were released, respectively, and saturation was reached within 3 days. Conversely, approximately 58.3 mg of C was released, with a saturation time of approximately 7 days. The gradual release of the nutrients indicates a continuous nutrient supply to the microbes over time. The final mass ratio of the C:N:P released into the water was approximately 10:4:1, providing substantial N and P to stimulate the growth of the microbes. The results of oxygen release using recycled CaO₂, reagent-grade CaO₂,

and encapsulated eggshell-derived CaO₂ in 600-mL flasks are given in Figure 5. All three cases showed similar capacities for oxygen release and reached oxygen saturation within 2 days. The recycled and reagent-grade CaO₂ exhibited similar oxygen release behavior, and the encapsulation of the CaO₂ had little effect on the oxygen release into water. Therefore, the recycled CaO₂ was encapsulated to make the biopellets. The results shown in Figure 5D demonstrate that, with capsulation, the oxygen concentration was nearly 1 mg/L, and oxygen would theoretically be released continuously with up to 56 mg of oxygen from each biopellet; this oxygen release was deemed sufficient for the microbes' needs. Thus, recycling eggshells and providing a steady oxygen supply through encapsulation are both innovative steps in the process of manufacturing biopellets.



Figure 4. Release of C, N, and P over the treatment period.



Figure 5. Oxygen released from (A) eggshell-derived CaO_2 , (B) reagent-grade CaO_2 , (C) encapsulated eggshell-derived CaO_2 , (D) eggshell-derived CaO_2 in a biopellet, and a blank.

3.3. TPHd Removal

Figure 6 shows the results of the TPHd removal during the first 8 days, depicting the degradation of TPHd by the novel biopellet. The TPHd levels at various depths showed similar trends over time. A spike of 500 mg/L TPHd, with and without the addition of the biopellet, yielded daily TPHd removal rates of 64.1 and 7.2 mg/L per day, respectively (see Figure 6 (II,III) at a depth of 10 cm, for a nearly 9-fold removal rate with the addition of the biopellet. Table 2 shows residual chromatograms of TPH at a depth of 10 cm for Runs I–III after 0, 1, 2, 4, and 8 days. Little change is observable in the chromatograph of Run II (diesel only). By contrast, the concentration decreases over time in Run III (pellet provided). By Day 8, approximately 99% of the spiked TPHd had been removed through the

addition of the biopellets, and a significant minimization of the peak area was also observed (Table 2). Further GC-MS results of the residual TPHs on Day 8 of Run III are given in Table 3. The remaining substances included C13-C18, all of which were more than 98% degraded after 8 days; 100% TPHd removal appears likely with sufficient treatment time. The microbial counts over the first 8 days are plotted in Figure 7. In Run I, the count increased through Day 2 before leveling off at approximately 3.6×10^6 CFU/mL. In Run II, no microbes were detected due to the absence of biopellet. In Run III, the count increased through Day 8, reaching 8.1×10^7 CFU/mL. Thus, the microbes thrived because of the TPHd removal. A great number of microbes appearing at depths of 30 and 50 cm, where no diesel existed, might be due to the gravity settling of microbes from the top. The C, N, P, DO, and pH values recorded over 8 days are shown in Table 4. TPHd removal due to microbial degradation resulted in the pH dropping to 5.5 by Day 4 and 4.7 by Day 8. In Runs I and II, the pH value was near neutral and changed little over time. Run I (biopellet only) yielded a DO level of 2.10 mg/L on Day 8, Run II with diesel yielded low DO at 0.39 mg/L throughout the treatment, and Run III (with both the diesel and biopellet) maintained DO of approximately 2.06 mg/L by Day 8. These results indicated that the supply of oxygen provided by recycled CaO₂ was sufficient for the TPHd removal. A similar trend was observed for C, N, and P release, which decreased from Day 4 to 8 in Run III, serving as strong evidence that the microbes were thriving by consuming system C, N, and P during the TPH removal period.



Figure 6. TPHd removal from Day 0 to 8 in the mimicked groundwater system.

Table 2. Residual constituents of TPHd over time in the mimicked groundwater system at a depth of 10 cm.

Runs	0 Day	1 Day	2 Day	4 Day	8 Day
I—no diesel, w/pellet					
II—w/diesel, w/o pellet					
III—w/diesel, w/pellet					

Table 3. TPHd constituents on Days 0 and 8 of Run III at a depth of 10 cm.

C #	Compounds Left	Peak Area/% Area at Day 0	Peak Area/% Area at Day 8	% Removed on Day 8
C13	Tridecane	24,135,133/1.6	275,068/14.6	98.9
C14	Tetradecane	44,592,741/2.9	592,722/31.5	98.7
C15	Tetradecane, 2-methyl-	13,138,933/0.9	100,706/5.4	99.2
C15	Pentadecane	38,815,206/2.5	628,999/33.4	98.4
C18	Octadecane	29,464,709/1.9	283,232/15.1	99.0
Percent of total peak areas		9.8%	100%	

Table 4. Water quality at a depth of 10 cm during the first 8 days of TPH removal.

Time Elapsed (Day)	Runs	TOC (mg/L)	TN (mg/L)	TP (mg/L)	DO (mg/L)	pН
0	All runs	0.0	0.0	0.0	0.39	7.08
4	I—no diesel, w/pellet	119.1	396.7	178.8	2.35	6.58
	II—w/diesel, w/o pellet	2.5	0.0	0.0	0.39	6.91
	III—w/diesel, w/pellet	68.1	119.7	6.3	2.14	5.46
8	I—no diesel, w/pellet	91.5	289.0	214.3	2.10	6.51
	II—w/diesel, w/o pellet	2.3	0.0	0.0	0.39	6.88
	III—w/diesel, w/pellet	10.1	37.3	2.1	2.06	4.65

For the second spike of TPHd at 1500 mg/L, the results from Run II in Figure 8 show a TPHd removal rate of 7.2 mg/L per day over 22 days; this rate is similar to that observed in the first 8 days. The decrease in TPHd removal in Run II may have resulted from the minimal microbial activity or the volatilization of the TPHd over time. In Run III, the TPHd removal rate reached 45.9 mg/L per day over the last 22 days, resulting in a 6-fold removal rate increase compared to that in Run II and strongly suggesting the feasibility of using manufactured biopellets for treating TPHd-contaminated water.



Figure 7. Microbial counts from Day 0 to 8 in the mimicked groundwater system.

4

8

2

Time, day

 1.0×10^{6}

0

1

The results of this study strongly suggest that there is potential for the use of the reported biopellets alone or in combination with other technologies. Currently, the real in situ applications of biopellets in treating TPH-contaminated groundwater are rarely reported, which partially may be due to the wide adaptation of P&T technology. Poi et al. [10] reported a large-scale treatment of TPH-contaminated groundwater using bioaugmentation. Additional microbes were added, and the groundwater TPH concentration dropped from 1564 to 89 mg/L in 32 days. As a comparison, the use of biopellets in this study removed all 1500 mg/L in 22 days, showing rapid TPH removal when the biopellet was applied. Kucharzyk et al. [18] applied ligninolytic enzymes encapsulated in beads to treat various types of crude oils. About 70% of THPs as crude oils were removed in 14 days, and the removal rate increased to ~90% if weathered crude oil was treated. The encapsulation of ligninolytic enzymes could have helped in prolonging the enzymatic activities, thus enhancing their efficiencies. Although these two examples operated differently, the inclusion in our pellet of all of the components necessary to support the microbes could be the major cause of its rapid and complete removal of TPHs and might serve as protection, allowing the microbes to adapt in the field. In addition to treatment efficiencies, the recycling of the fermented fruit peels to provide nutrients and eggshells to make CaO₂

for oxygen supply would simultaneously achieve waste minimization and pollution remediation in such operations.





Figure 8. TPHd removal over time in the mimicked groundwater system.

As was previously mentioned, P&T technology is the most dominant technology in treating groundwater contamination [2,19–21]. The P&T operation creates an active driving force that makes groundwater flow and eases the applications of other treatments for targeted pollutant removal. However, the lengthy remedial time, consumption of energy, and possible secondary environmental problems like emission of carbon dioxide and vaporization of some pollutants into the air are major concerns when using this technology. On the other hand, the use of the biopellet is a passive means, needs minimal energy, and has little secondary pollution. Thus, the biopellet might work well alone as a treatment supplement used in an in situ treatment or incorporated into a flow-through

treatment barrier. Furthermore, compared with traditional bioaugmentation and biostimulation means, the use of the biopellet has more advantages. With hydraulic conductivity at around 0.001–0.002 cm/s, the groundwater moves around 1–2 m/day. Since the proposed pellet could provide the TPH degraders with oxygen and nutrients for up to 30 days at a fixed water level, the components needed to degrade the target pollutants might mix with the plume of the pollutants and prolong the degradation.

A combination of P&T and the use of biopellets could be beneficial. With the rapid removal of TPHs if biopellets are applied, using P&T strategies to drive flowing groundwater through a biopellet-filled flow-through barrier has several advantages, including faster movement of groundwater with high TPH removal efficiency, in situ treatment of TPHs, and minimization of TPH volatilization. As for treatment costs using the biopellets, besides the use of recycled materials and the energy costs saved by eliminating the need to pump groundwater and supply oxygen, the consolidation of all the required TPH-degrading components in one biopellet will avoid the labor-intensive operation of adding those components one at a time during the remedial works. The premade biopellets would also avoid the necessity of transporting liquid nutrients or setting up pipelines for air pumping. For further applications of biopellets in the field, a pilot test of real TPH-contaminated groundwater is suggested. In addition, knowing the existing depth of the pollutants and the necessary quantity of pellets are some prerequisites before a full-scale treatment can be applied.

4. Conclusions

Based on the results and the discussion above, a number of conclusions were reached and are listed as follows:

- 1. Novel biopellets made from acclimated microbes, fermented fruit peels, and CaO₂ recycled from eggshells appeared to effectively treat TPH-contaminated groundwater. The saturated C:N:P ratio reached 10:4:1 (by weight), with oxygen being released at approximately 1.0 mg/L after the addition of biopellets. Furthermore, triple alginate coating yielded a pellet floating time of up to 25 days.
- 2. Microbes acclimated through gradually increasing TPHd additions up to concentrations of 1600 /mg/L over a 60-day period were considered adequate, and this operation can be adopted to acclimate TPHd degraders. Through this acclimation process, the TPHd removal rate reached 46.2 mg/L per day.
- 3. The biopellet treatment of TPHd in water at an initial concentration of 500 mg/L removed nearly 99% of the spiked TPHd at a removal rate of 64.1 mg/L per day. The remaining TPHd mainly consisted of carbon (C13–C18), which was more than 98% degraded after 8 days. When the TPHd spike was raised to 1500 mg/L, the daily removal rate increased to approximately 45.0 mg/L per day, and all spiked TPHs were completely removed by 22 days.
- 4. During the first 8 days of treatment, the microbial count increased from near zero to 8.1×10^7 CFU/mL, the microbial consumption of N, P, and oxygen was considerable, the oxygen level remained high at 2.1 mg/L, and the pH was low at approximately 4.7.

Though the use of the novelly manufactured biopellets showed rapid TPH removal in days, the lack of applications to real TPH-contaminated groundwater and some minor adjustments to the pellet ingredients based on various TPH-contaminated groundwater cases still deserve further investigation. It is also interesting to acknowledge the potential of using this proposed method to make other biopellets to treat other groundwater-polluting substances like dense non-aqueous phase liquids (DNAPL) such as trichloroethylene (TCE).

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