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Effects of co-present cations and anions on hexachlorobenzene removal by activated carbon, nano zerovalent iron and nano zerovalent/activated carbon composite

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ABSTRACT

Activated carbon, nano zerovalent iron (nZVI), and nano zerovalent iron/activated carbon (nZVI/AC) have all been found to be effective for hexachlorobenzene (HCB) removal either through adsorption, dechlorination, or both. Detailed investigations on the effects of several anions and cations normally present in aqueous streams on the removal of HCB were carried out to evaluate the potential performance of these materials in field treatment. Effects of ions were analyzed from the perspectives of changes in pH, ionic strength, and redox conditions. Results showed that ions that facilitate zerovalent iron corrosion, i.e. bicarbonate, chloride, chloride, ferrous, and copper, could greatly enhance HCB removal by nZVI, while HCB adsorption by activated carbon was more a factor of solution pH and ionic strength. The effects of ions on nZVI/AC were more complicated since both nZVI and activated carbon played a role in HCB removal. The results lead to a better understanding of HCB removal by these materials and could be employed in the consideration of choosing materials and prediction of treatment efficiency.

Keywords: Hexachlorobenzene; Activated carbon; Nano zerovalent iron; Dechlorination; Copresent ions

1. Introduction

Hexachlorobenzene (HCB) was widely used in industries, such as fireworks, ammunition, fungicide, and rubber manufacturing, and is now banned for commercial production due to its hazardous effects on human being and natural environment [1]. Epidemiology studies have shown that HCB is carcinogenic [2]. Short- and long-term exposure could lead to kidney, liver damage, and damage in central nervous system (CNS). Stockholm convention in 2001 listed HCB as one of the persistent organic pollutants [3]. It was reported to have a half-life about 9 years. Due to its persistence, there are sites all around the world where HCB pollution is still a serious issue. For instance, HCB was found in many river sediments in China due to wastewater discharge from chemical plants [4].

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Biodegradation of HCB through aerobic and anaerobic processes is one of the methods that have been widely investigated. However, biological remediation often needs cultivation of specific microorganisms [5]. Compared with biological treatment, physicochemical treatment technologies are often more flexible in operation and adaptive to different circumstances. Physicochemical methods employed in HCB remediation include adsorption, oxidation, reductive dechlorination, thermal decomposition, chemical enhanced washing, and electrokinetic remediation [6]. Adsorption has attracted many attentions due to its low cost and easy operation. Studies have shown that HCB released into the environmental can be adsorbed on soils and sediments. However, it may take several months or even years to reach equilibrium suggesting the potential risk of transport in the environment [7]. In comparison, adsorption by activated carbon was more effective due to activated carbon's large surface area and sophisticated pore structure. In practice, activated carbon often was used with other technologies to enhance HCB removal. For instance, Wan et al. achieved a HCB removal of more than 90% by combining soil washing by rhamnolipid with powdered activated carbon adsorption [8].

Reductive dechlorination, especially reduction by zerovalent iron, was another technology that has been employed in both pilot and full-scale operations in recent years [9,10]. Nano zerovalent iron (nZVI) was especially attractive due to its special characteristics, for instance, high surface area to volume ratio [11]. However, the effectiveness of reduction was often impaired by iron particles' strong tendency to agglomerate and low mobility. Depositing iron on porous materials, such as activated carbon, chitosan bead, silica, zeolite, usually could greatly alleviate the agglomeration and mobility problems [12–14]. Combination of activated carbon and nZVI was revealed to be beneficial to the reductive dechlorination of various organics [15,16].

In our previous research, a nano zerovalent iron/activated carbon (nZVI/AC) composite was synthesized through a liquid reduction method and used to remove HCB [17]. Results indicate that a synergistic effect was created and HCB was removed both through adsorption by activated carbon and reductive dechlorination by nZVI. Thus, synthesized material achieved a higher HCB removal than nZVI and activated carbon alone.

However, both adsorption and reductive dechlorination are affected by many factors such as pH of the target water, copresent ions, or organic compounds, etc. Among them, the presence of interfering cations and ions are of enormous significance since they are ubiquitous in real water or wastewater. However, the impacts of cations or anions on adsorption or dechlorination varied. The presence of ions may affect adsorption through competition or changing adsorption chemistry [18,19]. As for dechlorination, Liu et al. indicated that reactivity of SO_4^{2-} had a negative effect on trichloroethyl dechlorination by nZVI but have no influence on dechlorination of trichlorobenzene [20]. Rajasekar et al. reported that trichloroethylene dechlorination by sulfidated nano iron was affected by solution pH and high dechlorination rate was observed at higher pH [21]. Kim et al. studied the effect of water chemistry on dechlorination trichloroethylene by FeS-coated iron nanoparticles and found that the presence of Ca^{2+} and Mg^{2+} changed the ionic strengths of the solution thus changing dechlorination efficiency [22].

The main purpose of this research is to study the impact of copresent ions on HCB removal by activated carbon, nZVI and nZVI/AC composite. The ultimate goal is to provide essential information in the discussion of the applicability of these for HCB removal in aqueous streams.

2. Materials and methods

2.1. Chemicals

Sodium borohydride, sodium salts of chloride, sulfate, bicarbonate, sulfate of ferrous, magnesium and copper, ethanol and n-hexane were purchased from Sinopharm Chemical (Shanghai, China). HCB, ferrous chloride, and chlorobenzene standard solutions were obtained from Aladdin Industrial Co. (Shanghai, China). All chemicals were of analytical grade and used as received. All the reagents were prepared with deionized water.

2.2. Preparation of activated carbon, nZVI- and nZVI-activated carbon composite

Lignite-activated carbon was purchased from Sinopharm Chemical, Shanghai, China and was ground to particle size of 88–150 μm, washed thoroughly with deionized water and dried.

nZVI was synthesized using a modified $NaBH_4$ reduction method [23]. About 21.36 g of ferrous chloride was added to a mixture of 37.5 mL of ethanol and 37.5 mL of water. The solution was added slowly to 400 mL of 1 mol/L $NaBH_4$ and then shaken for 2 h on a rotary shaker at 25°C. After that, particles were separated by filtration and washed thoroughly with ethanol, dried, and stored in N_2 purged container.

In the preparation of nZVI/AC, ferrous salt was loaded onto activated carbon (88–150 μm in size) by an adsorption method. Specifically, 2 g of activated carbon was added to 75 mL of 1 mol/L of ferrous chloride solution which is made of 37.5 mL of pure ethanol in 37.5 mL of water. The mixture was shaken for 24 h on a rotary shaker at 25℃. Fifty milliliters of 1 mol/L $NaBH_4$ was then added to the suspension dropwise and stirred vigorously. Zerovalent iron was formed through chemical reduction of preloaded iron salts by $NaBH_4$ according to the following reaction (1):

$$2Fe^{2+} + BH_4^- + 2H_2O = 2Fe^0 + BO^{2-} + 2H_2 + 4H^+ \tag{1}$$

The mixture was then filter to separate solid material from liquid and the resultant solid material was washed thoroughly with ethanol to remove any loose nZVI on the surface of activated carbon. The final material was named as nZVI/AC.

Analysis of iron content showed that activated carbon contained 0.30 mg Fe/g, while nZVI/AC had 217.38 mg Fe/g.

2.3. Effect of pH on HCB removal

Activated carbon, nZVI or nZVI/AC, 0.16 g in mass, was added to 20 mL of 6.0 mg/L HCB solution. pH of the solution was adjusted to 3, 5, 6, 7, 9, and 11 using 2 mol/L HCl or NaOH. The mixtures were then shaken for 8 h at 150 rpm and 25℃. Solids were separated by filtration. About 10 mL of filtrate was extracted with 10 mL of n-hexane and analyzed for HCB concentration.

2.4. Effect of ions on HCB removal

Effects of copresent ions on HCB removal were investigated in batch experiment. Anions included SO_4^{2-}, HCO_3^-, Cl^-, and NO_3^-. Cations included Mg^{2+}, Fe^{2+}, and Cu^{2+}. Solutions of sodium salt of anions and sulfate salts of cations were added to 100 mL of HCB solution. Initial HCB concentration was set at 6.0 mg/L (or about 0.02 mmol/L). Concentrations of anions and cations varied from 0.2 to 10 mmol/L. About 0.16 g of activated carbon, nZVI or nZVI/AC was added next and the mixture was sealed and put on a shaker for 8 h at room temperature. Controls without salt addition were conducted. After 8 h of reaction, mixture was filtered. About 10 mL of filtrate was then extracted with 10 mL of n-hexane for 0.5 h and HCB was analyzed.

Triplicates were done for all the experiments. Results shown are averages with error bars.

2.5. Chemical analysis

HCB was analyzed with an Agilent 7890A-5975C gas chromatography-mass spectrometry (GC/MS) (Agilent Technologies, USA) equipped with an HP-5MS capillary column. About 1 μL of extraction was injected automatically in splitless mode. The temperatures of injector and detector were set at 320 and 350℃, respectively. Separation was controlled with a temperature program that started at oven temperature at 40℃, held for 5 min, then ramped at 20℃/min to 200℃, and next ramped at 5℃/min to 250℃, held for 2 min.

3. Results and discussion

3.1. Effects of initial pH on HCB removal

Fig. 1 is the effect of initial pH on HCB removal. Removal by activated carbon peaked at around pH 7–8 and was lower both at high and low pH. Aromatic compounds are physisorbed on carbon materials essentially by dispersion interactions between the π-electrons of the aromatic ring and those of the graphene layers [24]. Nonelectronic interactions are the driving force for the adsorption. Activated carbon used in this study had a pHpzc (pH of point of zero charge) of about 7.2 which means that surface charge is near neutral at pH around 7.2, while it is positively charged at pHs lower than 7.2 and negatively charged at pHs greater than 7.2. It appears that physiosorption of HCB by activated carbon was strongest when carbon surface was not charged.

As for nZVI, removal was favorable at acidic pH. Taha and Ibrahim believed that low pH resulted in the dissolution of the passivating oxyhydroxide layer on nZVI and reactivity of nZVI increased as a result

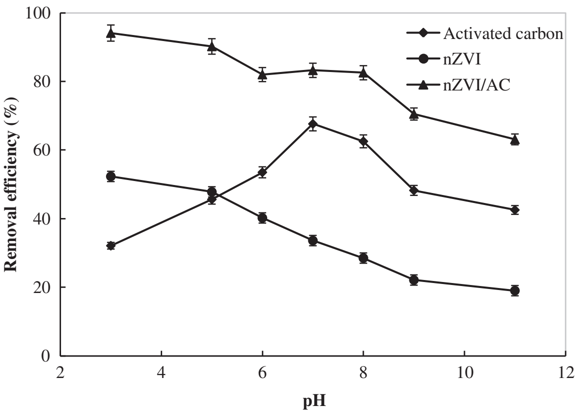

Fig. 1. Effects of pH on HCB removal by activated carbon, nZVI, and nZVI/AC.

[25]. While at high pH, Fe(II) and (III) hydroxides started to form and this could result in hydroxide covering the Fe^0 surfaces and hampering electron transfer.

In addition, statistical analysis revealed that variations in HCB removal by nZVI/AC were not significant at $\alpha = 0.05$ level (p-value > 0.05), when pH was lower than 9. Significant drop in HCB removal by nZVI/AC occurred only when pH was raised above 9. nZVI/AC appears to be quite robust against pH change and this could be explained by the synergistic effect of nZVI and activated carbon. nZVI performed best at low pH, while adsorption by activated carbon was favored at neutral pH. Acting together, removal capacity of nZVI/AC was inhibited only at high pH.

3.2. *Effect of copresent anions on HCB removal*

Identifying the effects of interfering anion and cations would have significant impact on the material's applicability since many anions and cations are omnipresent in surface or groundwater streams. In this research, four anions and three cations were selected. Sodium salts of anions were used since Na^+ had no effect on the degradation reactivity of zerovalent iron [26]. The standard reduction potential of Na^+ is −2.71 V which is much lower than that of Fe^{2+} (−0.44 V).

3.2.1. *Effect of bicarbonate*

The influences of bicarbonate at different concentration on HCB removal by activated carbon, nZVI and nZVI/AC are shown in Fig. 2.

In general, HCB removal was enhanced by the presence of bicarbonate as bicarbonate increased from 0.2 to 1 mmol/L (12–63 mg/L) for all three materials and then leveled off at higher concentration.

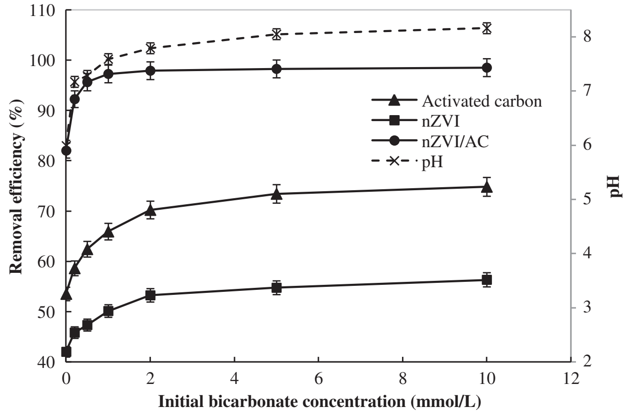

Fig. 2. Effect of bicarbonate on HCB removal by activated carbon, nZVI, and nZVI/AC.

Secondly, y axis in Fig. 5 shows the initial pH of solution after bicarbonate was added. As bicarbonate concentration increased from 0 to 10 mmol/L, pH increased from around 6.0–8.1 (dashed line). HCB removal by activated carbon increased as pH approached 7–8. This was in good agreement with results from effects of pH on HCB by activated carbon, that is, HCB removal was best at pH around neutral. In addition, the increase in HCB removal after the addition of $NaHCO_3$ could be due to the change in ionic strength. There are studies showing that adsorption by activated carbon of HCB were favored at high ionic strength [27].

For nZVI, the improvement was attributable to the promotion of nZVI corrosion by bicarbonate [28]. Le et al. reported increase in para-chloronitrobenzene (p-CNB) reduction by nZVI at bicarbonate concentration less than 100 mg/L (~1.6 mmol/L) [29]. Klausen et al. also reported that the dechlorination efficiency of trichloroethylene (TCE) was enhanced by bicarbonate with concentrations between 2–20 mmol/L [30]. However, Le et al. [29] observed a suppression effect as bicarbonate concentration exceeded 100 mg/L. The suppression effect at high bicarbonate concentration was attributed to the formation of Fe-carbonate which blocked the active sites on iron surface as shown in Eqs. (2) and (3):

$$Fe + 2HCO_3^- \rightarrow Fe^{2+} + 2CO_3^{2-} + H_2 \tag{2}$$

$$4Fe^{2+} + 2Fe^{3+} + CO_3^{2-} \rightarrow Fe_6(OH)_{12}CO_3 + 12H^+ \tag{3}$$

No suppression effect was observed as bicarbonate concentration increased beyond 1 mmol/L in this study. As a matter of fact, HCB removal did not change much as bicarbonate concentration continued to increase.

As for nZVI/AC, it manifested enhanced HCB removed at low bicarbonate but reached plateau as concentration reached above 1 mmol/L. The increase in HCB removal could be attributed to both increases in adsorption and dechlorination based on bicarbonate's effects on nZVI and activated carbon.

3.2.2. *Effect of chloride*

The effect of chloride is shown in Fig. 3. Compared with HCB removal without any salt, removal efficiencies improved with nZVI and nZVI/AC as chloride concentration rose from 0.2 to 2 mmol/L and the enhancement effect leveled off after that. Gotpagar et al. reported that chloride could act as a corrosion promoter [31]. The presence of chloride accelerated the generation of electrons from iron and induced corrosion pit formation. Such effects had been assumed to be the main reasons for improved TCE reduction and carbon tetrachloride dechlorination.

For activated carbon, HCB removal was statistically larger only when chloride reached beyond 5 mmol/L probably due to changes in ionic strength since pH change is insignificant with the addition of chloride. However, it appeared that impact of ionic strength on HCB removal was detectable only if chloride concentration is high enough.

3.2.3. Effect of nitrate

Fig. 4 shows that nitrate ions inhibit HCB removal by both nZVI and nZVI/AC. Devlin and Allin [32] observed in batch experiments that nitrate inhibited the degradation of 4-chloronitrobenzene. The presence of nitrate was believed to produce stable protective iron oxide and oxyhydroxide species on the iron surface, which in return inhibited electron transfer [33]. Monitoring of the nitrate concentration confirmed that nitrate decreased at the end of HCB removal with nZVI. Nitrate obtained electrons from iron surface and was reduced to nitrite and ammonia as shown in Eqs. (4) and (5):

$$NO_3^- + Fe^0 + 2H^+ \rightarrow Fe^{2+} + NO_2^- + H_2O \quad (4)$$

$$NO_3^- + 4Fe^0 + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O \quad (5)$$

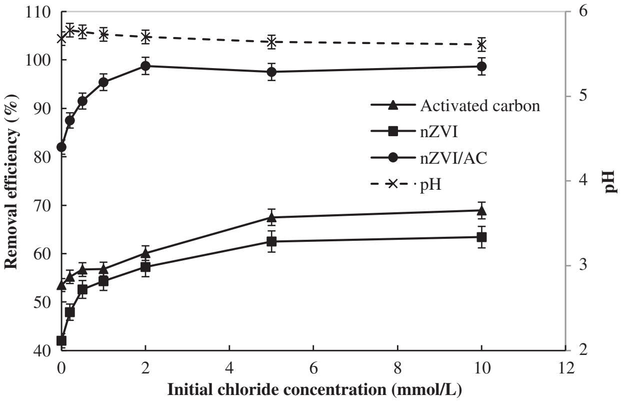

Fig. 3. Effects of chloride on HCB removal by activated carbon, nZVI, and nZVI/AC.

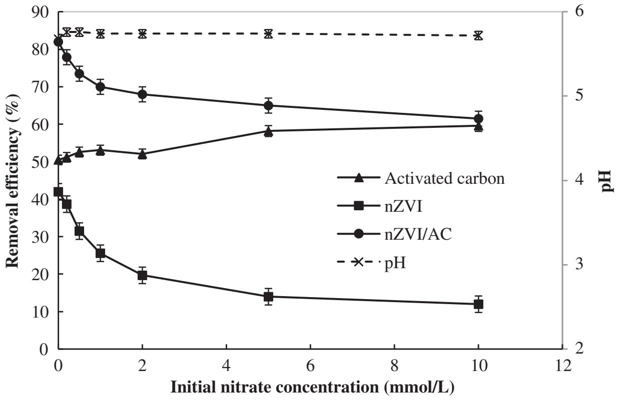

Fig. 4. Effects of nitrate on HCB removal by activated carbon, nZVI, and nZVI/AC.

The inhibitory effect was probably caused by the competition between nitrate and HCB for the same reactive sites. As nitrate concentration increased from 0.2 to 10 mmol/L, HCB removal by nZVI dropped sharply from 42% to about 12%. By comparison, decrease in nZVI/AC by nitrate inhibition occurred in a lesser degree. About 62% of the HCB was removed even with nitrate concentration of 10 mmol/L.

The effect of nitrate on HCB by activated carbon was similar to that of chloride. HCB removal was significantly greater only when nitrate concentration was higher than 5 mmol/L.

For nZVI/AC, the effect of nitrate followed the same pattern as that of nZVI, indicating that the effect of nitrate of nZVI overrides that on activated carbon. The increase in adsorption was cancelled off by negative effect of nitrate on nZVI.

3.2.4. Effects of sulfate

Fig. 5 shows the effect of sulfate ion on HCB removal. Sulfate enhanced the removal by nZVI and nZVI/AC. Fan et al. reported that sulfate could remove iron oxides and hydroxides from the iron surface, thereby compromising the passivating film which led to the increase in the number of reactive sites [34]. Sulfate enhancement was also observed in studies on nZVI for carbon tetrachloride and trichloroethylene removal [35].

Since variation in pH is negligible with the addition of sodium sulfate as shown in Fig. 5, improvement in HCB removal by activated carbon could also be a result of change in ionic strength. HCB removal was improved at sulfate concentration greater than 2 mmol/L.

In summary, from the results of anions on HCB removal, there is a general increase in HCB removal

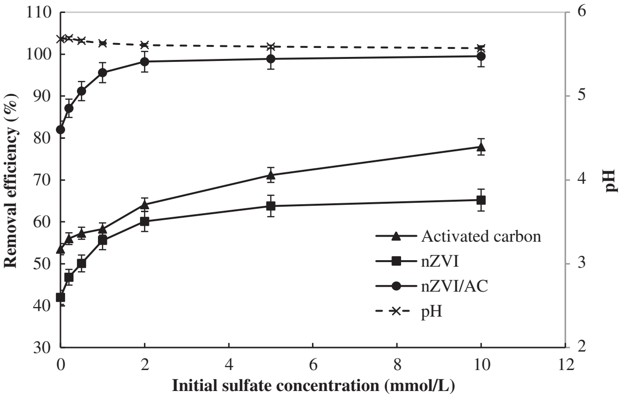

Fig. 5. Effects of sulfate on HCB removal by activated carbon, nZVI, and nZVI/AC.

by nZVI/AC with the presence of anions except with nitrate where competition resulted in inhibition.

3.3. *Effects of cations on HCB removal*

Sulfate salts of cations were employed. Assuming that the effect of sulfate was consistent, the differences in HCB removal between sodium sulfate and sulfate of magnesium, ferrous and copper were used in the discussion of effect of cations.

3.3.1. *Effect of magnesium ion*

The effect of Mg^{2+} ions at different concentration is shown in Fig. 6. Mg^{2+} ions had no significant effect on nZVI. The standard reduction potential of Mg^{2+} ions (−2.37 V) is less than that of Fe^{2+} ions (−0.44 V). Like Na^+, Mg^{2+} ions cannot affect reactivity of iron metal by the reduction of ions.

As for activated carbon, the presence of Mg^{2+} improved HCB removal. pH was ruled out as the main contributor to this change since pH change was not significant. The difference could be attributed to changes in ionic strength.

Effect of Mg^{2+} on nZVI/AC followed closely that of activated carbon since Mg^{2+} had no effect on nZVI. Therefore, effect of Mg^{2+} on adsorption was the dominant factor in HCB removal by nZVI/AC.

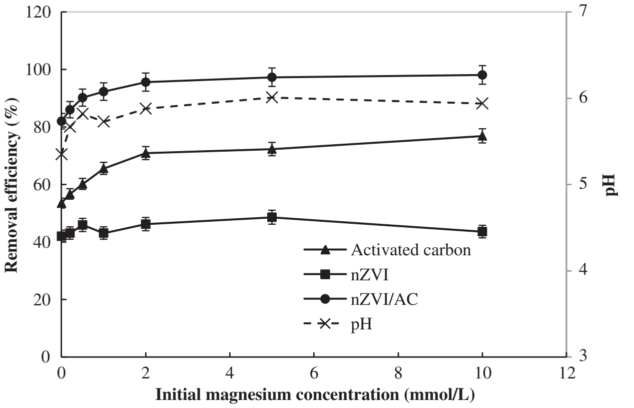

Fig. 6. Effects of magnesium ions on HCB removal by activated carbon, nZVI, and nZVI/AC.

3.3.2. *Effect of ferrous iron*

The effect of Fe^{2+} ion is shown in Fig. 7. Ferrous ions enhanced HCB removal for nZVI. Change in solution pH in Fig. 7 indicates that increases in ferrous ions concentration caused decrease in the pH. Shih et al. reported that pH decrease was likely the main factors of HCB removal by Pd/Fe bimetallic nanoparticles, not ions [36]. As shown in Fig. 1, HCB removal was favored in acidic condition, especially with nZVI. pH dropped to under 3 when ferrous ion concentration reached beyond 5 mmol/L. In addition, Fe^{2+} could act as a reducing agent which provided electrons and induced dechlorination [37].

HCB removal by activated carbon dropped with the increase in ferrous ions. As had been discussed above, HCB removal was dependent on pH and ionic strength. Removal was favored at near neutral pH and high ionic strength. Compared with sodium sulfate, addition of ferrous sulfate led to a drop in pH while increase in ionic strength. Based on results from this research, it appears that pH change played a more dominant role when adsorption was concerned. As pH decreased, HCB removal dropped even though ionic strength increased.

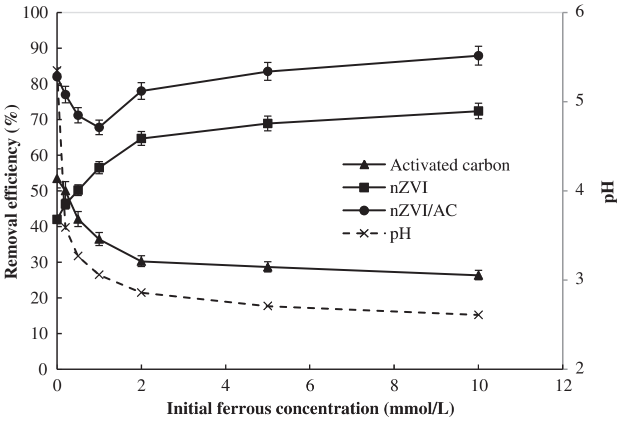

Fig. 7. Effects of ferrous ions on HCB removal by activated carbon, nZVI, and nZVI/AC.

Effect of ferrous ion on nZVI/AC is a balance of effects on nZVI and activated carbon. At low ferrous concentration, the inhibition of adsorption predominated, HCB removal by nZVI/AC decreased with the increase in ferrous concentration and drop in pH. There is a turning point at ferrous ion concentration around 1 mmol/L, HCB removal increased with the increase of ferrous ion above that. At higher concentration, ferrous ion's facilitating effect on nZVI became prominent and nZVI/AC's behavior was more close to that of nZVI.

3.3.3. Effect of copper ion

Fig. 8 is the effect of Cu^{2+} ion. HCB removal was enhanced by Cu^{2+} ions for nZVI. The standard reduction potential of Cu^{2+} ions (+0.34 V) is above that of Fe^{2+} ions (−0.44 V), so a redox reaction of the Cu^{2+} ions could take place [38]. Karabelli et al. observed the deposition of reduced copper on iron particles [39]. The deposited copper was believed to facilitate the degradation of halogenated compounds by promoting electron and promote corrosion of Fe^0. That is, the formation of bimetallic produced a galvanic corrosion at the surface thus enhance electron transfer.

In addition, pH decreased with the increase in copper concentration due to hydrolysis of copper as shown in Eqs. (6)–(7) [40,41]:

$$Cu^{2+} + 2H_2O \rightleftharpoons Cu(OH)_2 + 2H^+ \tag{6}$$

$$[Cu(OH_2)_2]^{2+} \rightleftharpoons [Cu(OH)(OH_2)]^+ + H^+ \tag{7}$$

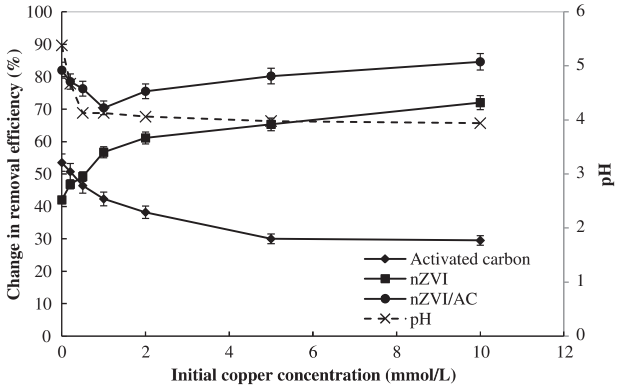

Fig. 8. Effects of copper ions on HCB removal by activated carbon, nZVI, and nZVI/AC.

The drop in pH is considered to be the main reason that HCB removal by activated carbon dropped with the increase of copper ions.

Effects of copper ions on nZVI/AC were similar to that of ferrous ions. Overall impact is a balancing act between nZVI and activated carbon and varied at different concentration. Lowest HCB removal was observed at a copper concentration of around 1 mmol/L.

4. Conclusions

HCB removal by activated carbon, nZVI and nZVI/AC in the presence of different cations and anions was examined. Bicarbonate, sulfate, chloride, ferrous, and copper ions were all able to facilitate HCB removal by nZVI through the promotion of corrosion while nitrate competed with HCB for reactive sites, and thus, its effect was inhibitory. Mg^{2+} had no influence on nZVI due to its redox state. In contrast, for activated carbon, HCB adsorption was affected by ions by changing the solution pH (bicarbonate, ferrous, and copper ions) or ionic strength (sulfate, chloride, nitrate, magnesium). Effects of ions on nZVI/AC were a combination of both nZVI and activated carbon. In the case where effects of ions on nZVI and activated carbon were both facilitating, HCB removal by nZVI/AC was also promoted. However, when effects of ions were opposite (as in the case of nitrate, ferrous and copper ions), it seems that effects on nZVI predominated. nZVI/AC would follow more closely the pattern of nZVI.

Acknowledgments

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