Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1035674

57 (2016) 9679–9689
May

Taylor & Francis
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Investigation of petroleum-contaminated groundwater remediation using multi-stage pilot system: physical and biological approach

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Received 6 April 2014; Accepted 17 March 2015

ABSTRACT

In this paper, a pilot-scale system including various process steps was investigated in order to treat contaminated groundwater supplies which have been exposed to oil pollutants for a long time as they are located near the Tehran oil refinery company (TORC). For achieving this goal, a combination of dissolved air flotation unit that is followed by activated sludge bioreactors (ASBRs) and an activated carbon filter was chosen. The crude oil combined with tap water was applied to synthesize contaminated groundwater. Activated sludge taken from wastewater treatment plant at TORC was used to supply oil-degrading bacteria. Besides, the solution of mineral salts was added to the bioreactor as nutrients amendment. The optimum design parameters such as hydraulic retention time, return activated sludge rate of the ASBRs, and total residence time for all steps were 14 h, 100%, and 21 h, respectively. The operation of the pilot system which was implemented in different initial crude oil concentrations (206 ± 1,412 ± 3,1590 ± 10 mg l^{-1}) finally led to total petroleum hydrocarbons removal of 97, 97.25, and 98.57%, respectively. The reduction efficiency of chemical oxygen demand during the experiment was more than 97%. Furthermore, the quality of the treated groundwater was clearly improved, as the turbidity reduction through the experiment exceeded 90%. According to the results of the study, this treatment system can be considered as a reliable and efficient approach that is recommended to be used in case of extremely contaminated groundwater.

Keywords: Bioremediation; Activated sludge; Crude oil; Groundwater; TPH

1. Introduction

Petroleum hydrocarbons spills due to activities such as extraction, refining, leaks from underground storage tanks or pipelines, transportation accidents, and improper disposal of industrial wastes can be considered as the main reasons for spreading groundwater contamination [1–7]. The further spreading of contaminants resulting from groundwater pollution is remarkably concerning because of potential effects on drinking water supplies and possible toxicity towards human beings [8]. Petroleum pollutants release in the land areas located at south of Tehran especially those villages which are adjacent to Tehran oil refinery company (TORC); therefore, it

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leads to underground waters and surrounding environments to be polluted. In addition, pollution of these water supplies is caused many problems for the local residents. By considering these conditions, innovative, safe, trustworthy, and productive technologies can be applied to remediate contaminations of groundwater [9].

Remediation technologies for petroleum hydrocarbon treatment can be classified into three general categories known as chemical, physical, and biological approaches [10]. Among the most common technologies to clean up petroleum hydrocarbons, bioremediation methods offer beneficial solutions which are so cost-effective, energy efficient, and environmentally sound approach [11–17].

Bioremediation is explained as the elimination, attenuation, or transformation of contaminants by taking advantage of biological processes [18].The given technologies use microbes to treat contaminants by degrading and detoxifying organic compounds to less harmful products such as CO_2, methane, water, and inorganic salts [19]. Bioaugmentation and biostimulation are mainly employed as major kinds of bioremediation techniques which are defined as adding cultured bacteria with specific hydrocarbon-degrading potential and adding essential nutrients for enhancing the existing natural bacterial population, respectively [20]. The utilization of bioaugmentation approaches have been applied for remediating contaminated groundwater, which generally have a low potential for biological treatment as they suffer from some lacking sufficient substrate and nutrients that cannot support a viable biomass [21]. *Ex-situ* bioremediation using biological reactors, both under aerobic and/or anaerobic conditions, has been prosperously applied in the treatment of contaminated water with fuel hydrocarbons such as oil, gasoline, and diesel [19]. Moreover, aerobic bioremediation is regarded as an excellent approach to fulfill biodegradation processes, with respect to the fact that the majority of the commonplace micro-organisms would be able to degrade hydrocarbons belong to the aerobic species [22,23].

Several studies have already been done regarding the removal of petroleum compounds using activated sludge systems. Tellez et al. [24] investigated the performance of an activated sludge system for removing petroleum hydrocarbons from Southwestern US oilfield. The treatment process consisted of a skimming and pre-aeration unit followed by biological treatment step. Furthermore, a filtration unit was also placed on the downstream at the end of the clarifier. They concluded that an activated sludge system can successfully remove total petroleum hydrocarbons (TPH) from oilfield produced water. This treatment system maintained a removal efficiency of 98–99% at solid retention time of 20 d and mixed liquor suspended solids concentration of 730 mg l^{-1}. Chang et al. [25] studied the naphthalene (NAP) biodegradation using enriched activated sludge in the oil refinery wastewater. The bio-treatment process conducted in a 3-l constant flow stirred tank reactor was employed under different influent chemical oxygen demand (COD) and flow rates of wastewater containing NAP. They reported that the enriched activated sludge was properly able to biodegrade the NAP up to 15 mg l^{-1} and also mentioned that the bio-treatment efficiency on NAPs increased up to 87.9% with the decrease in inflow rate from 19.2 to 7.92 l d^{-1}.

Besides, the combination of the biological treatments along with physical or chemical methods could be used to speed up the pollutant removal efficiency, and helpful to decrease the contamination to a safe and acceptable amount as well [26,27]. Lu and Wei [28] used a combination of chemical pretreatment and biological degradation in a batch activated sludge reactor to treat oilfield-produced water. They concluded that the total removal efficiencies of TPH and COD after chemical oxidation using zerovalent iron, ethylenediaminetetra acetic acid, and air process combined with 40 h of bioremediation were 97 and 92%, respectively. Wirthensohn et al. [29] applied a pilot-scale plant including an aerated sedimentation/flotation basin, a submerged fixed film reactor, and a multimedia filter followed by an activated carbon filter (ACF) for remediation of contamination groundwater resulting from a manufactured gas plant (MGP) site in Vienna, Austria. This pilot-scale plant was operated for six months at flow rates of 1 and 2 l s^{-1} with the total hydraulic retention time (HRT) of 7 and 3.5 h over the treatment steps. They found that the treatment system was effective in reduction of typical MGP contaminants, PAHs, and BTEX more than 99.8%. The enhanced coagulation/flocculation study was also conducted by Zhao et al. [30], to assess the oily wastewater treatment using combining synthetic polymers with diatomite as an adsorbent and a coagulant aid. They investigated the influences of coagulant dose, initial pH, and settling time on COD/turbidity removal. They found that the combination of poly aluminum chloride (PAC) as a preferential polymer and diatomite effectively reduced more than 70% of COD and 90% of turbidity, accomplished at the optimum dose of PAC 50 mg l^{-1} and diatomite 1,250 mg l^{-1}, pH range (7–10) within 20 min of settling time.

In this study, a set of biological and physical steps was conducted in a pilot-scale system to operate under continuous flow regime of synthetic groundwater feedstock. Activated sludge bioreactors (ASBRs) were employed as a core stage of the remediation procedures, supported by dissolved air flotation (DAF) compartment. The aim of the DAF establishment as a pretreatment step was to streamline the biological processes through ASBRs. Finally, an ACF was applied as a complementary treatment to improve the treated groundwater standards.

The main objectives of this study were as follows: firstly, to assess the petroleum-contaminated groundwater treatment by utilizing the multi-stage pilot system; secondly, to optimize the significant design parameters of the ASBRs such as HRT and rate of return activated sludge (RAS) to reach desirable biological treatment; and finally, to investigate the reliable performance of such a treatment approach in a large-scale use under organic loading fluctuations.

2. Materials and methods

2.1. Synthetic petroleum-contaminated groundwater

In this study, the crude oil (specific gravity = 0.858 g cm^{-3}) was taken from TORC. The combination of the crude oil and tap water, applied to synthesize contaminated groundwater, was used as pilot influent over the experiments period.

2.2. Selection of the multi-stage treatment system

The aim of the pilot-scale system establishment was to treat such contaminated groundwater supplies that were exposed to oil pollution for a long time period due to locating near the TORC. There were some priorities needed to be considered for selecting the treatment system units, such as accessibility of clean-up facilities, easy construction, and operation as well as providing noticeable removal efficiency. By studying the different process combinations, biological treatment was selected as a key element of the treatment concept [29]. In addition, the primary treatment step is essential since it allows for the efficient and extended use of the secondary treatment unit. Physical separation of oil, colloids, and suspended solids is used as the preferred pretreatment method because of its efficiency in separating heavier fractions of the waste [31]. As one suggestion, the configuration of the treatment process steps was derived from the wastewater treatment system at TORC. It is operated in extended aeration activated sludge system and supported by DAF unit. Therefore, a combination of DAF compartment followed by ASBRs was chosen. Besides, an ACF was also added to the end of the treatment system in order to obtain significant removal efficiency as well as high-quality effluent.

2.3. Characteristics and performances of each pilot step

As mentioned above, the pilot plant encompassed various treatment steps that were designed to operate in a continuous flow. The technical properties of the pilot stages are listed in Table 1. In addition, the scheme of all treatment steps is illustrated in Fig. 1.

2.3.1. Feed tank

Simulation of petroleum-contaminated groundwater was accomplished in a cylindrical barrel with working volume of 200 l. A mixer with a long shaft was also installed on the top of feed tank produced suitable rotational gradient to make an appropriate mixture of contaminated groundwater. During this study, this action was regularly used to ensure that specific amount of polluted groundwater is introduced into the following process steps. The prepared feed was delivered to the following step with pH of around 7.5–8, modified by 1.0-M HCl solution.

2.3.2. Dissolved air flotation

The process of flotation was implemented in a cylinder shaped vessel (effective volume = 28 l). The synthetic oily groundwater was pumped into the DAF compartment from the bottom. Two round disc diffusers (external diameter = 10 cm) were placed at the base of the DAF and connected to the air pump to provide fine air bubbles. Amount of air was forced to the reactor was at 3.5–4 l min^{-1} approximately. If needed, small particles floated on the surface were manually skimmed and removed. Since the physical pollutant reduction was only considered; no additional chemical agents were applied such as acidification, coagulation, etc.

2.3.3. Activated sludge bioreactors

In this study, an aerobic biological treatment was carried out in an activated sludge system. It consisted of a rectangular aeration basin (working volume = 175 l) and a settling/clarifying tank with an effective volume of 35 l. The aeration basin was equipped with four narrow bar diffusers with 47 cm length, connected to the air pump, which were fixed at the bottom. An aquarium heater also located at the inside wall of the reactor near to the surface. Furthermore, the ending part of the settling/clarifying tank was built like a funnel-shaped vessel in order to facilitate the processes of settlement and accumulation of biomass during the operational procedures.

Table 1
Technical data of pilot stages

	Feed tank	DAF	ASBRs		ACF
			Aeration basin	Settling/clarifying tank	
Diameter (cm)	54.5	27		29	25
Effective height (cm)	86	49	60.5	63-14*	51
Free board (cm)	10	5	15	5	12
Length (cm)			59		
Width (cm)			49		
Volume (l)	200	28	175	35	25

*The height of the funnel-shaped part at the ending of the settling/clarifying tank.

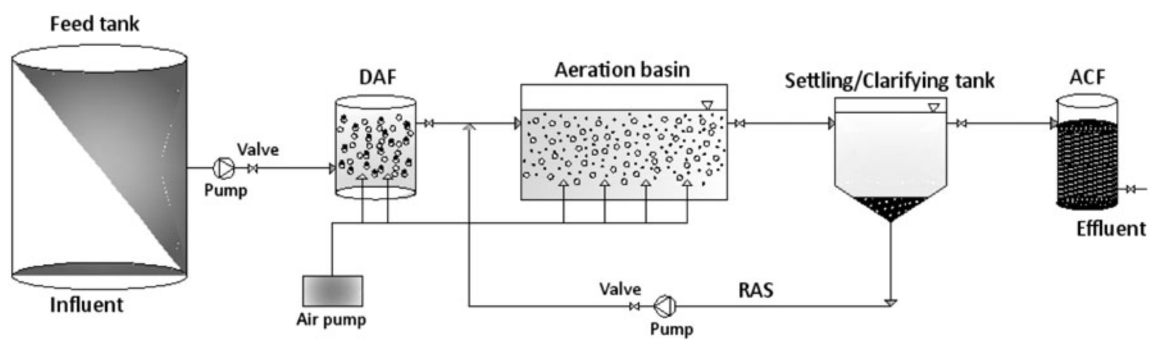

Fig. 1. Schematic diagram of pilot stages: Feed tank; DAF; ASBRs including aeration basin and settling/clarifying compartments; ACF.

To set up pilot system, around 55 l of activated sludge was taken from wastewater treatment plant at TORC, which was closely compatible to petroleum hydrocarbons. It was used as a source to supply bacteria with biodegradation capabilities and also considered as a crucial facet of bioremediation approaches [32,33]. An air flow rate of about 8–10 l min^{-1} was produced to the basin through bar diffusers in order to create uniform mixing and aeration conditions. During the experiment, temperature of the aeration basin was retained at a range of 28–30˚C through aquarium heater. To amend the nutrients, a solution of mineral salts was prepared and added to the bioreactor. The combination of the nutrients medium to meet the C:N:P ratio of 100:10:1 is as follows [34]: 8.79 mg l^{-1} KH_2PO_4, 30.55 mg l^{-1} NH_4Cl, 72.82 mg l^{-1} $NaNO_3$, and 25 mg l^{-1} Nutrient Broth as the routine cultivation of bacteria (containing Gelysate TM peptone and Beef Extractives) dissolved in purified water.

2.3.4. Activated carbon filter (ACF)

A cylindrical container with working volume of 25 l, filled with granular activated carbon, was used to improve the quality of final effluents. The surface adsorption of small particles and even the residuals left from the previous treatment process steps was assessed by a vertical column of activated carbon materials. It was operated in a down-flow regime, provided adsorption of organics and filtration of suspended solids in a one step as well as decreases the accumulation of particulate material in the bottom of the activated carbon bed where it would be difficult to remove by backwashing [35].

2.4. Data sampling and analysis

After each experiment, water samples were taken from the influent, and each effluent of the different pilot steps. They were collected in glass bottles and stored in 4.5–5˚C for subsequent analytical examinations. COD and mixed liquor volatile suspended solid (MLVSS) quantities were measured in accordance with Standard Methods [36].

In this study, the reduction of TPH was considered as a significant parameter to evaluate the effectiveness of treatment steps. Water samples were extracted using dichloromethane solvent according to Method

3510C [37]. The TPH was determined by gas chromatography (Agilent 7890), equipped with a mass selective detector, (5975C, MODE EI) and a capillary column (DB5-MS, 30 m, 0.25 mm, 0.5 μm) was applied. The both injector and detector temperature were 290˚C. Helium was served as the carrier gas at flow rate of 1 ml min^{-1}. During the experiments, temperature changes were as follows: initial temperature was set at 60˚C maintained for 1 min, raised to 100˚C at a rate of 10˚C min^{-1}, then elevated by 6˚C min^{-1} to 285˚C and held for 5 min. Accordingly, the TPH determination was calibrated with the standard solutions for the C_{10}–C_{35} carbon range.

3. Results and discussion

3.1. Start-up procedure of the ASBRs system

It is inevitable to allocate sufficient time for microbial community acclimation to petroleum-contaminated environment. In addition, it is very significant to allow the bacteria to adapt with petroleum substances, regarded naturally as the hazardous and carcinogenic materials. Hence, as to start-up, the operation of the bioreactors was initiated in a batch system to reach the steady-state condition. Any changes in pH were also monitored on a daily basis and maintained in a range of 7–7.5 which was adjusted by making use of 0.1 M NaOH solution. After a while, some alterations including the process of fading suspended oil fragments were observed and floated at the surface of the aeration basin as well as dispersing to the small separated particles which vanished finally. Moreover, the contents' quality of the settling/clarifying tank especially those were crystal and clear early, converted into turbid aquifer, accompanied with formation of biomass at the base and other inside walls of the tank. These evidences indicated that the present ASBRs could be beneficial for conducting bioremediation approaches. Meanwhile, adding the nutrients and petroleum-contaminated groundwater were carried on to the bioreactors. The stable removal amounts of COD and MLVSS for 2–3 d and in steady-state condition were more than 90% and 2,550 mg l^{-1}, respectively. The activated sludge system took about four weeks to reach the biological balance condition. Thus, the bioreactors batch performance turned into the continuous flow and fed by DAF effluent constantly. During the pilot operation in a continuous system, the nutrient solution was added to the bioreactors periodically, excluding Nutrient Broth which was not used any longer.

3.2. Optimization of HRT and rate of RAS

The pilot system performance to achieve the favorable TPH removal was investigated under various HRTs and RAS rates. An appropriate HRT has a remarkable impact on the removal efficiency, by providing good enough meeting time between cells (bacteria) and substrates (petroleum hydrocarbons). Because of this reason, the operation of the pilot system was investigated in different flow rates of 10.94–14.58 l h^{-1}, accounting for diverse HRTs of 16–12 h in the aeration basin. Moreover, the assessment of the appropriate HRT for fruitful biological treatment was carried out while the RAS was delivered to the aeration basin at an identical flow rate of each HRT experiment. Table 2 shows the TPH removal procedure based on changes in the parameter of HRT. The initial concentration of crude oil applied for preparing the pilot influent as only source of carbon was 206 ± 1 mg l^{-1} approximately.

According to the results, increasing in HRT led to higher TPH reduction at first. Nevertheless, the higher the HRT, the lower the removal efficiency was achieved. This result could be attributed to the depletion of substrates and decreasing the F/M ratio which cause exogenous respiration processes and increasing the decay rate of biomass [35].

Moreover, sufficient amount of RAS is required to keep adequate concentrations of biomass in the aeration basin in a good condition, so desirable biological treatment would be acquired in the given time [35]. In this way, ASBRs operation was tested in varied RAS rates. The inflow rate was fixed at specific amount exactly corresponded with the optimum HRT. In addition, the percentage of the RAS circulated between bioreactors, through control valve installed on the circulation line, was chosen 60, 80, and 100, respectively. The results of the ASBRs' examinations in different RAS rates are presented in Table 3.

Based on the data analysis, increasing in RAS rates met the more satisfactory regarding amounts of removal efficiency. It could be concluded that quite high concentrations of capable biomass should be served and maintained to the bioreactors to achieve favorable biological treatment.

Hence, the optimum design parameters of HRT and RAS rate to reach the highest TPH reduction was determined 14 h and 100%, respectively, resulting in 97% of TPH removal efficiency. Accordingly, the total retention time through the remediation steps was equal to 21 h as treatment of total contaminated groundwater, accounting for initial flow rate of 12.5 l h^{-1}. The procedure of TPH removal at optimum amounts of given parameters is illustrated in Fig. 2.

Table 2
The reduction of TPH in varied HRTs of the ASBRs (aeration basin)

Flow rate ($l\ h^{-1}$)	HRT (h)	TPH* ($mg\ l^{-1}$)	Number of samples (N)	Removal efficiency (%)
14.58	12	54 ± 3	3	72.86
12.50	14	20 ± 1	3	90.00
11.67	15	23 ± 2	3	88.56
10.94	16	29 ± 2	3	85.50

*TPH: is the outflow TPH concentration of the ASBRs. The concentration of TPH in the influent was 200 ± 1 $mg\ l^{-1}$, while it was variable between 103 and 120 $mg\ l^{-1}$ passing through the DAF unit.

Table 3
The investigation of effects of different RAS rates on aerobic biological treatment

RAS rate* (%)	TPH* ($mg\ l^{-1}$)	Number of samples (N)	Removal efficiency (%)
60	33 ± 2	3	83.58
80	24 ± 2	3	88.06
100	20 ± 1	3	90.00

*RAS rate: The ratio of (RAS flow rate/ inflow rate) × 100. Moreover, its determination was conducted at fixed continuous flow rate of 12.5 $l\ h^{-1}$obtained from previous tests.

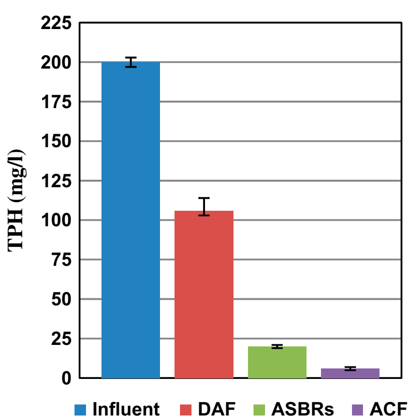

Fig. 2. The removal of TPH using pilot stages at optimum values of HRT and RAS rate of the ASBRs.

3.3. Effects of initial crude oil concentrations on the TPH removal

In order to evaluate the influence of organic shock loading on the pilot performance, it was operated in some different oil substances concentrations. The influent contaminated groundwater with crude oil concentrations of 412 ± 3, 1,590 ± 10 $mg\ l^{-1}$ was prepared in the feed tank to assess TPH removal while the treatment system is exposed to high amounts of oil pollutants. Fig. 3 shows how pilot system responded to the changes in oil concentrations. Similar performance was experienced when it was fed by a synthetic sample, made up with crude oil concentration of 412 ± 3 $mg\ l^{-1}$. Although, the total removal efficiency was obtained equivalent to 97.25%, the contribution of ASBRs as a main stage of treatment processes was slightly decreased from 43 to 40.5%. It could be derived from the fact that the activated sludge system may be affected by doubling crude oil concentrations in a short period of time. Moreover, feeding the pilot system with higher concentrations of crude oil (1,590 ± 10 $mg\ l^{-1}$) led to satisfying results. The contribution of biological treatment step was increased up to 47.44% of the whole TPH removal, supported the removal efficiency of 98.57% in total. Besides, the highest amount of MLVSS (3,500 $mg\ l^{-1}$) was taken over the entire experiments. It could be resulted from the correlation between the amount of biological treatment and the rate of available biomass. On the other way, the community of adapted microbial, possessed the potential to biodegrade oil substances, was developed when the amount of crude oil was increased at high rate in the influent.

In spite of the fact that noticeable TPH removal efficiency was achieved, there were still some oil particles remained in the final effluent. On the one hand, it could be assumed that some constituents of crude oil that was used in this study were strongly recalcitrant to any biodegradation processes. On the other hand, the mineralization of some particles could not be accomplished in the given conditions, so intermediate products might be generated along the experiment duration.

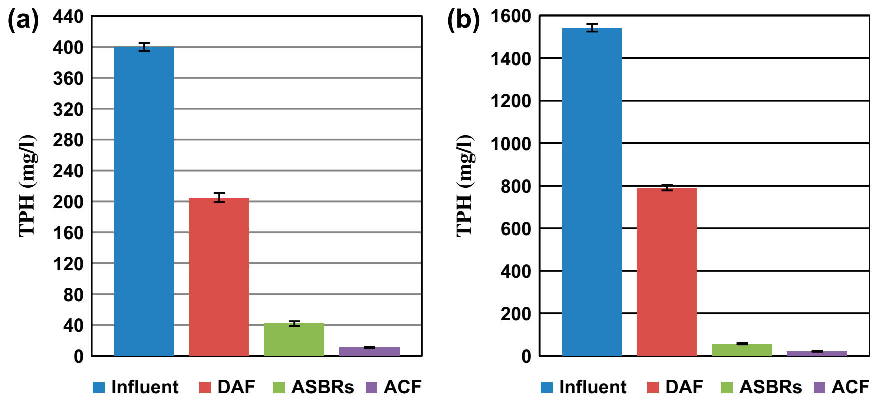

Fig. 3. Elimination of TPH content at different crude oil concentrations of (a) 412 ± 3 mg l^{-1} and (b) 1,590 ± 10 mg l^{-1}.

Furthermore, not being adsorbed of petroleum hydrocarbons thoroughly by activated carbon materials could be taken into account as another cause.

The biological treatment efficiencies with regard to the influent and effluent TPH concentrations of the ASBRs were 81.1 and 80.4%, respectively, when the contaminated groundwater containing 206 ± 1 and 412 ± 3 mg l^{-1} of initial crude oil concentrations was introduced into the process steps. The ASBRs exhibited a good performance in TPH reduction (at highly polluted groundwater experience) up to 93.2% as the TPH in the treated groundwater, leaving the ASBRs, was efficiently eliminated from 789 to 54 mg l^{-1}. The TPH removal efficiency is almost comparable to the Tellez et al. [24] findings while they assessed the activated sludge performance for the produced water treatment containing 126 ± 30 mg l^{-1} of TPH. The results indicate that the activated sludge system used in this study have a great biological potential to degrade the high concentrations of petroleum compounds. A comparison with Lu and Wei [28] study shows that the overall TPH reduction of 98.57% is relatively better than their achievements (97% removal of 62 mg l^{-1} of TPH). Moreover, the data analysis shows that TPH was suitably removed up to 49% by the aeration and flotation processes in the DAF unit, while Lu and Wei obtained 59% removal efficiency, including chemical oxidation in addition to air process. They also reported that the residual oxidant agents needed to be removed through additional settling/filtration process which had toxic potential to micro-organisms.

3.4. Improvement of the groundwater quality

3.4.1. COD removal

The declining trend of COD removal through the pilot steps was considered as an index to display the performance of each treatment process units. The proportional contribution of different pilot steps has been shown in Fig. 4. The separation process of the suspended particles which floated on the surface could be responsible for decreasing total COD through the DAF. The bioremediation processes took place in the ASBRs, and had a significant effect on the COD removal, although it stayed relatively high because of the biomass existence in the outflow from the ASBRs. The ACF as a complementary treatment step reduced the rest of the total COD as could as possible, through the surface adsorption of organic materials. Thus, using ACF caused to obtaining high-quality effluent for discharging issues. However, the biodegradation of petroleum hydrocarbons was not investigated in the ACF since it was no essential requirement for aerobic biological treatment.

At initial crude oil concentrations of 206 ± 1 and 412 ± 3 mg l^{-1}, the similar COD reductions were obtained which were 97.54 and 97.05%, respectively. In addition, the data corresponding to heavy oil pollution case (1,590 ± 10 mg l^{-1}) showed that 98.51% of the total COD was eliminated through the pilot steps and properly matched with the result of the TPH removal. Therefore, the presented data demonstrated that high COD removal could be efficiently obtained despite feeding the high concentrations of petroleum-contaminated groundwater. The treatment system in this study worked much better in the COD reduction, compared to the Lu and Wei [28] approach (92% removal of 1,130 mg l^{-1} of COD), while the COD concentrations were up to three times as high as their experiments. Furthermore, they reported that prolonging biological treatment time could not enhance the COD removal efficiency. The COD reduction was also considerably higher than Wirthensohn et al. [29] achievements, investigated a pilot-plant experience for remediation of contaminated groundwater with

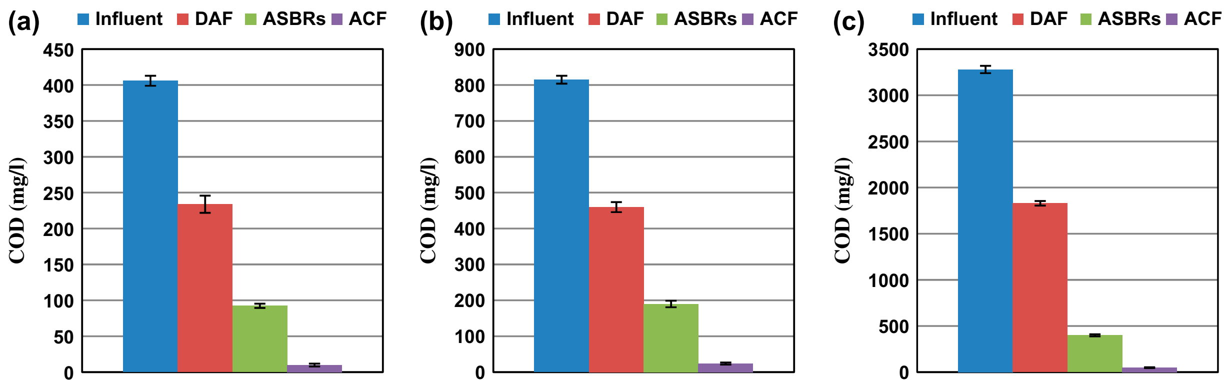

Fig. 4. The COD reduction through remediation steps at initial oil feeding of (a) 206 ± 1 mg l^{-1}, (b) 412 ± 3 mg l^{-1}, and (c) 1,590 ± 10 mg l^{-1}.

maximum COD influent of 61 mg l^{-1}. They reported that a significant amount of COD was not removed after all process steps. They also found some deposits of tar compounds in the bottom layers of the SSFR mentioned that using small size carrier materials make filters become more prone to clogging and cause operational problems subsequently.

3.4.2. Turbidity changes

To assess the treated groundwater quality, the turbidity of samples was measured throughout the experiments. It was observed that the synthetic oily groundwater experienced various amounts of remediation by passing through the process steps and its quality was subsequently improved. The physical process of floating small particles in the DAF unit, aerobic biological treatment using capable oil-degrading bacteria through the ASBRs, and particularly physical adsorption of particulate materials through the ACF, all contributed to enhance the quality of final quality effluent. Table 4 shows general changes in process steps turbidity with different crude oil feedings. Although the turbidity amounts of the synthetic contaminated groundwater were significantly more than Wirthensohn et al. [29] experiments, this treatment system also showed much better performance in turbidity reduction compared to their achievements. The turbidity reduction obtained over this study exceeded 90%.

3.5. The correlation between TPH and COD

The average data of TPH vs. COD corresponding to each process steps are illustrated in a chart series from A to D (Fig. 5). By comparing charts A and B, it is clear that the both TPH/COD ratio in the feed tank and the DAF unit remained relatively constant. It indicates that biological treatment process has not occurred in the pretreatment step and the pollutant reduction was just accomplished through physical flotation process. Afterwards, the mentioned ratio dropped considerably in the activated sludge system as it has been shown in chart C. In fact, the majority of the COD is comprised of suspended solids and biomass rather than oil pollutant particles. It confirms the significant role of biodegradation for removing and converting the contaminants to the less harmful products. Moreover, as it is observed in chart D, the residual TPH/COD ratio in the ACF unit returned to the initial ratio. Increasing in the given ratio is likely related to those suspended solids removal which directly contributed to the COD production. This results show that the ACF unit had an appropriate

Table 4
Amounts of turbidity during process steps in different crude oil concentrations

Influent	DAF	ASBRs	ACF	Initial crude oil concentration (mg l^{-1})	Number of samples (N)
Turbidity (NTU)					
145 ± 5	79 ± 4	48 ± 3	9 ± 1	206 ± 1	3
293 ± 9	149 ± 5	81 ± 4	17 ± 1	412 ± 3	3
915 ± 16	465 ± 10	184 ± 6	28 ± 2	1,590 ± 10	3

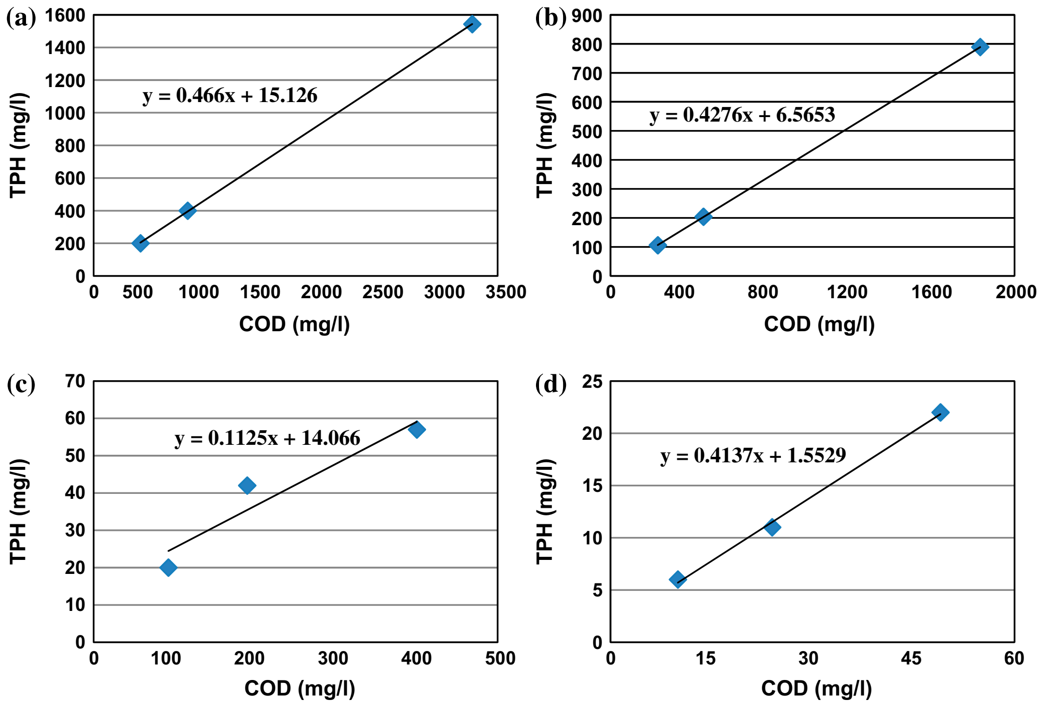

Fig. 5. The correlation between TPH and COD in all process steps.

performance in adsorption of small particles as well as TPH reduction.

The high TPH and COD removal efficiencies during the high contaminated groundwater experiments are considered as the distinguished characteristics of the investigated treatment system. In addition, the assessment of the pilot performance under different crude oil concentrations demonstrated that the treatment system is a reliable and effective approach for a large-scale use. This is related to the fact that the petroleum compounds reduction was kept quite high in spite of increasing the oil pollutant loading rate.

3.6. Monitoring of pH along the experimental period

After sampling of each treatment step, the pH measuring process was accomplished based on daily data. In comparison to the pH range in the feed tank, no remarkable pH changes were observed through the DAF. The bioremediation processes in the ASBRs apparently declined the pH parameter. As a matter of fact, alkalinity consumption and increasing the concentration of [H^+] ion were the main reasons for the pH drop during biodegradation activities [35]. Additionally, along the observations, the amount of the pH parameter was slightly altered in the effluent from the ACF. The range of pH changes in different pilot steps over the experiments is presented in Table 5.

Table 5
Variations of pH along experiment duration

Process unit	Range of pH changes
Influent	7.6–8.0
DAF	7.7–8.1
ASBRs	6.8–7.3
ACF	7.2–7.5

4. Conclusions and recommendations

The present multi-stage pilot consisting of DAF, ASBRs, and ACF units, turned out to be reliable and effective for treatment of petroleum-contaminated groundwater. The results show that the optimum HRT and RAS rate in the activated sludge system to reach the highest TPH removal were 14 h, 100%, respectively, accomplished at continuous flow rate of 12.5 l h^{-1}. The TPH reduction was efficiently achieved up to 98.57% and the activated sludge system played a significant role through biodegradation of petroleum hydrocarbons in high concentrations.

In spite of the crude oil feeding at high rates, the amount of COD removal was taken more than 97% throughout the treatment steps. Besides, the integrated pilot system was successful to enhance the remediated groundwater quality, as the turbidity reduction was more than 90%. Moreover, the results hold the fact that this pilot system has a sustainable performance in case of organic shock loading. Regarding the outcomes of this study, discharge to the sewage system could be considered as an appropriate option for the final effluent.

It is highly recommended that the operation of the pilot system to be evaluated with actual samples of groundwater polluted by oil products to assess the efficiency of the pilot performance in real circumstances. Further analyses are also needed to determine the structures of oil residuals or other intermediate products, generated during the experimental period. As another suggestion, the ACF could be replaced by some other natural adsorbents which hold similar capacity of particle adsorptions to reduce disposal problems.

To sum up, the DAF effectively contributed to the reduction of TPH as the petroleum pollutants were degraded by pretreatment processes up to 49%. More than 47% of the overall TPH reduction was achieved through ASBRs, while the influent contained 1,590 ± 10 mg l^{-1}crude oil concentration. Accordingly, the results indicated that the ASBRs have the high potential to fulfill aerobic biological treatment at high contaminants concentration as long as adequate dosages of nutrients (such as N, P, etc.) are provided to the bioreactors. Finally, using the ACF, represented as complementary treatment step, clearly improved the quality of the remediated groundwater. Based on the results, the investigated treatment system exhibited a great potential on the removal of petroleum compounds, recommended to be used in case of extremely polluted groundwater.

Acknowledgments

The authors would like to thank the Tehran Oil Refinery Company (TORC) and its staffs for their cooperation and kindly supplying sources of crude oil and activated sludge substances.

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