Study on Adsorption-Desorption of Benzene in Soil

Jing Sun1,2*, Guoqing Lin1,2, Henghua, Zhu3, Xiaomeng Tang1,2 and Lichun Zhang1,2

1Key Laboratory of Marine Environment and Ecology, Ministry of Education, Ocean University of China, Qingdao, Shandong, 266100, China
2Key Laboratory of Marine Environmental Geology Engineering of Shandong Province, School of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China
3Shandong Institute of Geological Survey, Jinan 250013, China
*Corresponding author’s e-mail: sunj0718@126.com

Abstract. Groundwater near the Qilu petrochemical plant in Zibo City is polluted by oil for over thirty years, which seriously threaten the local ecological environment. The results of GC-MS analysis of water samples show that benzene was the most abundant and toxic organic pollutant. The adsorption-desorption behaviour of benzene in soil was studied through batch experiments. The results indicated that the adsorption amount of benzene in the local soil showed a trend of increasing first and then decreasing with the increasing of the initial concentration of benzene. There existed an optimal initial concentration of benzene in the adsorption experiments. The desorption concentration of benzene was proportional to the initial concentration of benzene. Particle size of the soil was inversely related to adsorption and desorption concentration of benzene. The soil with the average particle size of 0.08 mm had the largest adsorption capacity for benzene, which could reach 376.39 mg/kg. The results could provide a theoretical basis for the local groundwater remediation.

1. Introduction
With the exploitation of petroleum resources, the harm of petroleum hydrocarbon pollutants to groundwater becomes increasingly prominent, causing severe environmental problems[1]. The vast majority of petroleum hydrocarbon pollutants are organic compounds which are characterized by long duration and strong stability in the environment, making them hard to be degraded[2]. Pollutants can take different forms in the groundwater environment, partly dissolved in water, adsorbed on solid particles or in the form of gas in soil pores[3]. Many petroleum hydrocarbons can be easily adsorbed by soil and sediment due to high affinity and hydrophobicity[4].

Benzene is a common pollutant among petroleum hydrocarbon pollutants. It is extremely harmful to human health. Even lower concentration can cause chronic toxicity and permanently damage the central nervous system of humans and other organisms, leading to cancer, deformity and mutation[5,6,7]. Adsorption of benzene on soil can effectively delay the migration of benzene and affect the fate of benzene. Studies show that there are many factors affecting adsorption and desorption. The adsorption of natural soil to benzene series is linear adsorption, and there is a significant lag in the desorption process[8,9]. Ma[10]et al found that the soil adsorption of low concentration of BTEX reached equilibrium in 16h. The adsorption isotherms were coincident with the Henry linear adsorption model after fitting. Zhang[11] et al found that there were different degrees of
hysteresis in the desorption of BTEX on different particle size components of red soil. Hysteresis coefficient increased as the particle size decreased. BTEX desorption hysteresis was more pronounced than polycyclic aromatic hydrocarbons and petroleum hydrocarbons. However, there are few studies on the adsorption-desorption of benzene in this area, especially the effect of particle size on adsorption and desorption of benzene. Therefore, the local soil was selected to study the adsorption-desorption law of benzene at the initial concentration of benzene and soil particle size, which provides a scientific basis for protecting local groundwater.

2. Materials and methods

2.1 Soils
The soils used in the experiment was taken from the uncontaminated soil layer below 40-50 cm on the surface of the arable farmland near Qilu Petrochemical plant (Figure 1). The soil samples were air-dried, decontaminated and crushed, then passed through a 2 mm sieve and stored in a labelled milled bottle for later use.

Figure 1. Location map of the study area; Figure 2. GC/MS full scan plasma diagram of water sample

2.2 Water samples
Determination of organic pollutants in groundwater by GC-MS and the collected mass spectrum data was retrieved by using the NIST08 spectral library so as to analyse the type and content of contaminants (Figure 2).

2.3 Batch experiments
Conducted in several 50 mL polyethylene centrifuge tubes, the test contains two groups: One group was added with 2 g soils and different initial concentrations of benzene solution to the headspace while the other group was also added with 2 g soils but in a different particle size and benzene solution with the same concentration to the headspace. All the tubes were sealed with solid paraffin and placed in a constant temperature oscillator.

Samples were taken at different time to determine the concentration of benzene and calculate the amount of adsorption. The desorption test was carried out 48 hours after the adsorption test in according to the procedures below: the supernatant was removed, methanol aqueous solution was added to the headspace, samples were taken at different times, and after centrifugation at 4000 r/min for 10 min, the supernatant was taken to measure the benzene concentration in the solution. In the above experiments, three groups were set in parallel, and controls were set at the same time.

3. Results and discussion

3.1 Water analysis results
Figure 1 was the results of groundwater organic matters. Totally 86 types of organic pollutants have been detected in the groundwater. Among them, aromatic hydrocarbons, halogenated hydrocarbons and aliphatic hydrocarbons accounted for a large proportion about 92%. The highest proportion of all pollutants was benzene, so benzene was taken as a characteristic pollutant.

3.2 The effect of initial concentration on adsorption-desorption

Figure 3(a) showed that as the initial concentration of the benzene solution increased, the adsorption capacity showed a trend of increasing first and then decreasing. When the initial concentration increased from 5 mg/L to 20 mg/L, the adsorption capacity of the soil increased from 119.44 mg/kg to 369.44 mg/kg (Figure 3a). The reason may be that the initial concentration of benzene increase in the solution can provide it a driving force to overcome the resistance between the liquid phase and the solid phase. Therefore, benzene molecules can continue to enter the interior of the soil pores[12,13], increasing the amount of adsorption. When the initial concentration was greater than 20 mg/L, the adsorption sites on the surface of the soil particles were filled up, and then the process of desorption occurred, so the adsorption capacity began to decrease.

Figure 3(b) showed that the concentration of benzene in the solution during the process of desorption increased as the initial concentration of benzene increased. When the initial concentration of benzene increased from 5 mg/L to 25 mg/L, the concentration of benzene in the solution after desorption increased from 2.44 mg/L to 8.56 mg/L (Figure 3b). It was because that when the adsorption of benzene reached equilibrium, the performance of benzene desorption improved with soil adsorption capacity of benzene and concentration gradient of benzene between methanol aqueous solution and soil increasing.

3.3 The effect of particle size on adsorption-desorption

Figure 4(a) showed that the adsorption basically reached equilibrium after 48 h, as the soil particle size increased, the amount of benzene adsorbed by the soil gradually decreased. When the soil particle size increased from 0.08 mm to 0.85 mm, the adsorption capacity of the soil decreased from 376.39 mg/kg to 244.44 mg/kg (Figure 4a). The reason was that the smaller the soil particle size was, the larger surface area of the soil particles had, providing more sites for adsorption[14,15].

Figure 4(b) showed that as the soil particle size increased, the concentration of desorbed benzene showed a downward trend. When the soil particle size increased from 0.08 mm to 0.85 mm, the benzene concentration in the solution after desorption decreased from 8.56 mg/L to 5.20 mg/L (Figure 4b). Two reasons accounted for this phenomenon. First, during the oscillation process, the smaller particle size of the soil had the more violently particles collide, facilitating the process of desorption.
Second, the smaller particle size of the soil had the more adsorption capacity of benzene, resulting in greater concentration gradient between the methanol aqueous solution and concentration of benzene in the soil, driving benzene to desorb. When the concentration reached equal, the desorption process stopped and the concentration of benzene in the solution became stable in the end.

![Figure 4. Effect of different particle sizes of soils on adsorption (a) and desorption (b)](image)

4. Conclusions
Among all the organic pollutants in the groundwater, the pollution level and toxicity of benzene was the highest. The results showed that the soil adsorption of benzene reached maximal value when the initial concentration of benzene solution was 20 mg/L. With the increased of the initial concentration of benzene, the amount of benzene desorption gradually went up, reaching the highest concentration of 25 mg/L. The particle size of soil was inversely proportional to the adsorption capacity and desorption concentration of benzene. The soil with the average particle size of 0.08 mm had the largest adsorption capacity for benzene, which could reach 376.39 mg/kg.

Acknowledgments
This study was supported by Zibo Key Financial Project (Zi (Water Resources Project [2017] No. 1). Thanks to Zibo Water Conservancy Bureau for sampling assistance.

References
[1] Rosell-Mele, A., Moraleda-Cibrian, N., Cartro-Sabate, M., et al. (2018) Oil pollution in soils and sediments from the Northern Peruvian Amazon. Science of the Total Environment., 610-611: 1010-1019.
[2] Gennadiev, A. N., Pikovskii, Y. I., Tsibart, A. S., et al. (2015) Hydrocarbons in soils: Origin, composition, and behavior (Review). Eurasian Soil Science., 10(48): 1076-1089.
[3] Logeshwaran, P., Megharaj, M., Chadalavada, S., et al. (2018) Petroleum hydrocarbons (PH) in groundwater aquifers: An overview of environmental fate, toxicity, microbial degradation and risk-based remediation approaches Environmental. Technology & Innovation., 10: 175-193.
[4] Ossa, I. C., Ahmed, A., Hassan, A., et al. (2019) Remediation of soil and water contaminated with petroleum hydrocarbon: A review, Technology & Innovation., 8: 1-80.
[5] Baghani, A. N., Sorooshian, A., Heydari, M., et al. (2019) A case study of BTEX characteristics and health effects by major point sources of pollution during winter in Iran. Environmental Pollution., 247: 607-617.
[6] El-Hashemy, M. A., Ali, H. M. (2019) Characterization of BTEX group of VOCs and inhalation risks in indoor microenvironments at small enterprises. Science of the Total Environment., 645: 974-983.

[7] Kanjanasiranont, N., Prueksasit, T., Morknoy, D. (2017) Inhalation exposure and health risk levels to BTEX and carbonyl compounds of traffic policeman working in the inner city of Bangkok, Thailand. Atmospheric Environment., 152: 111-120.

[8] Wu, W., Sun, H. (2017) Sorption-desorption hysteresis of phenanthrene-Effect of nanopores, solute concentration, and salinity. Chemosphere., 81: 961-967.

[9] Ren, W. J., Zhou, W. J., Wang, M. E. (2009) Environmental behavior of BTEX in soil: A review. Chinese Journal of Ecology., 28: 1647-1654.

[10] Li, P., Wen, F., SU, Y. H., Cheng, Y. (2015) Sorption of BTEX at low concentrations onto arid soil in Xinjiang. Environmental Science & Technology., 38(2): 52-57.

[11] Zhang, X. L., Ma, F. J., W, B., et al. (2015) Effect of different particle sizes of red soil on BTEX sorption and desorption. Journal of Safety and Environment., 15(2): 210-215.

[12] Wang, D. B., Jia, F. Y., Wang, H., et al. (2018) Simultaneously efficient adsorption and photocatalytic degradation of tetracycline by Fe-based MOFs. Journal of Colloid and Interface Science., 519: 273-284.

[13] Li, S. S., Liu, Q. F., Lu, R. Z., et al. (2018) Effect of solution concentration on magnetic Ni0.5Zn0.5Fe2O nanoparticles and their adsorption behavior of neutral red. Journal of Nanoscience and Nanotechnology., 18(7): 4798-4804.

[14] Zhi, K. K., Wang, L. L., Zhang, Y. G., et al. (2018) Influence of size and shape of silica supports on the sol–gel surface molecularly imprinted polymers for selective adsorption of gossypol. Materials., 11: 1-16.

[15] Jia, L., Fan, B. G., Li, B., et al. (2018) Effects of pyrolysis mode and particle size on the microscopic characteristics and mercury adsorption characteristics of biomass char. BioResources., 13(3): 5450-5471.