Application of coupled zero-valent iron/biochar system for degradation of chlorobenzene-contaminated groundwater

Xu Zhang and Yanqing Wu

ABSTRACT

A novel iron-carbon micro-electrolysis system, bamboo-derived biochar coupled with zero-valent iron (ZVI), was investigated for chlorobenzene (CB)-contaminated groundwater removal. Influences of initial pH value, mass ratio of the ZVI/Biochar, initial CB concentration and ionic strength of the ZVI/Biochar micro-electrolysis were studied. The results indicated that the increase of initial pH led to the decrease of the CB removal efficiency. While the optimum mass ratio of ZVI to biochar was 2:1, the improved initial concentration and reaction time were 33.68 mg/L and 4 h, respectively. When pH of 2, mass ratio of 2:1 and reaction time of 4 h were applied, the CB removal efficiency was 99.92%. Enhanced degradation of CB was observed with increased Cl⁻/C₀ concentration. When the Cl⁻/C₀ concentration of 1,000 mg/L and reaction time of 1 h were applied, the CB removal efficiency arrived at 98.2%. Additionally, considering that biochar is cost-effective and readily produced, the coupled ZVI/Biochar micro-electrolysis could represent an effective approach for the treatment of groundwater containing chlorinated organic compounds in the future.

Key words | chlorobenzene, micro-electrolysis, removal, volatile organic compounds, ZVI/Biochar

INTRODUCTION

Volatile organic compounds (VOCs) originating from photochemical, microbial and other daily activities are frequently encountered soil and groundwater contaminants (Watson 2004; Fink 2007). These compounds are generally regarded as non-aqueous phase liquids generating a source zone for soil and groundwater contamination, which have been detected to contaminate the subsurface environment by emission and combustion (Liu & Zhou 2011). Chlorobenzene (CB), as a kind of ubiquitous VOC, has been widely used as a solvent, heat transfer agent, insect repellent, deodorant, and intermediate in the pharmaceutical industry, dye and pesticide synthesis (Oh & Bartha 1994; Blad et al. 2012). It is toxic, highly persistent and easily migratory in the water environment because of its volatility, difficult degradation and long history of utilization in industry and agriculture (Braune et al. 2005; Maria & Maria 2009). Accordingly, CB has been discovered in surface water and sediments as well as in groundwater and soils (Oliver & Nicol 1982; Harper et al. 1992). Moreover, CB may threaten human health and damage organs via different routes of exposure due to its widespread application. For instance, people can be exposed to CB-contaminated water via drinking, bathing, food or laundering. The high volatility of CB creates more possibilities for intake by people and animals, resulting in various severe effects, including headaches, neurasthenia, dizziness, cyanosis, hyperesthesia, muscle spasms and increased risk of cancer (Ogata et al. 1991). At present, the common concentration measured in some areas of China groundwater is 0.2–0.9 μg/L; however, the CB concentrations could exceed this by more than 100,000 times in the vicinity of some chemical plants. For instance, according to a report in 2015, a secondary school in Jiangsu Province (China) experienced a serious CB excess issue because the school was near to a chemical plant and the CB concentration measured in the groundwater of this school was 94,799 times higher than the normal level in the groundwater. Therefore, due to its potential risk and high toxicity to accumulate in the environment, CB has been listed as a priority pollutant by the United States Environmental Protection Agency (USEPA) (Jiade et al. 2008). Hence, increasing concerns...
about CB as a hazardous pollutant have raised various approaches for the removal of CB from groundwater.

In the last few decades, a large number of remediation strategies have been devoted to removing VOCs from soil and groundwater, including physical, chemical, biological methods or combinations of various methods such as thermal incineration (Lin et al. 2003), biodegradation (Grostern & Edwards 2006), phytoremediation (Van Aken 2008), physical adsorption (Wei & Seo 2010), advanced oxidation processes like photocatalytic oxidation (Zuo et al. 2006), and Fenton oxidation (Vilve et al. 2010). These strategies have their advantages and disadvantages in treating VOC-contaminated soil and groundwater. These technologies usually have satisfactory removal efficiency, and some of these technologies, like adsorption, are reliable due to a robust operating configuration and provide the possibility of recovering the pollutants for reuse. However, the drawbacks of these methods should be noted, that they are difficult to apply in the engineering field because these technologies require stringent reaction conditions and need relatively expensive treatment costs. Simultaneously, the subsurface environment is highly variable in its composition, and groundwater is within a complex geological structure and reductive environment. Due to the heterogeneity and complexity of the subsurface environment, the remediation of VOCs in soil and groundwater becomes extremely challenging.

Zero-valent iron (ZVI) has been reported as an ideal candidate for the remediation of organic compounds in soil and groundwater (Chatterjee et al. 2010). When added in aqueous solution, ZVI can degrade or transfer organic compounds through the reduction effect from Fe⁰ and Fe²⁺ and coprecipitation effect from the corrosion product (iron hydroxide) during the ZVI reactions. As the most often applied material in permeable reactive barriers (PRBs), ZVI particles with large surface area have been widely used in remediation of VOC-contaminated soil and groundwater (Busch et al. 2014). Additionally, ZVI has been proved very cost-effective for contaminated soil and groundwater (Calabró et al. 2012). Unfortunately, the utilization of ZVI alone to remove organic contaminants revealed some drawbacks. Initially, the ZVI particles are readily oxidized on surfaces in ambient atmosphere, leading to the loss of active reaction sites (Feitz et al. 2005). Moreover, fine-sized iron powders are usually unstable in aqueous solutions, which could bring inconvenience to their environmental application (Zhang 2003). Furthermore, the raw ZVI has low reactivity due to the innate passive layer generated during its manufacturing process and thus the degradation rate for contaminant removal will be decreased as time goes on, since its surface passivation will be increased by the corrosion products (i.e. iron hydroxide and oxides precipitant) (Feitz et al. 2005; Joo et al. 2005). Therefore, exploring novel materials or methods for micro-electrolysis to improve the deficiency of the traditional ZVI system is essential.

In recent years, the application of ZVI coupled with some materials, including zeolite (Fukuchi et al. 2014), resin (Ponder et al. 2000), clay mineral (Luo et al. 2013), graphene (Kumar et al. 2015) and active carbon (Zhan et al. 2009; Mackenzie et al. 2012), has been investigated as a promising method to remove organic contaminants. Although ZVI coupled with other materials has similar mechanisms to the ZVI process, it can decrease the contact between Fe⁰ particles by addition of these materials, consequently reducing surface passivation and prolonging the serving life of Fe⁰. Carbon materials are used as the common material that cooperates with ZVI to remove various types of organic contaminants. Also, this method is defined as the Fe⁰/C micro-electrolysis system (Fu et al. 2014). Fe⁰/C micro-electrolysis is primarily reliant on the reaction of galvanic cells. ZVI, serving as anode, releases electrons, and the carbon materials, serving as active cathodes or facilitators, are commonly used in combination with iron chips to generate numerous local batteries in multiphase mixtures. Accordingly, reactions for decomposing refractory organics are believed to occur on or adjacent to the carbon surface (Ruan et al. 2010).

Recent studies have shown that biochar can remove a great number of organic contaminants and can be considered as a significant material in the environmental remediation (Chen et al. 2008; Qian & Shen 2013; Gai et al. 2014). Biochar is a solid heterogeneous material rich in aromatic carbon and minerals that can be derived from a variety of biomass such as wood, leaves, bamboos and agricultural wastes through the pyrolysis under oxygen-limited conditions (Lehmann 2007). Also, further activation like activated carbon is not necessary for the production process of biochar (Ahmad et al. 2012). Due to its excellent properties such as low production cost, high surface area, and porous and stable structure, biochar has been considered as a promising material to facilitate the efficiency of micro-electrolysis for removing organic contaminants (Yao et al. 2013; Zhang & Gao 2015). When ZVI is coupled with biochar, the coupled system can effectively remove the organic contaminants by several effects according to previous study (Jou et al. 2010; Shih et al. 2011). Firstly, two important degradation processes play the main role in the
organic contaminants' degradation in the ZVI/Biochar system. One is the reduction effect by the reductants (hydrogen radical ([H]), Fe⁰ and Fe²⁺) generated from the iron corrosion process (Wu et al. 2016). The other is the oxidation effect by strong oxidants (hydroxyl radical ([OH]), Fe⁰ and Fe²⁺) generated from Fenton reactions in the ZVI/Biochar system when oxygen or water is introduced into the system (Hsiao & Nobe 1993b; Gallard & De Laat 2001). The above reduction and oxidation effect would both reduce the toxicity (Hsiao & Nobe 1993a). Secondly, the minor effect for organic contaminants' removal is the adsorption and co-precipitation from iron (hydro) oxides, which may be generated with longer reaction times or higher pH. Moreover, absorption from the biochar can remove some organic contaminants in the solution; however, this effect will be greatly weakened as the saturation adsorption is reached with longer reaction time. Therefore, it is essential to evaluate the feasibility of biochar as the assistant material combining with ZVI to remove CB in groundwater.

The purpose of this study was to evaluate the feasibility and potential of the combination of ZVI with biochar as reactive materials in PRB for remediation of CB-contaminated groundwater. Firstly, the coupled ZVI/Biochar system was prepared and properties of the coupled ZVI/Biochar system were tested via microstructure and mineral composition analysis. Secondly, the coupled ZVI/Biochar system was applied to degrade CB-contaminated groundwater in laboratory conditions, and to analyze factors influencing CB removal ratio, including initial pH value, mass ratio of ZVI to biochar, initial CB concentration, reaction time and chloride ion concentration. These factors were investigated to determine the optimal conditions for the application of the coupled ZVI/Biochar system for in situ remediation.

**MATERIALS AND METHODS**

**Materials and simulated CB-contaminated groundwater**

Biochar was prepared from pyrolysis of bamboo in the laboratory. The bamboo used in this work was collected from a park in Shanghai City, China. After washing several times with tap water to remove adhering impurities, bamboo was air-dried for 2 days and then oven-dried for 24 h at 120 °C. The dried bamboo was first chopped into small pieces and then milled by pestle followed by sieving through a 120 mesh. Subsequently, pyrolysis was conducted in a muffle furnace (SX2-4-10, China) that was supplied with nitrogen in order to maintain an oxygen-free atmosphere. During the pyrolysis process, the temperature was gradually increased at the rate of 45 °C per minute and finally maintained at 600 °C, while the nitrogen flow-rate was kept at 200 mL/min. After reaching the target temperature, the sample was shifted into the operating furnace and kept for 300 min. The resulting biochars were removed from the furnace, cooled, weighted and stored in airtight plastic containers until use.

Elemental analysis of bamboo-derived biochar was conducted using an elemental analyzer (Vario MACRO cube, Germany) to determine their element components. The element contents are shown in Table 1.

All other chemicals and reagents (CB, hydrogen chloride, sodium hydroxide and sodium chloride) were analytical grade and purchased from Shanghai Sinopharm Chemical Reagent Co. Ltd, China. The specifications of the main components of iron powder used in the study are as follows: iron ≥98%, insoluble sulfate ≤0.1%, sulfide ≤0.06%, and copper ≤0.005%. The average particle size of the iron powder was observed about 0.019–0.067 mm. The composition of real groundwater is complex, which generates some influences on the treatment process. Additionally, the utilization of real groundwater in the experiment will be the topic of future research work. In this paper, de-ionized water was used throughout the entire study. Synthetic groundwater containing CB was prepared by adding CB into de-ionized water before use.

**Characterization**

Scanning electron microscope (SEM) (Sirion 200, USA) images were utilized to analyze the micro-structure of the samples that were performed using a scanning microscope to compare the interior and surface characteristics of the samples.

The mineral compositions of samples were also characterized by X-ray diffraction (XRD) analysis to identify crystalline structures on ZVI/Biochar using a computer-controlled X-ray diffractometer (XRD, Shimadzu XRD-6100) equipped with a stepping motor and graphite crystal monochromator.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>0.79</td>
</tr>
<tr>
<td>C</td>
<td>81.4</td>
</tr>
<tr>
<td>H</td>
<td>2.64</td>
</tr>
<tr>
<td>O</td>
<td>8.67</td>
</tr>
<tr>
<td>S</td>
<td>0.012</td>
</tr>
</tbody>
</table>
Batch experiments

The ZVI powders and biochar particles were mixed together at a certain mass ratio by adequate mechanical agitation to obtain a uniform mixture. Based on investigation of the literature, it should be noticed that the initial pH, mass ratio of ZVI to biochar, initial concentration of CB and ionic strength may affect the removal efficiency of contaminants by the ZVI/Biochar micro-electrolysis system (Lai et al. 2015). Therefore, in order to evaluate the influences of different factors on the ZVI/Biochar micro-electrolysis system, experiments were conducted under different initial pH values, mass ratios of ZVI to biochar, initial CB concentrations, and chloride ion concentrations, respectively.

In order to investigate the effect of initial pH on the removal efficiencies of the system, initial pH of CB was adjusted to 2.0, 3.0, 4.0, 6.0, 8.0, and 10.0 with 1.0 M hydrogen chloride (HCl) or sodium hydroxide (NaOH), respectively. Then, three mass ratios of ZVI to biochar (1:1, 2:1 and 3:1) were applied to test the influence of ZVI/Biochar on CB degradation. Subsequently, three initial concentrations (33.68 mg/L, 71.49 mg/L and 134.14 mg/L) were selected to examine the influence of the initial concentrations on the removal efficiencies.

To study the influence of ionic strength on CB degradation, sodium chloride (NaCl) was added as ionic strength adjuster and the initial chloride ion concentrations were fixed at 100 mg/L and 1,000 mg/L, respectively. Each flask was sealed with a teflon-lined cap and then immediately put into a thermostatically controlled shaker working at 150 rpm. All batch experiments were conducted in three replicates and the average data were reported.

Analytical methods

The CB concentrations in the synthetic groundwater were measured by using 20 mL headspace samples that were analyzed by a gas chromatograph (GC-2010, Shimadzu, Japan) using a flame ionization detector with a split injector system and a flame photometric detector that were used for separation and determination of organic contaminants. The injection port was held at 200 ºC and used in the split mode. The GC oven temperature was held at the initial 50 ºC for 2 min, and then ramped at a rate of 15 ºC/min to 200 ºC.

RESULTS AND DISCUSSION

Characterization of the ZVI powders and biochar particles mixture

In this study, the surface morphologies of ZVI/Biochar before and after 6 h treatment were characterized by SEM. Figure 1 reveals that the surfaces of the ZVI/Biochar system were rough before treatment, and some small apertures existed with non-uniform pore distribution and different pore sizes, which contributed to the rough surface, thereby increasing their specific surface area. Meanwhile, it can be seen that small particles were unevenly distributed on the surface of biochar and inside the pores, suggesting the presence of iron powders on the surface. 

Figure 1 | SEM images of morphological structure of ZVI/Biochar sample: (a) before treatment, (b) after 4 h treatment.
surface of biochar. This can be thought to be the iron powder successfully mixed with biochar before treatment. After 4 h treatment, it was evident that some morphological changes and agglomerates occurred on the surface of the ZVI/bamboo biochar system because of the generation of iron oxides, which might restrain electron transfer and decrease the number of macroscopic galvanic cells.

The outcome of XRD analysis provided in Figure 2 depicts the structure and phase composition of the ZVI/Biochar system. The wide diffraction peak at a small angle might be attributed to the amorphous phase of the biochar that was apparent in the samples. The apparent peaks at 44.67, 65.02, and 82.33 were the characteristic diffraction peaks of ZVI, which confirmed the formation of iron in its zero-valent state.

**Effect of initial pH**

Initial pH is a crucial factor for the degradation of CB by ZVI/Biochar system due to the great effect of H⁺ concentration on the corrosion process of iron. During the iron corrosion process, the released ferrous ions collided with hydroxyl ions, generating ferrous hydroxide precipitate on the surface of iron powders, which might occupy the reactive sites and hinder the micro-electrolysis reaction (Zhang 2003). Therefore, the influence of initial solution pH on CB removal by the ZVI/Biochar system was investigated in a pH range of 2 to 10. The results in Figure 3 depict that a downward trend on the removal efficiency was presented with increasing initial pH value. When pH increased from 2 to 3, the removal efficiency of CB was almost constant, at about 95%. Subsequently, the removal efficiency decreased rapidly when initial pH increased from 3 to 8, followed by a rapid increase in efficiency as pH increased from 8 to 10. The removal efficiencies of CB were 97.8%, 95.5%, 91.8%, 87.9%, and 72.1% at pH 2, 3, 4, 6, 8 after 3 h treatment, respectively. The removal performance of CB was obviously pH dependent and the increase of initial pH values from 2 to 8 led to the diminution of CB removal efficiencies. Consequently, the optimal pH should be 2.0 to 3.0 on the basis of the CB removal efficiency. The results suggested that acidic conditions were beneficial to the removal of CB, because the macroscopic galvanic cells are responsible for the reductive degradation of CB by the ZVI/Biochar system; the biochar as a cathode could accept electrons released from the ZVI as an anode. Additionally, the electrons could react with the acidic functional groups on the surface of biochar particles to form [H], resulting in the consumption of H⁺. With the increasing amount of H⁺, the degradation capacity of ZVI was improved, and H⁺ was also involved in the reduction of CB (Lai et al. 2013). Therefore, the initial pH could affect the CB removal efficiency by the ZVI/Biochar system. Additionally, the activity of iron particles would be strengthened in an acid environment, since they could help to avoid forming iron oxide, which would block the access of target contaminants to active sites of ZVI and enhance the reductive degradation of CB (Shu et al. 2007; Tang et al. 2012). The reaction rate of micro-electrolysis reactions and the dissolving of iron decreased rapidly as pH increased, which led to the reduction of the CB removal efficiency.

Interestingly, a further increase of pH from 8 to 10 resulted in an enhancement of the CB removal efficiency. It is probable that CB could react with OH⁻ in alkaline conditions.
The reaction principle is as follows (Dalman & Neumann 1968):

$$\text{C}_6\text{H}_5\text{-Cl} + \text{OH}^- \rightarrow \text{C}_6\text{H}_5\text{-OH} + \text{Cl}^-$$

In general, in order to enhance the removal efficiency of CB, pH of 2 was selected as the optimum pH.

**Effect of the mass ratio of ZVI to biochar**

The mass ratio of ZVI to biochar is an important factor for the removal of CB, since the electrochemical reaction between the iron powder and biochar particles is an electrochemical corrosion process. To evaluate the effect of ZVI:Biochar on the removal efficiency of CB, the mass ratios were set as 1:1, 2:1 and 3:1, respectively. The effect of varying mass ratios of ZVI to biochar on the CB degradation at different reaction times is shown in Figure 4. The results showed that the removal efficiencies of CB exhibited similar trends as the reaction times increased. The removal efficiencies were 95.6%, 98.8%, and 95.3% at ZVI:Biochar of 1:1, 2:1, and 3:1 within a reaction time of 4 h. Evidently, CB degradation efficiency was enhanced as the ZVI:Biochar was increased from 1:1 to 2:1 and subsequently diminished with further increments of the mass ratio. In the ZVI/Biochar micro-electrolysis system, iron powder served as an anodic metal which provided electrons for CB destruction. Biochar particles worked as cathodes to generate macroscopic galvanic cells when in contact with iron particles, which could significantly accelerate the corrosion of iron and thus stimulate the release of more iron ions and electrons (Ruan et al. 2010). Therefore, mixing biochar particles with iron powder effectively increased the current efficiency of the ZVI/Biochar micro-electrolysis system (Lai et al. 2012). When the ZVI:Biochar ratio arrived at a certain value, the total surface areas of iron and biochar particles were similar, which could promote the electrode reactions.

As the ZVI:Biochar ratio increased, the micro-electrolysis effect was enhanced due to the increased dosage of iron powder, which made it possible to provide more iron surface-active sites for collision with CB molecules to accelerate CB degradation (Chang et al. 2011). However, further increase of the mass ratio from 2:1 to 3:1 represented that an excess dosage of iron existed, giving rise to the decline of CB degradation rate because the contact area between iron and carbon was reduced (Liu et al. 2007). These results indicated that either a higher or a lower mass ratio of ZVI to biochar is unfavorable for CB removal because the iron would affect the mass transfer efficiency. In summary, the mass ratio of ZVI to biochar at 2:1 would be beneficial for CB removal.

**The effect of initial concentration and reaction time**

The influence of initial CB concentrations on the CB removal efficiencies by the ZVI/Biochar system is shown in Figure 5. It was found that all the CB removal efficiencies were above 90% after 90 min by the ZVI/Biochar system treatment with different initial CB concentrations ranging from 33.68 to 134.14 mg/L. The results also indicated that the lower the initial CB concentration involved, the shorter the removal process needed. Due to the limited number of galvanic cells formed, the incomplete degradation of CB gradually occurred with the increase of initial CB concentration. Consequently, each pollutant molecule shared...
fewer reactive sites and electrons, which means that the activity sites of ZVI for the reduction of CB were insufficient. As a result, it induced a decrease in CB removal efficiency. Simultaneously, as the treatment process proceeded continuously, higher CB concentration might accelerate the consumption of ZVI, leading to the decline of the exposed active sites on the surface of the ZVI/Biochar system (Huang et al. 2015).

Likewise, the time history of CB concentrations under the micro-electrolytic conditions is displayed in Figure 5. According to the observations, the degradation of CB would be implemented more thoroughly with relatively longer reaction time. In general, the treatment proceeded rapidly within the first hour. The CB removal efficiencies increased significantly from 70.2%, 56%, and 51.9% to 99.5%, 96.9%, and 79.7% when the treatment time was increased from 10 min to 1 h, respectively. While extending the treatment time the removal efficiencies were almost constant. The possible reason for this trend is that CB molecules could readily migrate to the surface of the ZVI/Biochar system at the early stage due to the excellent absorption and reduction capacity of the ZVI/Biochar system; the electrode reactions proceeded rapidly at this stage and consequently induced the generation of [H] and the prompt release of plentiful ferrous ions, which were both indispensable for the reduction of CB. In addition, it can be inferred that the CB solution was under acidic conditions at the initial stage, which could enhance micro-electrolysis reactions and boost the dissolution of iron. When the reaction time exceeded 1 h, the CB solution arrived at neutral conditions, inducing the restraint of micro-electrolysis reactions and the dissolution of iron. Meanwhile, flocculation precipitation of ferric hydroxides onto the surface of the ZVI/Biochar system may also inhibit the micro-electrolysis reactions and the mass transfer effect (Wu et al. 2011). Therefore, the removal efficiencies of CB were almost constant when reaction time exceeded 1 h.

Regarding the above results and the cost of treatments, the improved initial concentration and reaction time were 33.68 mg/L and 4 h, respectively.

The effect of chloride ions

It has been known that chloride ions are ubiquitous anions in groundwater and the concentration might be different regarding the water origin; especially in contaminated areas, high levels of chloride ions could be found. Additionally, chloride ions may affect the reaction of micro-electrolysis (Zhou et al. 2013). Figure 6 plots the effect of chloride ion (Cl\(^-\)) concentration on the CB degradation in aqueous solution. The results in Figure 6 imply that the removal efficiencies within the immersion time of 60 min were 96.1%, 95.7%, and 98.2% when Cl\(^-\) concentrations were 0 mg/L, 100 mg/L and 1,000 mg/L, respectively. It was evident from these data that the Cl\(^-\) exerted little influence on the removal efficiency of CB when the Cl\(^-\) concentration was relatively low. However, the degradation efficiency was promoted significantly when the Cl\(^-\) concentration was relatively high. Thus, it can be concluded that the elevated Cl\(^-\) concentration accelerates the degradation of CB. It is most likely attributed to Cl\(^-\) used as the anodic depolarizer, which could accelerate the micro-electrolysis reactions and iron corrosion, resulting in improvement of the electron generation from metallic species and renew the reactive sites on the surface of the system. In the presence of chloride ions, the passive film on the iron surface would be undermined, which could trigger corrosion pit formation (Gotpagar et al. 1999). Due to iron surface irregularities, which could dissolve faster than the rest of the surface, localized positive charge regions on the iron surfaces were generated. The chloride ions are attracted to these sites and form metal chlorides to maintain electroneutrality, which could result in the reaction of iron corrosion in the environment (Su et al. 2012). Hence, the relatively high chloride ion concentration is beneficial to the removal of CB in aqueous solution.

CONCLUSIONS

This study undertook a series of laboratory experiments to assess the potential of the mixture of ZVI powder
and biochar particles as a novel iron-carbon micro-electrolysis material for CB treatment in groundwater. The ZVI/Biochar micro-electrolysis system exhibited outstanding CB removal efficiency, which was due to the numerous iron-carbon galvanic cells generated during the reactions. Moreover, the CB removal efficiency might be affected by several factors. The removal efficiency was strongly dependent on initial pH, and the optimum pH should be between 2 and 3. The increase of initial pH led to the decrease of the removal efficiency. The increase of the mass ratio of ZVI to biochar was initially favorable for the degradation of CB, but subsequently led to the decline of the removal efficiency. The mass ratio of ZVI to biochar at 2:1 appeared to provide the best performance for the CB degradation. The increasing initial CB concentrations exerted a negative influence on their removal. The removal efficiencies increased significantly within the initial treatment time of 1 h, while the removal efficiencies were almost constant with further extending the treatment time. The desired reaction time was 1 h. Enhanced degradation of CB was observed in the presence of and with increasing concentration of chloride ions, because chloride ions acted as the anodic depolarizer, which could boost electron generation from metallic species and renew reactive sites on the surface of metals. The reduction and oxidation effects might be the main mechanisms of CB degradation, which would efficiently reduce the toxicity of CB-contaminated groundwater. Additionally, when the coupled ZVI/Biochar system was applied, the optimum conditions for the CB degradation were initial pH of 2, reaction time of 4 h, and initial CB concentration of 33.68 mg/L, and 99.92% of initial CB could be removed under these conditions. The necessary biochar and iron weight per unit of CB contained in the liquid phase was 35.6 mg biochar/(mg CB) and 71.3 mg iron/(mg CB), respectively.

Given that biochar is environment friendly and readily produced, it could become a promising alternative to effectively improve CB degradation. This novel ZVI/Biochar micro-electrolysis provides an important insight into the development of new inexpensive and efficient approaches to groundwater remediation. The coupled biochar and ZVI system can be applied to in situ remediation of CB-contaminated groundwater. The biochar can serve as a carbon source for indigenous microorganisms. Thus, the biochar, microbe and ZVI combination will be a promising approach to degrade CB with bioPRBs in situ groundwater.

ACKNOWLEDGEMENTS

This research was supported by the National Natural Science Foundation of China (41272261) and Shanghai Science and Technology Project (15DZ1205803). The authors are grateful to the reviewers who helped us improve the paper by many pertinent comments and suggestions.

REFERENCES


First received 30 May 2016; accepted in revised form 8 October 2016. Available online 26 October 2016