

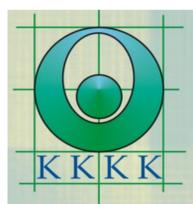
Study of chlorobenzene removal by ferrate treatment from groundwater applying GC-MS

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Since chlorobenzenes (CBs) were widely used as solvents in the chemical industry, they are the most frequently detected organic pollutants in groundwater. Their biodegradation is limited therefore, their removal needs different technologies based on adsorption or oxidation processes. Our research groups developed an electrochemical procedure for continuous production of ferrate [Fe(VI)] solution that can be mixed directly with polluted groundwater in order to oxidize the chlorine-containing compounds. Our investigations focused on the degradation of monochlorobenzene (MCB), 1,2-dichlorobenzene (1,2-DCB), 1,3-dichlorobenzene (1,3-DCB) and 1,4-dichlorobenzene (1,4-DCB) applying model solutions and real groundwater samples.

Materials and methods

Chlorobenzenes (>99% purity) were purchased from Sigma-Aldrich. The potassium-ferrate solution was produced electrochemically. To determine the concentrations of CBs before and after the ferrate treatments, solid-phase – micro-extraction and a gas chromatograph – mass spectrometer system (SPME-GC/MS) were used (SCION SQ 436GC; Bruker). The SPME fiber (PDMS; 100 μ m) was purchased from Supelco. The operating conditions of GC-MS system are listed in the *Table 1*.

Table 1. Operating conditions of GC-MS system

| |
|---|
| Injector: splitless |
| Injector temperature: 250°C |
| Column: BR-5; 30m 0,25 mm ID; 1 μ m thickness |
| Temperature gradient: 60 °C hold 1min →10°C/min rate to 160°C hold 5 min |
| Ion source temperature: 200 °C |

Ferrate treatment

10 ml model solutions containing CB in concentration of 0.1 mg l⁻¹ were treated with different amount of ferrate (10, 20, 30 and 50 mg l⁻¹) in septum sealed vials. The pH value was adjusted with 1 M sulfuric acid. In order to establish the optimal pH value of ferrate treatment, model solutions with 0.1 mg l⁻¹ CB concentration were treated with 50 mg l⁻¹ ferrate at pH of 4.5; 6.7; 8.2; and 12.7. The solutions were stirred with Teflon coated magnetic stirrer bar for 30 min. The CB concentration was determined after 1 min stabilization time. The ferrate treatment of groundwater spiked with CBs was similar to that of model solutions.

Results

The highest removal efficiency was achieved at neutral pH for all CBs (*Fig. 1*). Considering these results, all further ferrate treatments were carried out at pH = 7.

Removal efficiency values of 33, 57, 38 and 38 % were achieved for MCB; 1,2-DCB; 1,3-DCB and 1,4-DCB with concentration of 0.1 mg l⁻¹ using 50 mg l⁻¹ ferrate dosage, respectively (*Fig. 2*).

Lower removal efficiency was achieved, when the model solution contained simultaneously the four CBs at the same ferrate dosage (*Fig. 3*).

The ferrate treatment of spiked groundwater resulted in lower removal efficiency due to the matrix effect. The removal efficiency of MCB, 1,2-DCB, 1,3-DCB and 1,4-DCB amounted to 16, 27, 18 and 15 %, respectively (*Fig. 4*).

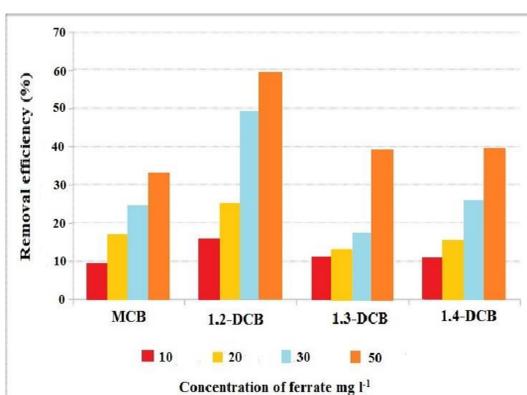


Fig. 2. CB removal efficiencies using different ferrate dosage in model solutions, containing compounds separately

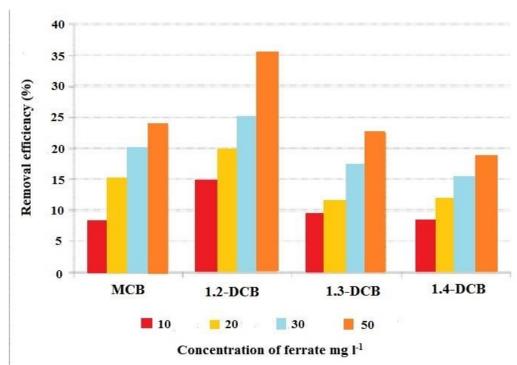


Fig. 3. Removal efficiencies using different ferrate dosages in model solutions containing 4 CBs simultaneously

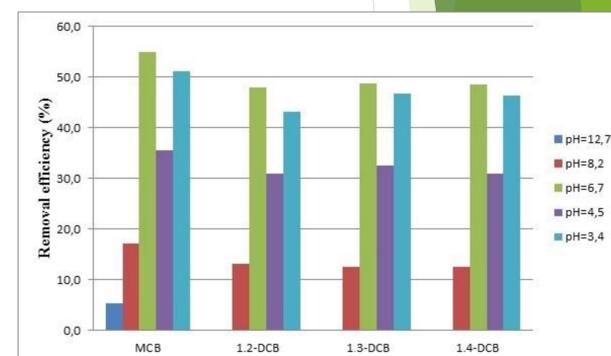


Fig. 1. The pH-dependence of ferrate treatment using 50 mg l⁻¹ ferrate concentration in model solution having 0.1 mg l⁻¹ CB concentration

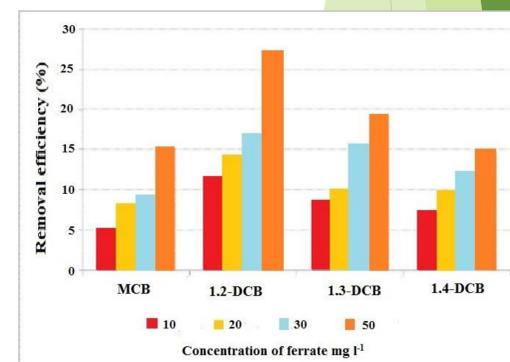


Fig. 4. CB removal efficiencies from spiked groundwater using different ferrate dosages

Conclusions

The optimal pH value of the ferrate treatment is the pH=7 and is recommended to apply ferrate in concentration of 50 mg l⁻¹. 1,2-DCB can be removed with highest efficiency and 1,4-DCB is relatively resistant to the oxidation process. The efficiency for groundwater is lower due to the matrix effect, since ferrate is consumed for oxidation of all organic matrix compounds.

