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Fe^0/Zn^0 PRB Technology for the Remediation of PCBs Contaminated Groundwater

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Abstract: The vast majority of PRB currently in use utilize zero valent iron (ZVI) as the reactive medium. In this paper, three laboratory columns were set up and operated under conditions simulating those anticipated in the groundwater to investigate the feasibility and efficiency of the enhanced Fe^0 PRB for the remediation of the PCBs contaminated groundwater. Operating under 10°C and an effective porosity of 61% to 67% and infiltration velocity of groundwater of 0.7 to $0.8 m\cdot d^{-1}$, the average iron concentration of effluent was $0.241 mg\cdot L^{-1}$, $0.129 mg\cdot L^{-1}$ and $0.201 mg\cdot L^{-1}$, respectively, and the average dechlorination efficiency reached 49.6%, 72.6% and 58.6%, respectively, the Fe^0/Zn^0 based columns can accomplish 94% of PCBs removal and pH value raised from 6.87 to 10.2. Comprehensive consideration suggested that Fe^0/Zn^0 based PRB technology is feasible for the remediation of PCBs contaminated groundwater.

Introduction

Polychlorinated biphenyls are a class of 209 synthesized compounds with chlorine atoms at different positions on two benzene rings and used in a wide variety of applications such as dielectric fluids in capacitors and transformers, hydraulic and heat transfer fluid, lubricating oil, etc[1]. Since the late 1920s, PCBs have been found to be highly toxic to humans[2-3] and a portion of them are released to the aquatic environment damaging our groundwater system, therefore, measures must be taken to remove PCBs from the groundwater.

Permeable reactive barriers (PRB) technology has been successfully applied for reductive treatment of various organic and inorganic groundwater contaminants, which are an emerging alternative to pump-and-treat systems. The main advantage of PRB is the passive nature of the treatment. Its operation does not depend on any external labor or energy inputs and is simple and low cost. Until 2010, more than 150 PRBs have been installed in the world, mainly distributed in the United States. 1994, Gillham et al[4] first proposed Fe^0 dechlorination technology, since then Fe^0 based PRB has drawn great attention concern for its low cost and significant treatment. At present, more than three fourths of the PRB using Fe^0 as reaction medium in the world [5-6]. However, Fe^0 based PRB is still in its initial stage in China. Therefore this paper aimed at

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remediating PCBs contaminated groundwater using PRB filled with iron powder, iron + zinc powder, iron powder and active carbon, respectively. The performance of the PRB is evaluated by monitoring of PCBs concentration, pH, Eh and other parameters, and PRB exhibited good effect.

Materials and methods

Materials Arcolor1242 (1000μg·mL^{-1}), iron and zinc powder (particle size>200 mesh, purity>98%), hexane (HPLC pure, >99.9%), activated carbon, hydroxypropyl- β-cyclodextrin(HP-β-CD) powder. GC-ECD 2010(SHIMADZU), ICP-MS (Agilent 7500c), Acidity meter (PHS - 29A).

Column studies The glass columns (500 mm length, 50 mm ID) provided a funnel-like effluent end. The upper layer was filled with 10cm thick sand, with the particle size of 0.6 mm-0.90mm, isolating the reaction medium from the air and preventing contaminant volatilize; the bottom layer was filled with 5cm thick sand, with the particle size of 0.6 mm-0.90mm, for filtration and buffering; The medium layer was filled with 35mm thick reaction medium, as the main part of the reaction column. Sampling ports at different levels (from the bottom up 15, 25 and 35 cm) within the column were used to sample aliquots of groundwater and continuous monitor pH, Eh, PCBs concentrations, Fe^{2+}, Zn^{2+} and Cl^- concentration.

The PCBs contaminated groundwater used for experiments was simulated by adding a certain amount of Arcolor1242 and HP-β-CD to groundwater sampled from somewhere in Changchun with pH 6.87 and PCBs concentration 821μg·L^{-1}. The simulated groundwater feed the column from the bottom to the top using a peristaltic pump. The penetration rate was controlled between 0.7 and 0.8m/d, effective porosity: 61% ~ 67% , coefficient of permeability：27.51~28.34m/d.

Table 1 Media configuration of reactors

Column	Component	Particle size/mm	Content/%
column1(C1)	iron powder	< 0.40	65
	sand	0.60 ~ 0.90	35
Column2(C2)	iron powder	< 0.40	55
	zinc powder	< 0.40	35
	sand	0.60 ~ 0.90	10
Column3(C3)	iron powder	< 0.40	55
	activated carbon	0.60 ~ 0.90	35
	sand	0.60 ~ 0.90	10

Results and discussion

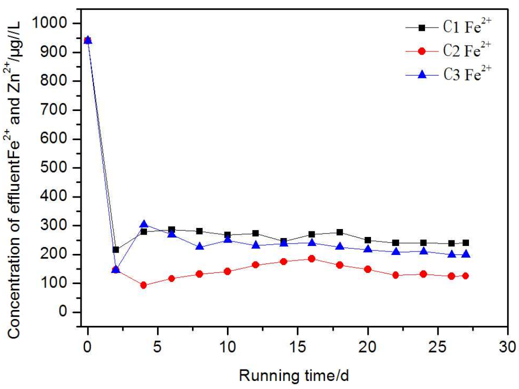

Fig. 1 The concentration of Fe^{2+} and Zn^{2+} of different columns

Fe^{2+}, Zn^{2+} concentration in the columns The Fe^{2+}, Zn^{2+} concentration in the effluent was shown in Fig.1, the Fe^{2+} concentration in C1 and C3 declined sharply at first then fluctuated in a small range. Owing to the adsorption by activated carbon, the Fe^{2+} concentration in C3 effluent is relatively low. After 25th day, the Fe^{2+} concentration in C1 and C3 were 241μg/L and 201μg/L, respectively. In C2, Zn was more reactive and reductive than Fe, so Zn had the priority to integrate with PCBs. With the passage of time, a large portion of the Zn had been used up except a little portion formed into micro cell with Fe, hence, iron began to dominate the redox reactions, with the Fe^{2+} concentration increased from 141μg/L on 14th day to 186μg/L on16th day. After 20 days, with the increasing of pH, Fe and Zn formed into compound in the system, attached to the reaction medium; in addition, the SO_4^{2-} in the systems was reduced to S^{2-}, formed into sediment with Fe^{2+} and Zn^{2+}, and the average Fe^{2+} concentration was 129μg/L, without causing groundwater pollution.

Cl^- concentration in the columns Cl^- concentrations all increased in the three columns, among which C2 exhibited the most significant increase. Due to the adsorption by activated carbon, Cl^- concentration in C3 effluent decreased at first until the activated carbon reached saturation adsorption, then Cl^- concentration in C3 exceeded that in C2 after 15 days. Cl^- concentrations variation indicated that bimetal and galvanic cell comprised Fe and activated carbon both enhanced the dechlorination efficiency in PRB. C2 had the most significant effect, hence, the subsequent work was done with C2.

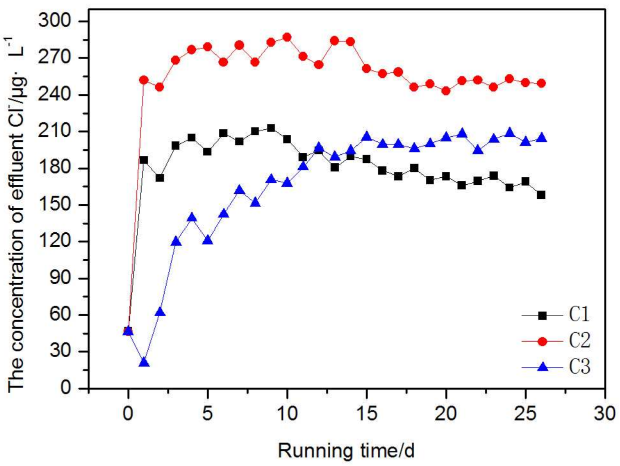

Fig. 2 The concentration of Cl- of three columns

PCBs removal Fig. 3 showed the removal efficiency of PCBs in three columns, the reaction wasn't stable in the first 5 days. From the 5th day, the reaction system became stable, the average removal efficiency is about 94%, and except individual points, the average fluctuations was less than 1%.The reasons are chiefly as follows:

Firstly, Fe^0 and Zn^0 has strong reducibility to provide electronic ability which reduce chlorinated organic compounds to simple less toxic organic compounds, (See the formula (1) and (2)). Secondly, as for the Fe^0-Zn^0 PRB, the formation of numerous tiny primary battery reduced the activation energy of reaction which accelerated the reduction reaction of the PCBs in the metal surface, and then strengthened the treatment effect. Thirdly, the iron oxide hydrate which was changed by iron pillar through the reaction had strong adsorption-flocculation performance，mass-adsorbing organic pollutants， further reducing the PCBs content in the water. Thus, the oxidation reduction reaction, micro electrolysis reaction played a major role in the PCBs removal process.

$$M^0 + 2H_2O \rightarrow 2OH^- + M^{2+} + H_2 \tag{1}$$

$$Fe^0 + 2H_2O + 2RCl_X \rightarrow 2ROHCl_{X-1} + Fe^{2+} + H_2 + 2Cl^- \tag{2}$$

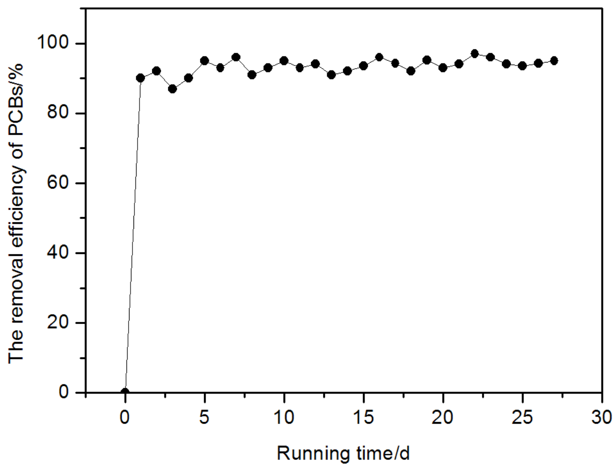

Fig. 3 The removal efficiency of PCBs in three columns

Conclusions

C2 achieved 94% PCBs removal efficiency, indicating that bimetal can enhance the PRB performance. Besides, the presence of Zn had inhibited Fe^{2+} concentration, with 241μg/L, 201μg/L and 129μg/L in the three column respectively, causing no harm to the groundwater, hence, PRB can be proposed as a promising technique for in situ treatment of PCBs contaminated groundwater.

Acknowledgements

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