Design of Permeable Reactive Barrier for Petroleum Polluted Groundwater

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ABSTRACT

Groundwater pollution caused by oil spill accidents has been reported occasionally, and the groundwater remediation of petroleum hydrocarbons is an important research direction. In the process of in-situ groundwater remediation, a permeable reactive barrier can effectively prevent the spread of contamination plume. However, selecting the optimal material and estimating the width remains critical and challenging problems in the design of permeable reactive barrier. Meanwhile, the site environment is also an important part to consider. In this study, aimed at the oil pollution site of a military base in South Korea, the best adsorption material was determined through batch and column experiments, and a PRB with the best width in line with the service life was designed through various design methods. In the width design, based on the material balance equation, the method of using the width of the material transport area is innovated.

Keywords: Permeable reactive barrier, Design methodology, Total petroleum hydrocarbon

NONMENCLATURE

Abbreviations	
PRB	Permeable Reactive Barrier
TPH	Total Petroleum Hydrocarbon
BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
TSS	Total suspended solid
TDS	Total dissolved solid
GC	Gas chromatography
MTZ	Mass Transfer Zone
Symbols	
q_e	Equilibrium concentration of adsorbed adsorbate (mg g^{-1})

C_e	Equilibrium concentration of TPH (mg L^{-1})
V	Volume of solution (L)
M	Mass of adsorbent (g)
K_L	Langmuir constant related to the energy of adsorption
q_{max}	Maximum adsorption capacity
K_F	Freundlich model constant
n	Correction factor
W_t	Width of total PRB (m)
W_{MTZ}	Width of MTZ (m)
W_e	Width of equilibrium zone (m)
R	Retardation factor

1. INTRODUCTION

Groundwater accounts for approximately 50% of the global water withdrawal[1]. As a scarce resource that is difficult to regenerate, groundwater faces many risks, such as contaminants discharged from industry and agriculture[2]. The petroleum industry accounts for a huge proportion of the industrial structure. However, onshore oil spill accidents occur from time to time, posing a huge threat to the local groundwater ecology[3]. The main contaminant total petroleum hydrocarbon (TPH), which includes monoaromatic hydrocarbons like BTEX and polycyclic aromatic hydrocarbons, is resistant to natural decomposition in the subsurface. Over time, contaminants in groundwater will spread over a wider area, causing immeasurable damage[4]. Due to geological heterogeneity, contaminant plumes, and long-term effects, remediation of contaminated groundwater is a challenging and necessary task[5].

Permeable reactive barrier (PRB) has unparalleled advantages in preventing further spread of pollution and protecting important areas, compared with common groundwater remediation technologies such as pumping treatment, biological ventilation, and chemical oxidation[6–8]. Well-designed PRB systems have also been

shown to reduce costs and maintain long-term operations from some reports[9–11]. However, some PRB systems still do not meet their intended purposes, and these failures may be caused by insufficient reactive materials, insufficient widths or thicknesses of PRB, and reduced porosity[5,12]. Hence, it is crucial to address potential risks and prevent PRB failures during the design phase.

Based on the information disclosed by the public management department and reports, the main design process of PRB typically includes preliminary feasibility studies, site characterization, reactive material selection, and engineering design[13,14]. Feasibility studies are crucial in determining whether the PRB method can be applied effectively to remediate the site[15]. On-site investigations involve the identification of target pollutants, collection of geochemical information, and assessment of hydraulic characteristics[16]. The selection of reactive materials usually relies on extensive engineering practices, primarily following mechanisms such as adsorption or reduction for the removal of pollutants[17]. The engineering design of PRB requires consideration of both lifetime and construction. Among these, the key factors in PRB design are primarily the reactive materials selection and thickness of PRB.

The selection of reactive materials is determined by performance evaluation based on the capture of specific contaminants by reactive materials[13]. Due to the heterogeneous and geochemical properties of soils, column experiments are commonly used to determine residence times[18]. For the remediation of petroleum hydrocarbon contaminated groundwater, there have been relevant reports using zeolite and granular activated carbon as reaction materials[19,20]. These studies indicate that the operation of PRB facilitates the growth of microorganisms on the reactive materials, thereby accelerating the degradation of petroleum hydrocarbons. However, the biodegradation process is susceptible to various environmental factors, including temperature, dissolved oxygen, etc., which are considered unstable[21]. Consequently, in this design process, only physical and chemical processes are taken into account. To the best of our knowledge, utilizing adsorption reactive materials for groundwater remediation proves effective in cost control, but there is a scarcity of comprehensive reports on the entire design process.

Aiming at a real groundwater site polluted by petroleum hydrocarbons, this paper completes comprehensive processes from site analysis, and material screening to engineering design. In terms of material screening and PRB width design, our goal is to (1) assess site contamination and select the right treatment method, (2) identify optimal adsorption materials via batch and column experiments, and (3) calculate PRB width based on material transfer area for innovative design.

2. MATERIAL AND METHOD

2.1 Material and chemicals

Two adsorbents were purchased from the public market, including granular activated carbon (CGAC model 830 W, American) and biochar-based graphitic carbon nitrate (BGCN 1240 PLUS, g-C3N4, Norit Netherlands). The maximum particle size of the two materials was less than 3 mm. In order to evaluate the impact of the particle size in adsorption, different size range carbon adsorbents (0.25–0.6, 1–1.4, 1.7–2, and 0.25–2 mm) were separated by manual sieving. Because the content of fine particles had a significant effect on permeability, the particle size of original adsorbents smaller than 0.25 mm were also separated and marked as 0.25–2 mm. Raw groundwater was collected from a site in Korea and stored at 4℃. Sodium bromate (99%, chemical grade) and hydrochloric acid (37%, chemical grade) were purchased from Daejung in Korea. The n-hexane (99%, GC grade) and TPH standard samples were purchased from Sigma Aldrich. The simulated TPH was mixed gasoline and diesel (m:m = 1:1), and all petroleum products were purchased from S-soil company in Korea. The simulated groundwater was synthesized referring real groundwater and the geochemical characteristics of groundwater are presented in Table 1.

Table 1. Characteristics of groundwater

Parameter	Value	Parameter	Value
pH`	6.2	NO_3^- (mg L^{-1})	2.2
Temp. (℃)	15	Na^+ (mg L^{-1})	9.54
TSS (mg L^{-1})	94	K^+ (mg L^{-1})	1.61
TPH (mg L^{-1})	3.4	Ca^{2+} (mg L^{-1})	52.61
Cl^- (mg L^{-1})	9.1	Mg^{2+} (mg L^{-1})	15.54
SO_4^{2-} (mg L^{-1})	2.8	Fe (mg L^{-1})	15.17
HCO_3^- (mg L^{-1})	300	Mn (mg L^{-1})	1.91

2.2 Experiments

For the adsorption isotherm experiment, different amounts (0.5, 1,2, 4, 6, 8, 10 and 15 mg) of adsorbent (CGAC or BGCN) was added in a 2000 mL beaker, respectively. The adsorption tests were conducted in raw groundwater and the stirring speed was at 150 rpm. During the experiments, 100 mL groundwater was

sampled by a syringe and filtered through 0.22 µm cellulose acetate filter. Subsequently, this sample was extracted by an organic solvent for GC measurement. All batch adsorption experiments were performed at room temperature (23±1℃). The simulated groundwater was conducted to column adsorption test. Specifically, two types of column were used depending on different experiment test. The small size column (Φ3 cm × 30 cm) was made of glass for retardation factor analysis. The plexiglass column (Φ5 cm × 50 cm) was applied for column adsorption test. In order to minimize volatilization of hydrocarbon, the gas-guide tube was insert into the bottom of raw groundwater tank.

2.3 Analysis method

Specific surface area of different size CGAC and BGCN was determined by the Brunauer-Emmett-Teller method (Tristar II 3020). The concentration of total petroleum hydrocarbon TPHs (C10-C40) was measured by extraction-GC method following EPA method 8015B. TPHs were extracted from soil or groundwater using distinct methods: ultrasonic extraction (1 hour) for soil and vortex extraction (15 min) for groundwater. In each case, the extraction process utilized n-hexane as the organic solvent. The anions were analyzed by ion chromatography (Dinoex ICS-1100) and cations were measured by ICP-MS. A falling head permeability test was applied to determine hydraulic conductivity of adsorbent particles.

3.   MATERIAL AND METHODS

3.1 Site characterization

Based on our previous investigation, the remediation site (a military base near Seoul) revealed significant organic contamination in both soil and groundwater. The analysis of soil samples showed that TPHs as the main contaminant, originating from fuel and engine oil leakage, with a peak concentration of 7984 mg kg^{-1} in the central polluted area. Considering diffusion and precipitation, groundwater was investigated over 11 months, in which the TPH concentrations were as high as 3.4 mg L^{-1}. Fig. 1(A) indicated that the contaminant plume was much larger than the spill point, while the total contaminated area covered approximately 940 m^2.

The concentration distribution of TPH in groundwater in the vertical direction shows that the pollution area is mainly concentrated in the depth range of 4 to 5 m below the surface (shown in Fig. 1B). The investigation results reflected that the pollution center

was around UJMW10, which coincided with spill center. Given factors such as TPH's low water solubility and the unsaturated groundwater zone where the spill occurs, rainfall and gravity effects play a key role in contaminant dispersion, because TPH mainly forms a light non-
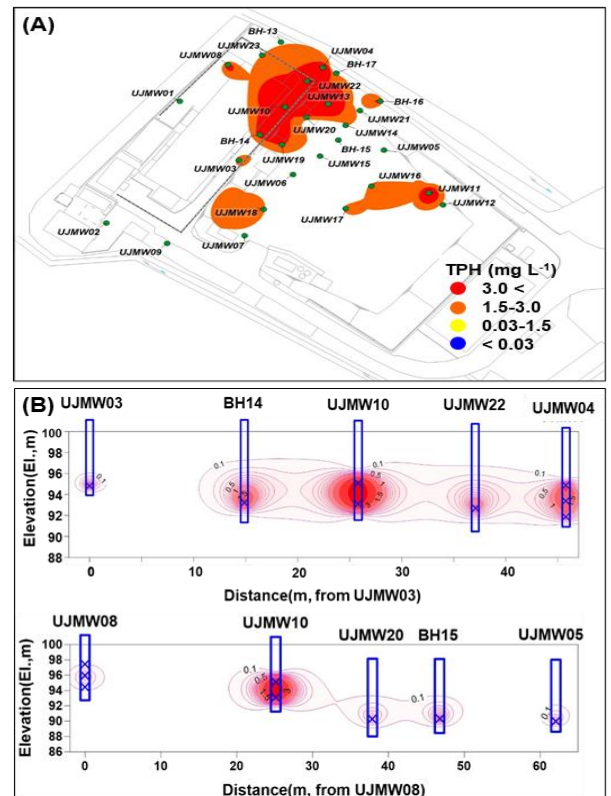

Fig. 1. Monitor wells and TPH contaminant plume in (A) horizontal direction and (B) vertical direction.

aqueous phase liquid[22]. Depending on the concentration distribution of pollutants in soil and groundwater, petroleum compounds are mainly transported in the soil medium in the form of dissolved molecules. Since the contaminated site is close to buildings, ex-situ remediation poses safety risks, so in-situ remediation of contaminated soil was first considered. However residual sources of contamination and soil spatial heterogeneity may hamper remediation efforts, making it critical to contain and limit the further spread of TPH[23]. In order to control concentration of TPH in the plume, PRB was selected as remediation technology in "treatment‐train".

3.2 Material selection by adsorption test

Batch and column tests were conducted to evaluate the adsorption capacity of potential reactive materials for the PRB. These materials should be readily available in the public market; thus, two common commercial

carbon-based adsorbents were chosen. To investigate the impact of particle size on adsorption, we sieved CGAC and BGCN into four different range sizes while keeping their surface chemical properties consistent. In Fig. 2A-B, the results presented that the adsorption capacity increased significantly with decreasing particle size. Smaller particle sizes yielded higher adsorption capacity of carbon materials due to increased specific surface area[24]. The Fig. 2A-B also presented the fitting results of the Freundlich model and the Langmuir model, showing good fitting degree (R^2 > 0.995). The fitting results unequivocally demonstrated that the adsorption efficacy of BGCN surpassed that of CGAC. According to the results of material surface analysis, the main reason was that the original size BGCN (1260 m^2 g^{-1}) had a larger specific surface area than that of the original size CGAC (996 m^2
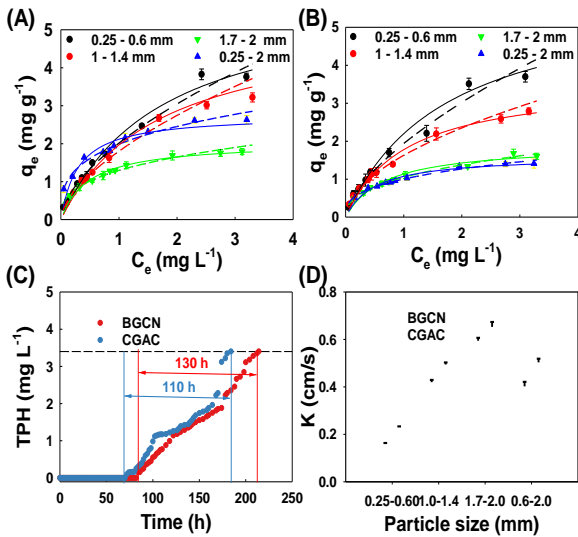

Fig. 2. Isotherm adsorption equilibrium curve of (A) BGCN and (B) CGAC (solid line: Langmuir model fitting, dash line: Freundlich model fitting), (C) breakthrough curve of adsorbent in actual groundwater, and (D) hydraulic conductivity with different particle size.

g^{-1}). More surface area of materials provided more abundant adsorption sites for petroleum hydrocarbon molecules[25]. Furthermore, it appeared that Freundlich model had a better fitting than Langmuir model. Additionally, CGAC had irregular square-shaped particles, whereas BGCN predominantly had flat particles. These differences in morphology are attributed to variations in raw materials and fabrication processes[26].

3.3 Design of width

Both the empirical method and mass balance method used in this study are summarized in Table 2[28,29]. For the calculation of width, column adsorption experiments were conducted to derive the necessary parameter (retardation factor R)[28,30,31]. The experimental results of the simulated wastewater are shown in Fig. 3. Before the experiment, sodium bromide was used to conduct a tracer test on the adsorbents (shown in Fig. 3A), and the retention coefficient was calculated by comparing the simulated wastewater test results. The hydraulic conductivity coefficient of CGAC was better than that of BGCN but slightly inferior to BGCN in terms of retention coefficient. As shown in Fig. 3B, the retention coefficients of CGAC and BGCN are 134 and 144 respectively.
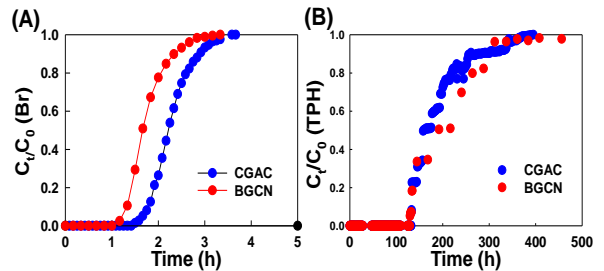
The key parameters in the width design of PRB

Fig. 3. (A) Tracer test (Br-) and (B) simulated TPH contaminated groundwater test in the small column.

directly determine the service life of PRB. Different reactive materials have different mechanisms for removing pollutants. Thus, choosing the appropriate calculation reaction is particularly important. For example, using zero-valent iron as the reaction medium for RPB is more like a plug flow reactor while using activated carbon or zeolite is more like a fixed bed adsorption tower. The experimental results will also be affected by water quality.

This study estimates the width of PRB using the methods of material conservation and mass transfer zone calculation. According to engineering experience, a larger width of PRB will have a longer service life, but will also be more expensive. The experimental results are shown in Table 3. The results showed that the PRB width calculated by the empirical method was significantly higher than that obtained by the material balance method and the experimental method. The results of the experimental method and the material balance method were more similar, which directly showed the accuracy of the material balance method.

Table 2. Design width of PRB by different methods.

Method	Equation	No.	Parameter
Empirical design	$W_t = \dfrac{t_{life} \times \mu_{Ground}}{R}$ [Eq. 1]	1	*Model retardation factor (R_M):* $Langmuir\ sorption\ R = 1 + \dfrac{\rho}{\theta}\dfrac{K_L q_{max}}{(1+K_L C)^2}$ [Eq. 3]
		2	$Freundlich\ sorption\ R = 1 + \dfrac{\rho}{\theta}K_F n C^{(n-1)}$ [Eq. 4]
		3	*Experiment retardation factor (R_E):* $R_E = \dfrac{t_p}{t_{Br}}$ [Eq. 5]
Mass balance design	$W_t = W_e + W_{MTZ}$ [Eq. 2]	4	*Equilibrium zone with (W_{MTZ}):* $W_e = \dfrac{Q_{in} \times C_{in} \times t_{life}}{q_e \times A \times \rho}$ [Eq. 6] *Mass transform zone with (W_{MTZ}):* $W_{MTZ} = t_{MTZ} \times \mu_{sh}$ [Eq. 7] $\mu_{sh} = \dfrac{\mu_{Groud}}{1+(1-\varepsilon_{bed}(1-\varepsilon_p)\rho_p(\frac{q_e}{c_0})}$ [Eq. 8]
		5	*Mass transform zone with (W_{MTZ}):* $W_{MTZ} = L \times (1 - \dfrac{t_{BR}}{t_{Equ}})$ [Eq. 9]

Table 3. The design of width of PRB

Method	1	2	3	4	5
CGAC	$3.29 \times t_{yer}$	$10.7 \times t_{yer}$	$3.80 \times t_{yer}$	$0.59 \times t_{yer} + 0.152_{MTZ}$	$0.59 \times t_{yer} + 0.15_{MTZ}$
BGCN	$3.04 \times t_{yer}$	$7.83 \times t_{yer}$	$4.17 \times t_{yer}$	$0.20 \times t_{yer} + 0.167_{MTZ}$	$0.20 \times t_{yer} + 0.158_{MTZ}$

(Unit: m)

4. CONCLUSION

In this study, two carbon-based materials were used as reactive materials for TPH-contaminated groundwater. The experimental results showed that BGCN with a larger specific surface area has stronger adsorption capacity than CGAC. Meanwhile, in the adsorption experiment, the breakthrough time of BGCN was also longer than that of CGAC. We compared the use of different width design methods to express the relationship between age and width through the material transfer zone method. This study demonstrates the process of experimentally determining PRB design for TPH-contaminated groundwater to promote the development of carbon materials for groundwater remediation.

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