



A novel integrated active capping technique for the remediation of nitrobenzene-contaminated sediment

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ABSTRACT

The objective of this study was to develop a novel integrated active capping system and to investigate its efficiency in the remediation of nitrobenzene-contaminated sediment. An integrated Fe(0)–sorbent–microorganism remediation system was proposed as an *in situ* active capping technique to remediate nitrobenzene-contaminated sediment. In this system, nitrobenzene was reduced to aniline by Fe(0), which has a much better biodegradability. The sorption capacity and structural properties of cinder was measured to examine its applicability as the sorbent and matrix for this integrated capping system. Indigenous microorganisms from Songhuajiang River sediment, which was contaminated by nitrobenzene and aniline in Chinese Petrochemical Explosion in Jilin, were acquired one month after the explosion and used in this active capping system to degrade nitrobenzene and its reduced product, aniline. A bench-scale remediation experiment was conducted on a mimicked nitrobenzene-contaminated sediment to investigate the efficiency of the integrated capping system and the synergistic effects of the combined components in the active capping system. The results show that this integrated active capping system can effectively block the release of target pollutants into the upper-layer water and remove the compounds from the environment.

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1. Introduction

Sediments become contaminated with organic compounds because of uncontrolled discharges of organic pollutant-containing wastewater or accidental leakages [1–3]. Remediation of contaminated sediments has aroused a great deal of scientific and public concern around the world since the contaminated sediment may act as an inner pollution source for the above water column. Current approaches to the remediation of contaminated sediments include *ex situ* and *in situ* treatments. The *ex situ* treatments rely heavily on dredging and disposal of the contaminated sediment, which are expensive and may cause secondary contamination by disturbing the contaminated sediment [4,5]. During the remediation processes of large-scale contaminated sediment sites, such as Hunters Point Naval Shipyard (San Francisco, CA, US) [6] and Songhuajiang River (Jilin, China), the *ex situ* remediation techniques have been proved ineffective to meet the economic, environmental, and technical challenges. Hence, developing *in situ* remediation techniques have recently drawn much scientific interest.

Approaches for *in situ* remediation of contaminated sediments, including capping, solidification/stabilization, chemical treatment,

and biological treatment, have been developed in the past few years [7]. However, each of these *in situ* remediation methods has limitations and the application of a single *in situ* remediation method alone cannot always remediate the contaminated sediment efficiently. For example, solidification/stabilization and chemical treatment may lead to secondary pollution and the complete mixing of treatment reagents with the contaminated sediments is difficult to achieve [8]. For these reasons, new innovative strategies need to be proposed in order to meet cleanup goals in sediment management while also to minimize costs and environmental impact [9–11].

Songhuajiang River was severely polluted with benzene, nitrobenzene (NB) and aniline (AN) in the winter of 2005 due to the “Chinese Petrochemical Explosion” in which over 100 t of NB and related compounds were released into the Songhuajiang River [12,13]. Among the contaminants, NB was the main pollutant. NB is a carcinogenic pollutant even at low concentration, and hence, it may present high risks to the ecosystem [14]. The highest detected NB concentration in the water phase of the Songhuajiang River was around 1.7 mg/L, which was 100 times greater than the criterion concentration in Environmental Quality Standards for Surface Water in China (GB 3838-2002). Sediment was also expected to be contaminated by NB. Hence, to avoid any chronic adverse effects of NB pollution, an *in situ* remediation technique for the NB-contaminated sediment was needed. The electron-deficient

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character of the nitro-group in the NB structure prevents oxidation of NB by microorganisms [15]. Therefore, conventional aerobic biological treatment processes are not effective for the treatment of NB-contaminated sediment [16], and comprehensive techniques integrating the conventional biological treatment with other techniques are required.

In recent years, zero-valent iron (Fe(0)) has been intensively studied for its capacity to reduce organic and inorganic pollutants [17–20], and Fe(0) has been used as the main active component in permeable reactive barriers (PRBs) for *in situ* remediation of contaminated ground waters and soils [19–22]. Elemental iron, together with ferrous ions and hydrogen generated in a Fe(0)–water system, has been regarded as a suitable reducing agent for reducible organic and inorganic pollutants [20,22]. Fe(0) was reported to reduce NB to AN [23], which has a better biodegradability than NB. Since the products of Fe(0) reduction often pose greater biodegradability, the combination of Fe(0) and microbial cells was proposed as a means to thoroughly remove organic contaminants [24–26].

Sorption of contaminants to contained sorbents cannot only remove target pollutants from the water phase quickly, but the sorbents can also provide an interface for biotic and abiotic processes [6,27]. Hence the addition of sorbents such as clays, carbonaceous materials (activated carbon and peat), or agricultural byproducts to the capping layer for remediation of contaminated sediments or their incorporation into PRBs has been studied and adopted in remediation engineering practices [6,27–29]. Strongly adsorbing sorbents, such as activated carbon, have been confirmed to yield much higher levels of substrate biodegradation and higher specific microbial growth rates when used as a bio-support matrix compared to non-adsorbing or weakly adsorbing media, such as sand [30,31]. Hence a support matrix with a great sorption capacity may improve remediation efficiency.

Aiming to remediate NB-contaminated sediments *in situ*, an innovative integrated active capping system containing Fe(0)–sorbent–microorganisms was proposed, and the feasibility of using this integrated system as an *in situ* capping technique for NB-contaminated sediments was evaluated in this study. In the integrated capping system, Fe(0) acted to reduce NB to AN. Cinder was selected as the sorbent and support matrix, based on preliminary sorption experiments. The biodegradation of NB and AN by indigenous microorganisms obtained from Songhuajiang River sediment was also investigated. Finally, the feasibility of the integrated technique was examined using a bench-scale microcosm set-up containing a mimicked NB-contaminated sediment.

2. Materials and methods

2.1. Chemicals and reagents

Nitrobenzene (analytical grade) was purchased from Tianjin Chemical Reagent Company, China. Aniline (analytical grade) was purchased from Tianjin Yongda Chemical Reagent Center. Cinder was collected from the stokehold of Nankai University, and a primary selection was conducted to avoid the coarse stone and to get cinder portion with particle size <2 mm. Organic matter content was determined by method of weight-loss-on-ignition (450 °C for 24 h) [32] and surface area was determined by BET analysis (Autosorb-MP, Quantachrome, USA). Commercial granular iron (purity >98.0%, 100 mesh, Tianjin North Tianyi Chemical Company, China) was used in batch experiments. The iron materials were treated with 1 M HCl solution for 24 h to remove impurities on the iron surface and dried under nitrogen protection [33] before use. Its surface area was measured to be 0.311 m²/g by the same BET analyzer described above. High permeability nonwo-

ven polypropylene-based geosynthetic fabric was purchased from Jiangxi Synthetic Fiber Plant (Jiangxi, China).

2.2. Selection of sorption and support matrix for the capping system

Preliminary sorption experiments were conducted on granular activated carbon, coke, diatomite, and cinder to select an optimum sorbent (results are not shown here). Though activated carbon exhibited a better sorption capacity on the target compounds, cinder is the most cost-effective sorbent and was therefore selected as the sorbent for the integrated capping system. The sorption isotherms of NB and AN with cinder were measured over a wide concentration range. In brief, 15 mg of cinder was weighed into 25 mL of test water solution (0.01 M CaCl₂, 200 mg/L NaN₃ as a biocide, and pH 7). Specific amounts of NB and AN in methanol were spiked into the vials and the methanol level was maintained at <0.05% to avoid any co-solvent effects. The vials were sealed by screw caps with Teflon-lined septa and placed on a shaker in the dark for 24 h at 20 ± 0.5 °C. Preliminary experiments indicated that apparent equilibrium occurred within 24 h. The solution was separated by centrifugation at 3000 × g for 15 min. Volatilization and sorption to vial walls of NB and AN during the sorption process was negligible; therefore, the amount of NB and AN sorbed by the sorbent was acquired by the difference of aqueous concentrations after and before the sorption.

Cinder is a good sorbent for many organic compounds, however, its application is often limited over concern that it may contain certain toxic elements, such as As, Pb and Se, causing secondary pollution during its application. Hence, leaching experiments were carried out to determine the possible release of certain elements from the cinder to the ambient environment. Leaching experiments were conducted by putting the cinder in deionized water and shaking for 40 days at 20 ± 0.5 °C. The ratio of cinder to deionized water was 1:20 (w/w) to mimic the remediation of sediment in a 4-m deep river with an integrated capping system using 20 cm thick cinder as the support matrix. The elements of As, Pb, Se and F are the secondary pollutants of greatest concern. Hence, the concentration of As, Pb and Se in the water layer was measured by ICP-MS (IRIS ER/S, Thermo Electric Corporation, Germany) and the concentration of F was detected by ion chromatography (DX-120, Dionex Corporation, CA, USA).

2.3. Batch reduction experiments

Batch reduction experiments were conducted using 25 mL US EPA glass vials with Teflon-lined screw caps at 20 ± 0.5 °C in the dark under anoxic condition. All the deionized water used in the reduction experiments was purged with N₂ for 10 min to remove dissolved oxygen immediately before the experiments. The initial concentration of NB was 1.75 mg/L, and 25 mL of this solution was added to the batch reactor. This concentration is about 100 times that of the environmental quality standard for surface water in China (GB 3838-2002), but represents the concentration of NB detected in Songhuajiang River after the “Chinese Petrochemical Explosion” in Jilin. Duplicate samples were prepared for each of the three different Fe(0) dosages (10, 40 and 100 mg). An additional control was prepared without Fe(0). All the vials were placed on a shaker and continuously shaken at 180 rpm. The nitrobenzene reduction kinetics by Fe(0) was obtained by determining the residual NB concentration remaining in the aqueous phase at different reaction times. The loss of NB in the control was negligible, so degradation of NB by Fe(0) was acquired by difference. The concentration of final reduction product AN was also monitored.

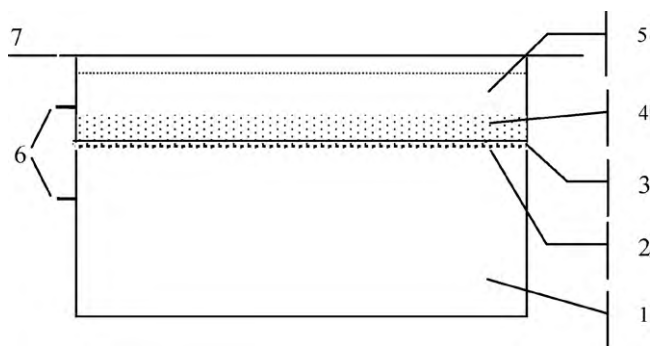


Fig. 1. Experimental set-up of bench-scale remediation microcosm system: (1) lower-layer solution (representing contaminated sediment); (2) acrylic plate with 30×100 pores (pore size 3 mm); (3) geosynthetic fabrics; (4) active capping layer; (5) upper-layer water; (6) sampling ports; and (7) glass cap.

2.4. Microorganisms

To mimic the real *in situ* environment, a mixture of indigenous microorganisms was obtained from sediment of the Songhuajiang River (Sifangtai, Jilin, China), which had been contaminated by the “Chinese Petrochemical Explosion” in Jilin, and was collected one month after the explosion. The microorganism mixture was obtained by incubating 50 g sediment in 1 L of inorganic growth medium containing K_2HPO_4 (0.8 g/L), KH_2PO_4 (0.2 g/L), $CaSO_4 \cdot 2H_2O$ (0.05 g/L), $MgSO_4 \cdot 7H_2O$ (0.15 g/L), $FeSO_4 \cdot 7H_2O$ (0.1 g/L), and 1 mL/L of a trace metal solution comprised of $MnCl_2 \cdot 4H_2O$ (2.5 mg/L); $CoCl_2 \cdot 6H_2O$ (0.5 mg/L); and $CuCl_2$ (0.1 mg/L). Nitrobenzene (20 mg/L) was spiked into each slurry to serve as the sole carbon and nitrogen source for the microorganisms. All the incubation experiments were carried out in the dark at $20 \pm 0.5^\circ C$. The pH of the medium solution was adjusted to approximately 7.0 using 20% H_3PO_4 . The concentration of NB was determined every 5 days until a degradation plateau was observed. Four replicates of this experiment were carried out. Next, the culture was diluted and spread onto agar (1.5%) plates with inorganic growth medium and NB, and incubated at $20^\circ C$ for 5 days. Colonies appearing on the agar plates were sub-cultured and purified for further degradation kinetics experiment and bench-scale remediation experiments.

Degradation kinetics of NB and AN by the isolated microorganisms were further determined by incubating the isolated microorganisms into the inorganic growth medium supplemented with NB and AN, respectively. The concentration of the target contaminant and the density of the cultures were measured every 24 h. The microorganism density was measured by optical sorption at 600 nm using a UV-vis spectrophotometer (SP-2000, Shanghai Spectrum Instruments Company, China).

2.5. Bench-scale integrated remediation system

Fig. 1 shows the experimental set-up of the microcosm used to test the feasibility of the integrated Fe(0)-sorber-microorganism system for the remediation of NB- and AN-contaminated sediments. The set-up consisted of the following sections: (1) a layer of nominal polluted sediment, which was mimicked by a solution spiked with specific concentration of NB. (2) An acrylic plate with 30×100 pores (pore size 3 mm) fixed in the chamber just above the nominal polluted sediment, acting as the supporter for the capping layer; (3) a layer of high permeability nonwoven geosynthetic fabrics expanded over the acrylic plate to hold the materials of capping layer; (4) the capping layer with different constituents (see below); (5) an upper-layer water without contaminants to mimic upper-layer water in the real river; (6) sampling ports, which were

sealed with Teflon valves and covered with rubber septa; and (7) a cap to avoid the loss of the target contaminants by volatilization. NB solution was used rather than contaminated sediment so that the possibility of NB sorption to the sediment was eliminated. This set-up has a length of 0.5 m, a width of 0.16 m, and the effective volumes of the lower-layer “sediment” and the upper-layer water solution were 12 and 3 L, respectively.

To investigate the remediation efficiencies of different systems, five different capping systems were designed: (1) 1 cm thick cinder; (2) 3 cm thick cinder; (3) 1 cm thick integrated layer of Fe(0)+cinder; (4) 1 cm thick integrated layer of Fe(0)+cinder+microorganisms; and (5) 3 cm thick integrated layer of Fe(0)+cinder+microorganisms. For each integrated capping layer, a 10:1 ratio of cinder to Fe(0) was adopted, based on the results of batch experiments, and 500 mL of the isolated indigenous microorganism mixture with an OD_{600} of 0.5 was inoculated to the capping layer in the last two systems. 10 mM KCl was prepared as background solution for the microcosm experiments to support microorganism growth. In this microcosm, the initial concentration of NB in the lower-layer water was 30 mg/L (360 mg NB mass in this microcosm) and no contaminant was added into the upper-layer water. The bench-scale experiments lasted for 40 days. The concentrations of NB and AN in the upper-layer water were measured every day for the first 15 days and every 5 days for the last 25 days. The concentrations of NB and AN in the lower-layer water were determined upon completion of the 40 days remediation experiments.

2.6. Analysis of the chemicals

The water phase concentrations of NB and AN were determined by HPLC (Waters 2487, US) equipped with a binary HPLC pump (Waters 1525), a Waters 717plus autosampler, a dual λ absorbance detector (Waters 2478), and a Waters C_{18} column (150 mm, 4.6 mm i.d.). All analyses were performed with a flow of methanol/water (v/v, 7:3) at a rate of 1.0 mL/min. The absorbance wavelengths for NB and AN were 270 and 285 nm, respectively. The NB and AN were eluted at 3.3 and 4.4 min, respectively, with detection limits of 1 and 10 $\mu g/L$. Both solutes were quantified using external calibration curves.

3. Results and discussion

3.1. Cinder as sorption and support matrix in the integrated capping system

Cinder exhibited great sorption capacity for NB and AN (Fig. 2), and this could be ascribed to its high content of organic matter (39.12%) and large surface area ($55.59 m^2/g$). Scanning electron microscopy showed that cinder contains many micro-pores (the image is not shown in this paper), which may also contribute to the great sorption capacity of cinder [34,35]. When the equilibrium solution concentration was less than $55 \mu g/L$, the sorption capacity of the cinder was similar for both NB and AN. However, when the equilibrium solution concentration was larger than $55 \mu g/L$, the sorption of AN become saturated, whereas sorption of NB increased continually (Fig. 2). The difference in the sorption of AN and NB could be ascribed to their different interaction mechanisms toward cinder. According to the Lewis acid-base theory, the nitro-group can be considered as Lewis acid, while the amino group can be viewed as Lewis base. As a result, over the low concentration range, NB and AN may undergo strong Lewis acid-base interactions with specific sorption sites on cinder surface. As the concentration increased, the specific sorption sites on the cinder surface became saturated by NB and AN. Then, hydrophobic inter-

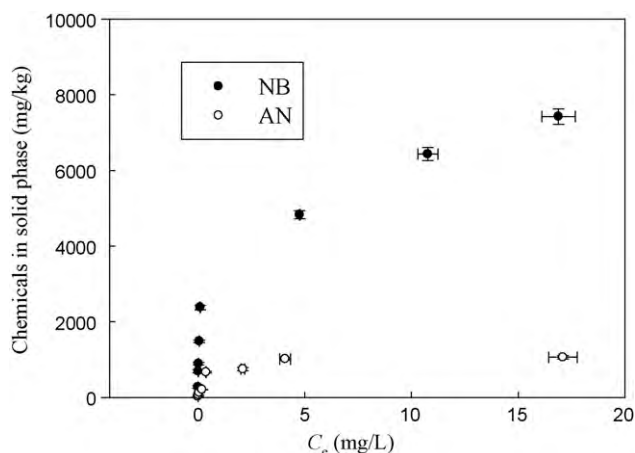


Fig. 2. Sorption isotherms of nitrobenzene (NB) and aniline (AN) to cinder. The isotherms were acquired in 25 mL 0.01 M CaCl₂ aqueous solution (with 200 mg/L Na₃N as a biocide, and pH 7) containing 15 mg cinder and series concentrations of the target compounds at 20 ± 0.5 °C.

actions dominated the sorption of NB and AN to cinder. Since the hydrophobicity of NB is much greater than AN, cinder has a larger sorption capacity for NB than AN at high equilibrium concentrations. Therefore, the reduction of NB to AN by Fe(0) may favor the transfer of pollutant from cinder to the water phase. According to the hypothesis that microorganisms can only utilize contaminants in the water phase, the conversion from NB to AN may favor the biodegradation and complete removal of NB from the environment [36].

Since cinder has a high sorption capacity for both NB and AN, the addition of cinder as the support matrix is expected to effectively block the transfer of contaminants from the “sediment” to the upper-layer water. The results of the leaching experiment for As, Pb, and Se, showed that no toxic element could be detected in the leachate except for Se, which was detected at 0.009 mg/L and this is below the Environmental Quality Standard Level I (0.01 mg/L) for surface water in China (GB 3838-2002). Hence, cinder can be used as the sorbent in the *in situ* remediation of NB-contaminated sediment.

3.2. The reduction of NB by Fe(0)

The reduction kinetics of NB by commercial granular Fe(0) at 20 ± 0.5 °C is shown in Fig. 3, the data were fitted to a pseudo-first-order kinetic model (Eq. (1)), and reduction rate coefficient (k_{obs}) was calculated.

$$\frac{dC_{NB}}{dt} = -k_{obs}C_{NB} \quad (1)$$

The k_{obs} is 0.98×10^{-3} , 3.40×10^{-3} , and 4.17×10^{-3} 1/min at Fe(0) dosage of 10, 40 and 100 mg, respectively. Although the k_{obs} values increased with Fe(0) loading, they were still in the same order of magnitude. The k_{obs} were not directly proportional to Fe(0) loading, which is consistent with other investigations [33,37]. Arnold and Roberts [33], and the references therein, ascribed this to inefficient mixing at the higher metal loadings. However, a linear increase of reduction rate constant with Fe(0) dose was reported in other literature [38].

The concentration of AN in the batch reaction system was also measured over time. The concentration of AN increased over time as NB decreased. The sum of NB and AN accounted for about 90% of the mass balance at the later period of experiment at Fe(0) doses of 40 and 100 mg. However, at Fe(0) dose of 10 mg and at the initial period of the reduction, the mass balance by NB

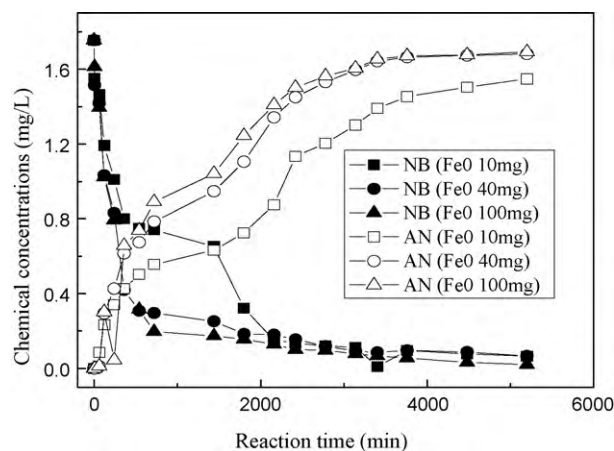


Fig. 3. The reduction kinetics of nitrobenzene (NB) by Fe(0) at 20 ± 0.5 °C with three different Fe(0) dosages (10, 40 and 100 mg) in 25 mL aqueous solution containing 1.754 mg/L NB.

and AN was not good. This may be explained by the mechanism (Fig. 4) proposed by Agrawal and Tratnyek [23], where NB is not reduced directly to AN by elemental iron, but rather through various intermediates. Hence there should be some hysteresis between the disappearance of NB and the production of AN [23]. Though some small peaks were observed in HPLC graph, attempt was not made to characterize the intermediates, since at the end of experiment, the mass balance was around 90% for all the three Fe(0) dosages.

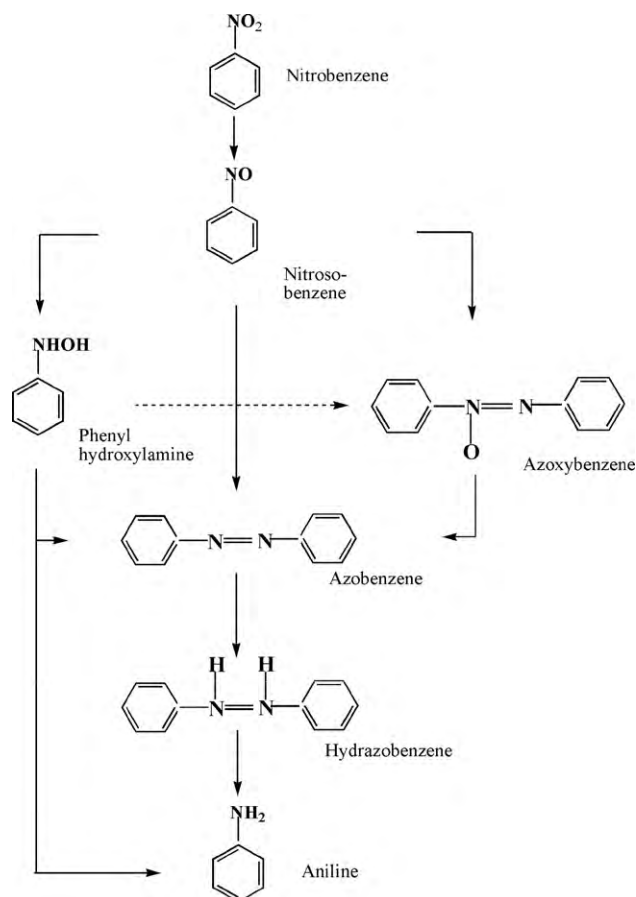


Fig. 4. Schematic diagram of the various possible transformation pathways for nitrobenzene (NB) conversion to aniline (AN) by Fe(0) [23].

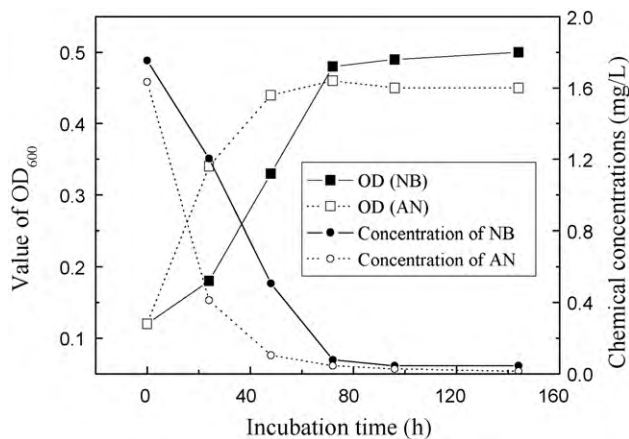


Fig. 5. Degradation of nitrobenzene (NB) and aniline (AN) and the corresponding growth curves of the indigenous microorganisms in batch experiment with initial concentration of NB or AN around 1.754 mg/L and initial density of the microorganisms (characterized by OD₆₀₀) of 0.1.

3.3. Biodegradation of NB and AN

The indigenous microorganism mixture extracted from a field-contaminated sediment could efficiently degrade NB and AN as demonstrated in Fig. 5. More than 90% NB and AN was removed over 3 and 2 days, respectively, and over 67% AN was degraded in the first day. As indicated by the OD₆₀₀ (Fig. 5), the microorganisms propagated correspondingly during degradation of the chemicals. These results suggest that both NB and AN could be degraded by the indigenous microorganisms, but that NB was a little more difficult to biodegrade than AN, which is consistent with the results of other studies [39,40]. Therefore, the remediation of NB-contaminated sediment could be favored by the Fe(0) reduction of NB to AN.

The technique described here is designed to enhance the applicability of *in situ* bioremediation processes by inoculation of adapted and enriched populations of indigenous microorganisms specifically capable of degrading the target contaminants. With degradation of the target chemicals, the indigenous microorganism mixture simultaneously propagated. In recent years, the use of field microflora rather than engineered species is the preferred method for the remediation of a contaminated site [41,42]. This may be because, despite displaying greater degradation capacity in laboratory experiments, the engineered species were shown, in most cases, not to propagate well under field conditions [43]. Moreover, the complete mineralization of a target contaminant usually needs successive degradation steps incorporating a mixture of microorganisms [44,45].

3.4. Bench-scale remediation experiment

The concentrations of NB and AN in the upper-layer water of five different remediation system microcosms, 1 cm cinder; 3 cm cinder, 1 cm integrated layer of Fe(0)+cinder, 1 cm integrated layer of Fe(0)+cinder+microorganisms system, and 3 cm integrated layer of Fe(0)+cinder+microorganisms, were measured and are shown in Fig. 6. For the 1 cm cinder and 3 cm cinder capping systems, NB in the upper-layer water increased within the first 15 days to a peak of 1200 and 1000 µg/L, respectively, then gradually decreasing to approximately 800 and 400 µg/L, respectively, by the end of the experiment. The values represent NB mass of 2.4 and 1.2 mg, respectively, based on the upper-layer water volume of 3 L, corresponding less than 1% of the total NB mass of 360 mg. This indicates that some but little amount of NB in the lower-layer water penetrated the cinder layer, and 1 and 3 cm cinder capping systems could not completely block the transfer of NB from the lower-layer

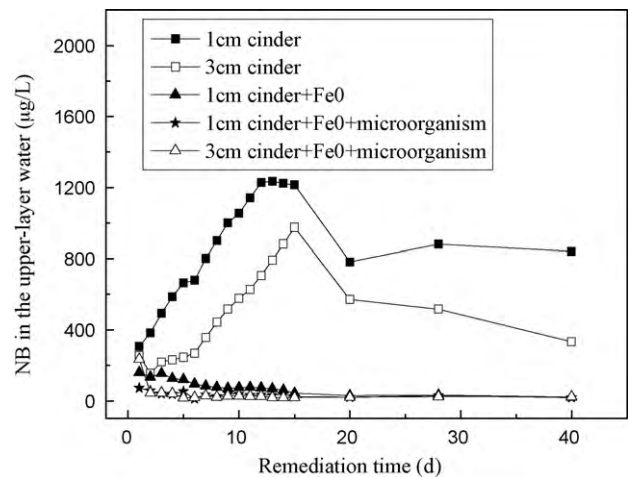


Fig. 6. Concentration of nitrobenzene (NB) in the upper-layer water of bench-scale microcosms employing five different capping systems ((1) 1 cm cinder; (2) 3 cm cinder; (3) 1 cm integrated Fe(0)+cinder system; (4) 1 cm integrated Fe(0)+microorganisms+cinder system; and (5) 3 cm integrated Fe(0)+microorganisms+cinder system) during the 40 days remediation period.

to the upper-layer in the case of high initial concentration of NB (30 mg/L) used in the present study. The decline of NB in the upper-layer water may be due to a slow adsorption process of NB to the cinder. The cinder layer used in the present study was thin (only 1 and 3 cm), some NB molecules might have not had enough contact time before they entered into the upper-layer. AN was not detected when only cinder was applied. In the real field, the concentration of NB would not be as large as that used in this study, and more importantly, the sorbed NB releases slowly from the sediment. Hence, using cinder alone could be an option for passive capping in the remediation of contaminated sediment. However, as discussed below, the main drawback of using cinder alone is that sorption cannot destroy the contaminant, and the capping layer may become saturated over time.

In the other three integrated active capping systems, the concentration of NB and AN in the upper-layer water was kept at a very low level at all times except at the beginning of the experiment (Fig. 6). Less than 0.02 mg/L NB was found for capping systems of 1 cm cinder+Fe(0), 1 cm cinder+Fe(0)+microorganisms, and 3 cm cinder+Fe(0)+microorganisms, respectively. The presence of NB in the upper-layer water at the beginning of the experiment may have been caused by the leaching from low-layer during the addition of the capping layer and the upper-layer water since the capping layers were thin. For Systems 3, 4 and 5, which had Fe(0) in the capping layer, AN was not detected in the upper-layer water. As indicated by the results of the batch reduction experiment, the reduction of NB to AN by Fe(0) is fast, and the dose of Fe(0) in the capping layer is far more than what was needed for the reduction of NB in the system. Hence, when NB in the lower-layer water contacts with underside of the capping layer, it was reduced to AN by Fe(0), and some of AN molecules dissolved into the lower-layer water due to its great water solubility. Moreover, AN was adsorbed by cinder in the upward diffusion path and/or degraded by the microorganisms therein, hence it cannot diffuse into the upper-layer water.

At the end of experiment, the concentrations of NB and AN in both lower-layer and upper-layer water were measured (Fig. 7A and B). By the end of the 40 day experiment, the concentration of NB in the upper-layer water was less than 20 µg/L in the last three capping systems containing Fe(0), which is much lower than those in the capping systems containing only cinder. This is very close to the value of National Environmental Quality for Surface Water (17 µg/L, GB 3838-2002) in China. In integrated active capping systems, Fe(0) could efficiently reduce NB to AN. Aniline has a higher

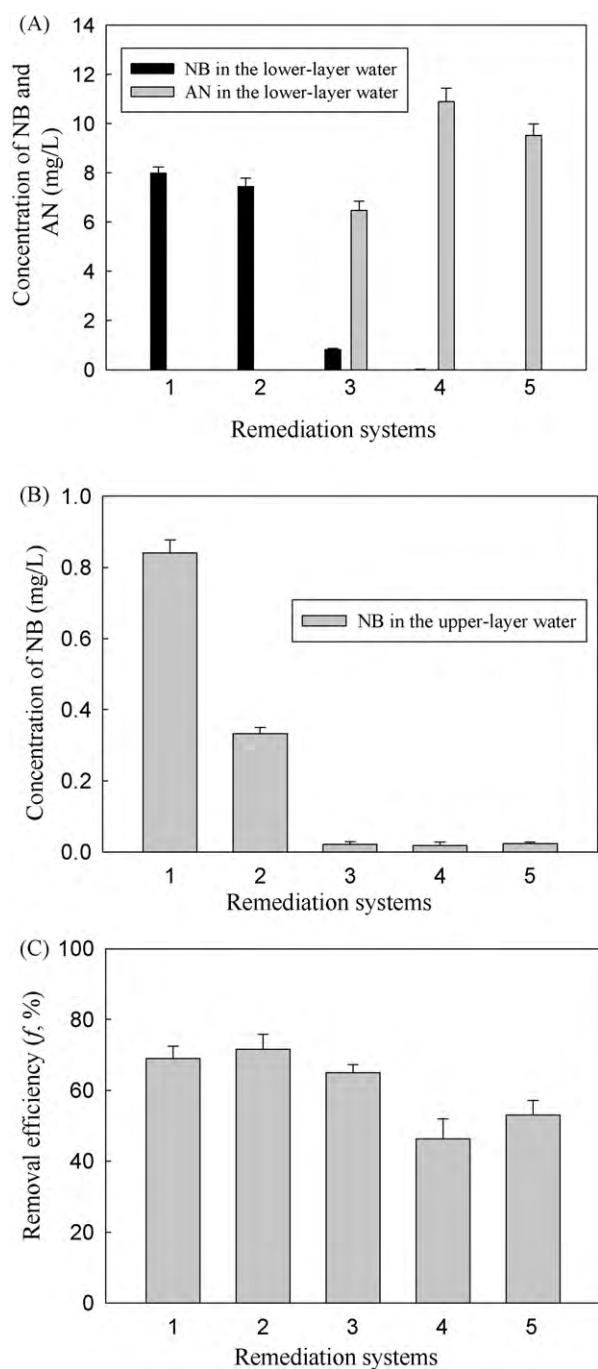


Fig. 7. Concentration of nitrobenzene (NB) and aniline (AN) in the aqueous phases (A and B) and the removal efficiencies (C) of the five different remediation systems: (1) 1 cm cinder; (2) 3 cm cinder; (3) 1 cm integrated Fe(0)+cinder system; (4) 1 cm integrated Fe(0)+microorganisms+cinder system; and (5) 3 cm integrated Fe(0)+microorganisms+cinder system.

solubility, lower sorption capacity on cinder and better biodegradability than NB. Hence, the reduction of NB to AN may favor the contaminant removal by microorganisms. Systems 3 and 4 have the same capping layer components except the microorganisms, and there was still residual NB in System 3 but none in System 4 (Fig. 7A) at the end of remediation experiment. This indicates that the microorganisms might be also involved in the reduction of NB. Biodegradation is a relatively slow process and complete removal of a high concentration of the contaminant (30 mg/L) could not be achieved in 40 days and about 10 mg/L AN remained in the lower-

layer water at the end of 40 days experiment (Fig. 7A). Hence, the incorporation of the quick reduction and sorption processes, and the slow degradation process is needed for quick prevention of the release of NB into the upper-layer water phase and its complete removal.

Based on the initial mass of NB and the residual mass of NB and its main degradation product, AN in aqueous phases, including upper-layer water and lower-layer water, the removal efficiency (f) of each remediation system was calculated (Eq. (2)) and is shown in Fig. 7C:

$$f_i = \frac{M_{\text{NB},0} - (M_{\text{NB,RE}} + M_{\text{AN,RE}})}{M_{\text{NB},0}} \times 100\% \quad (2)$$

where, f_i is the removal efficiency of System i , $M_{\text{NB},0}$ is the initial mass of NB, $M_{\text{NB,RE}} + M_{\text{AN,RE}}$ is the sum of NB and AN residue mass in aqueous phases at the end of the experiment. The efficiencies of the five capping systems were quite different, ranging from 46.3% to 71.6%. The capping systems containing Fe(0) did not show a better total removal efficiency based on aqueous phase NB and AN as compared to the capping systems containing cinder only. The dominant mechanism in each of these systems for the removal of contaminants from water phase over a short period is the sorption to cinder, the decrease in removal efficiency could be ascribed to the lower sorption of AN on cinder as compared to NB. The microorganisms also contributed to the removal of the contaminants in Systems 4 and 5, however biodegradation is a relatively slow process and longer time is needed to achieve higher remediation efficiency.

The main shortcoming of the capping layer containing only cinder is that sorption might become saturated over time. When saturated, the capping system needs to be replaced, and this is a big challenge in the field. Moreover, the contaminant saturated capping layer must be dealt with carefully so as that the contaminants are not desorbed in the replacement and disposal process leading to secondary pollution. Therefore, an active capping technique that could degrade the target compounds is still more advantageous.

Each of the remediation systems tested in this study can effectively retard the transfer of pollutants from lower-layer water (mimicked sediment) to upper-layer water. Due to the large sorption capacity and low cost, cinder was selected as the sorbent and support matrix of the integrated remediation system. However, a primary leaching experiment is recommended so as to optimize the application parameters of cinder and to ensure that no secondary pollution will occur. The sorption capacity of cinder may contribute most to the removal of contaminants from the aqueous phase at the outset of the remediation process, however, even though sorption of the contaminants to cinder can block the release of contaminants from the lower-layer water (mimicked contaminated sediments) to the upper-layer water, the sorbed contaminants are not really removed from the environment and the sorbent could be saturated. Furthermore, under certain conditions, the sorbed contaminant may be released to the environment again, causing secondary contamination. Hence, the addition of Fe(0) and microorganisms to the system is necessary. The Fe(0) reduction of NB to AN can enhance the solubility and biodegradability of contaminants, this further proved by the results of NB and AN biodegradation experiments. Hence the addition of Fe(0) and microorganisms may favor the complete removal of NB from the contaminated sediments. However, as indicated by the results of bench-scale remediation experiment, the complete removal of NB by microorganisms may need longer remediation period.

4. Conclusions

Cinder is a cost-effective sorbent for NB and AN, it can be used as the support matrix of the integrated remediation system. However, to avoid the secondary pollution caused by cinder, a primary

leaching test is recommended. Fe(0) can effectively transform NB to AN, which has better biodegradability, as proved by the results of biodegradation experiment. With the integrating of cinder, Fe(0) and microorganisms, the released NB from sediment can be effectively blocked to prevent the contamination of upper-layer water. NB can be completely removed from environment by this integrated cinder–Fe(0)–microorganisms system.

While the initial findings of this study are promising, further research is necessary. For example, the interactions between the support, Fe(0) and the microorganisms requires further investigation, and the parameters should be optimized to achieve better remediation efficiency. This study also provides an innovative remediation approach that can be applied to the remediation of other reducible organic pollutants such as organochlorines.

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