



Chemical–biological hybrid reactive zones and their impact on biodiversity of remediation of the nitrobenzene and aniline contaminated groundwater

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HIGHLIGHTS

- Hybrid reactive zones was studied to clean up NB/aniline contaminated water.
- Chemical reactive zone of ZVI transforms nitrobenzene producing aniline.
- Depredate rate and impact on bio-diversity revealed evidence for treatment efficiency.
- Identified novel strains demonstrated very competent in treating NB/aniline.
- Chemo-biological reactive zones continuously and effectively operate 40 days.

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ABSTRACT

The effectiveness and bio-implication of the chemical and biological hybrid reactive zones were investigated to treat contaminated water through two months simulation. The mechanism of the sequenced chemo-bio-hybrid reactive zones designed as a ZVI part for chemical treatment of nitrobenzene producing aniline and a biological membrane depredate organic pollutant using bioaugmentation in the bio-reactive zone. The results demonstrate that the hybrid system exhibited excellent efficiency in nitrobenzene and aniline removal, 91% ($P < 0.01$) and 85% ($P < 0.01$), respectively, for about 40 days without any extra cost. From the real time analysis of aniline and nitrobenzene, the chemo-bio reactive zone should be maintained at 40 days after the system set up. The PCR–DGGE molecular approach elucidated that the biological diversity of the membrane decreased with depth and two bioaugmentation bacteria could be immobilized at the membrane and have a high treatment efficacy by depleted aniline and nitrobenzene in the bio-reactive zone and form a stable community. This system indicates a higher efficacy, environmentally friendly and novel technology for remediation strategy of contaminated sites.

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1. Introduction

Nitrobenzene and aniline are common benzene compounds that are widely present in explosives, dyes and herbicides. Due to their high toxicity to the life forms, chemical instability, high water solubility and volatility, they are prone to spreading in the (sub)surface environment and pose a serious risk to health [7–9,6,18,19]. Nitrobenzene and aniline have been listed by the US Environmental Protection Agency (EPA) as the priority pollutants. Environmental problems caused by these have unfortunately

happened frequently in the past years; and a typical example is an explosion happened in November 2005 at an aniline-production factory in NE China, leading to serious nitrobenzene and aniline contamination in the nearby rivers and aquifer system.

Nitrobenzene (NB) is a member of the nitro-compound with the chemical formula $C_6H_5NO_2$ (Fig. 1b), which is the precursor to synthesize dyes and pesticides [24,6]. This compound is extremely toxic, easily absorbed through the skin causing liver or kidney damage. Due to the nitryl electrophilic effect, the electron density of benzene is decreased and makes the nitrobenzene more stable than benzene, and difficult to be biodegraded. Depending on investigations, approximately 95% of nitrobenzene was used to synthesize aniline [4]. Aniline consists of a phenyl group connected to an amino group with the formula $C_6H_5NH_2$ (Fig. 1b). It's mainly used

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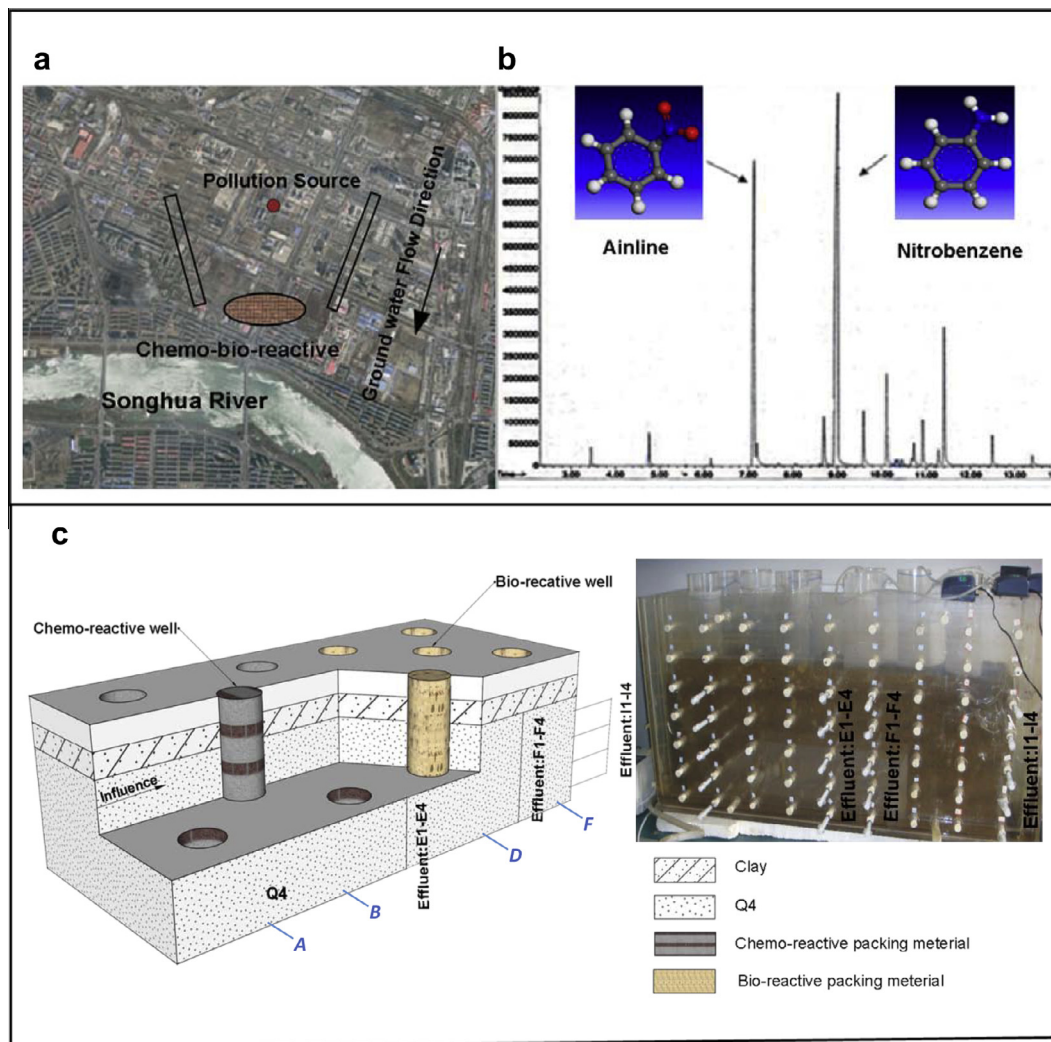


Fig. 1. The schematic diagrams for (a) setting of the contaminated site, (b) GC/MS profile of the organic contaminants in groundwater and (c) chemical and biological hybrid zones and stratigraphic profile.

in manufacturing other industrial chemicals, and toxic by inhalation of the vapor, ingestion, or percutaneous absorption. As a result of the above chemical properties of these compounds, their groundwater contaminants are persistent for a long time and prone to wide spreads.

The effective treatment technology of contaminated groundwater has been developed in the last decade, such as in-situ permeable reactive barriers (PRB) [7,8,9,16] and air sparging (AS)/bio-sparging (BS) [3,14,5,26]. PRB as a permeable treatment wall, normally consists of an underground trench installed with permeable reactive media, with sometimes hydraulic water collection systems [15,22]. Numerous studies have shown the selection of reactive media is subject to specific contaminants and the hydro-geological condition of the contaminated sites. Zero-valent iron has been successfully used in the full-scale remediation sites to treat groundwater contaminated by chlorinated solvents, nickel, dissolved inorganic carbon, nitrate etc. [7–9,1,17,16]. The PRB technology has been successfully demonstrated to clean up Trichloroethene (TCE) contamination in groundwater for over 18 years at the Monks Town site, Northern Ireland, as the Europe's oldest commercially-installed ZVI PRB [16]. The PRB case study shows the advantage of such an in-situ remediation strategy: (a) efficient and cost-effective, (b) almost maintenance free once installed, (c) little impact on land use and so forth. However, PRB

does require excavations at sites which may not be possible in cities due to the existing underground system; homogeneity of reactive treatment and effectiveness may be a limiting functioning factor for various sites and the permeable reactive barriers may have clogging problem by microbial or other fine materials with time therefore reducing performance [10]. These scientific issue shall be addressed for a more effective and efficiency application of the PRB technology. BS, another major economical in-situ remediation technology uses native microorganism to degrade the contaminants in groundwater with air or oxygen or nutrients injected into the saturated zone to increase the native microorganism efficacy [5,26]. Based on the investigation, BS can be an efficient technology to remediate BTEX contaminated groundwater and has removed more than 70% organic compounds in ten months at an averaged groundwater temperature of 18 °C at an abandoned petrochemical manufacturing facility [5]. Therefore integrated technologies, e.g. AS/BS and PRB, for deeper understanding of the contamination treatment and their molecular signature of microbial activities in the systems, call for more detailed novel research.

To treat the persistent pollutants like nitrobenzene and aniline under complicated site situation, e.g. occupied land uses and/or subsurface infrastructures, novel alternatives integrating more available and suitable technologies are timely needed. Based upon previous critical literature review on related remediation

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