

# Adsorption behavior of the iron-hydroxide precipitation formed during ferrate treatment of polluted groundwater

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## Introduction

Ferrate (FeVI) is a well-known oxidation agent to remove organic pollutants from water matrices. During the ferrate treatment the Fe(VI) is reduced to Fe(III) resulting in amorphous Fe(OH)<sub>3</sub> precipitation. In the literature this step is characterized by excellent coagulation and flocculation ability of ferrate and in addition the adsorption capacity of Fe(OH)<sub>3</sub> plays a dominant role in the removal of oxidation by-products and other pollutants. Considering the fact that the groundwater contains not only organic pollutants to be removed but simultaneously different inorganic compounds (e.g. cations, anions), as competitors in the adsorption process, it is necessary to clarify their effect on the efficiency of ferrate treatment and the role of Fe(OH)<sub>3</sub> precipitation in the removal of by-products and other dissolved compounds from the treated water.

In this study the influence of Ca, Mg, Zn and Ni cations on the removal of three chlorobenzene pollutants [mono-chlorobenzene (MCB); 1,2-dichloro-benzene (1,2-DCB) and 1,3-dichloro-benzene (1,3-DCB)] from model solutions and the adsorption of cations on the Fe(OH)<sub>3</sub> precipitation were investigated applying ferrate and FeCl<sub>3</sub> treatments.

## Materials and methods

Chlorobenzenes (>99% purity) were purchased from Sigma-Aldrich. The sodium-ferrate solution (6 g/L) was produced by electrochemical method applying cast iron anode and 15M NaOH solution. To determine the concentrations of CBs before and after the treatments, headspace gas chromatograph coupled with mass spectrometer (HS/GC-MS) was used. The cation concentrations in the treated groundwater was measured by flame atomic absorption spectrometer (FAAS). Purgable organic carbon (POC) content and chloride concentrations were determined by TOC analyzer and ion chromatograph (IC), respectively.

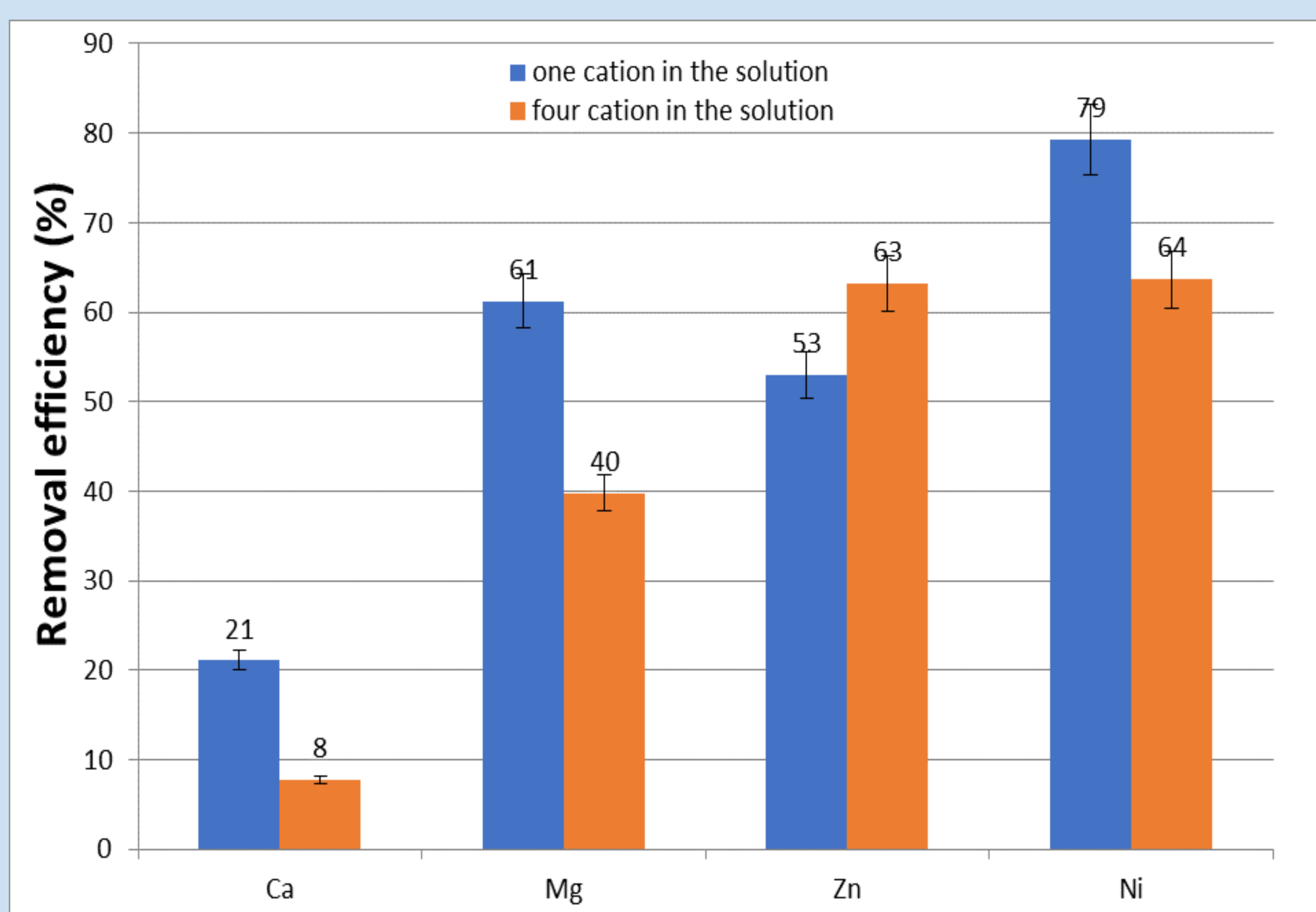


Fig. 2. Cation removal efficiency using ferrate at molar ratios of 1:1:5 and 1:4:5 (organic compounds: cation: iron) depending on the number of cations in the solution

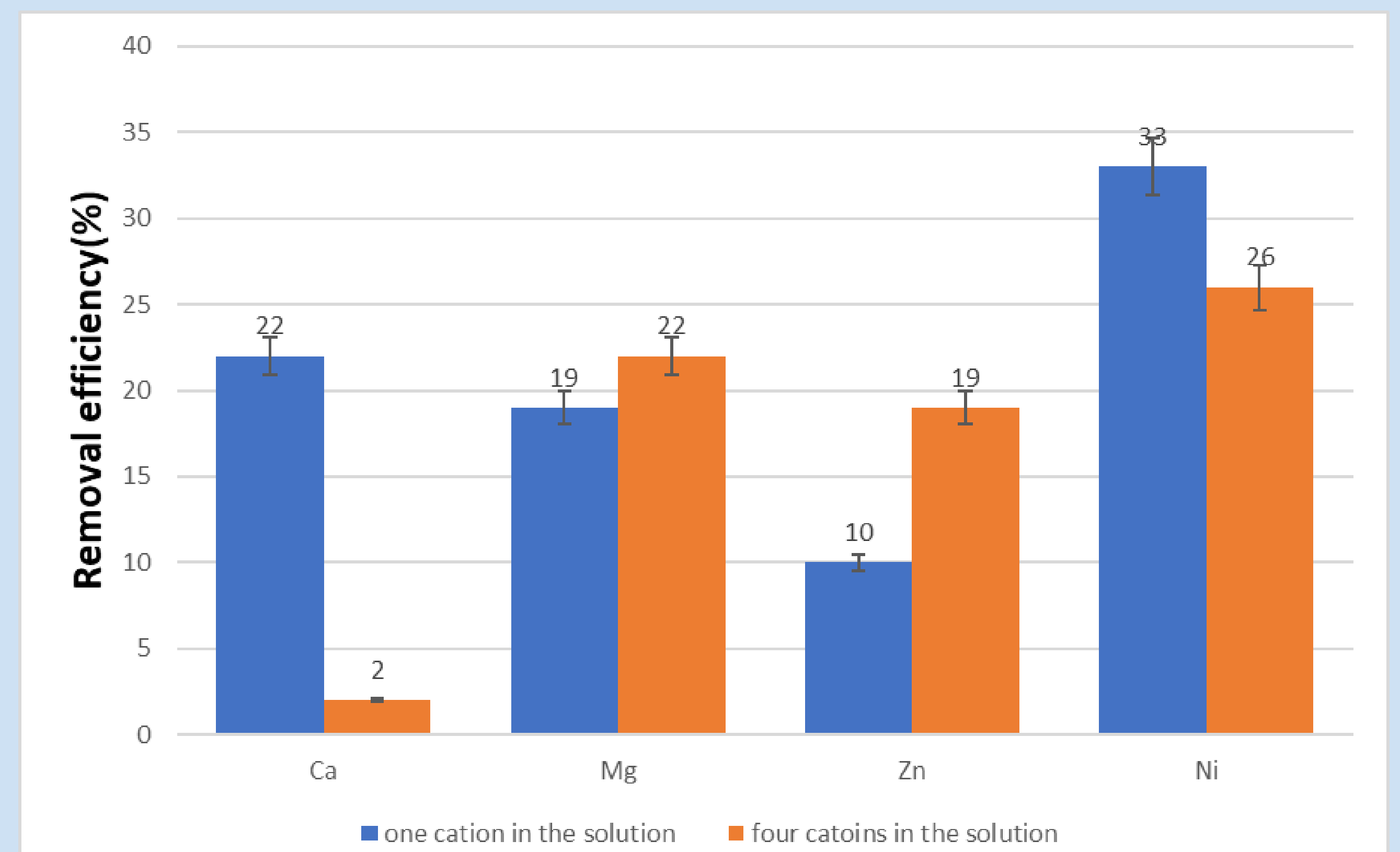


Fig. 1. Cation removal efficiency using iron-chloride at molar ratios of 1:1:5 and 1:4:5 (organic compounds: cation: iron) depending on the number of cations in the solution

## Treatment

Two experiments were carried out with two different solution series containing chlorobenzene compounds, NaHCO<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, MgSO<sub>4</sub>, ZnSO<sub>4</sub> and NiSO<sub>4</sub>, as well as FeCl<sub>3</sub> or Na<sub>2</sub>FeO<sub>4</sub>. The molar ratio of chlorobenzene compounds related to cations and iron were selected to 1:1:5 or 1:4:5 depending on the number of cations added to the solutions. In the case of experiment with FeCl<sub>3</sub>, NaOH was added to the solution in order to simulate the change of pH similarly to the ferrate treatment. After the formation of Fe(OH)<sub>3</sub> the pH was adjusted to 7 by addition of 5 M H<sub>2</sub>SO<sub>4</sub> and the suspension was mixed for 30 minutes.

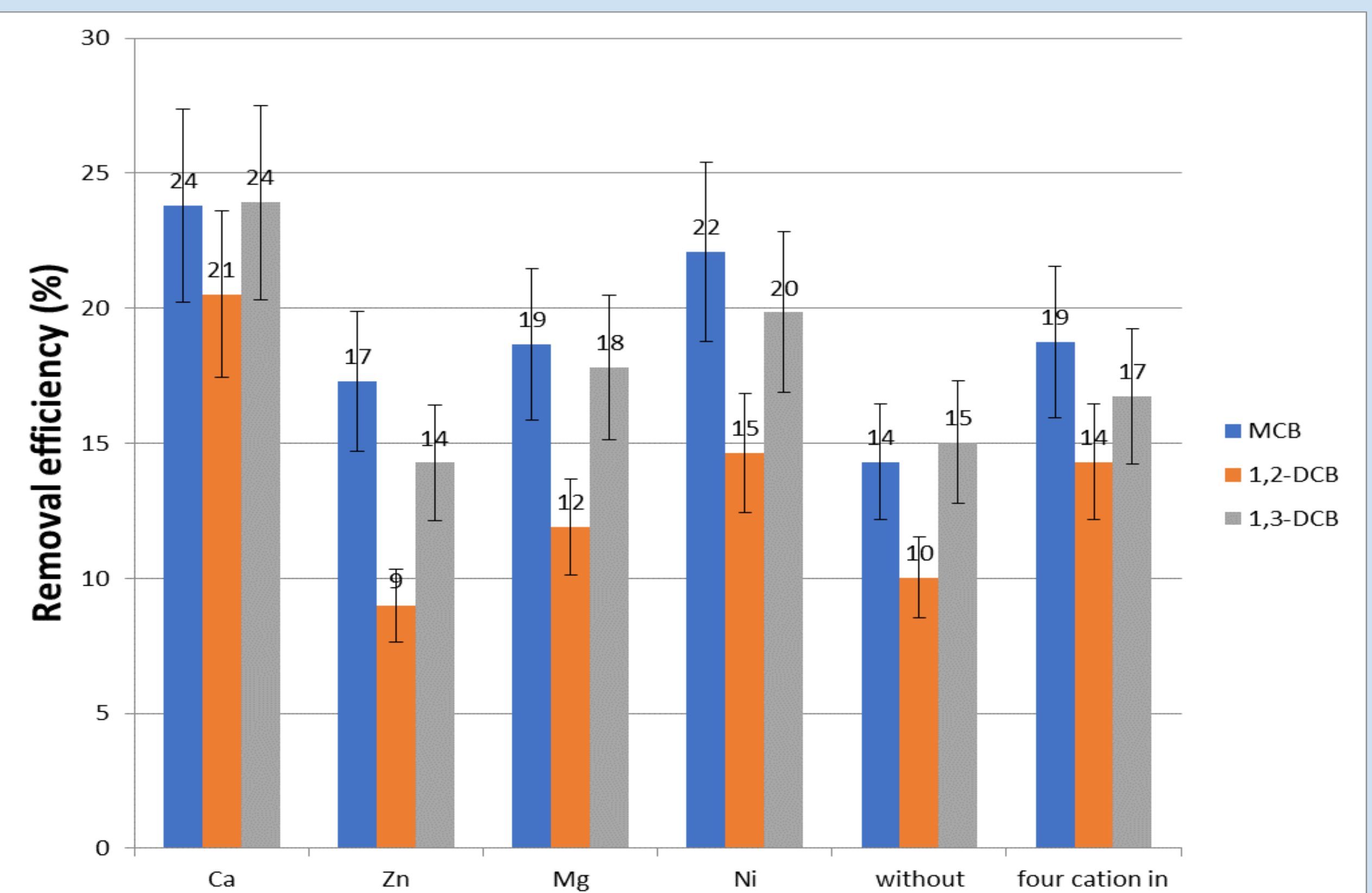


Fig. 3. Removal efficiency of chlorobenzene compounds after ferrate treatment at molar ratios of 1:1:5 and 1:4:5 (organic compounds: cations: iron) in absence or presence of one or four cations

## Results

### Treatment by iron-chloride

The formation of Fe(OH)<sub>3</sub> precipitation had not any influence on the concentration of chlorobenzene compounds in the solutions. This observation was stated both by HS/GC-MS and POC measurements. However, the precipitation adsorbed cations at added cation/iron molar ratio of 1:5 and 4:5 in the following order, Ni > Ca > Mg > Zn, and Ni > Mg > Zn > Ca, respectively (Fig. 1).

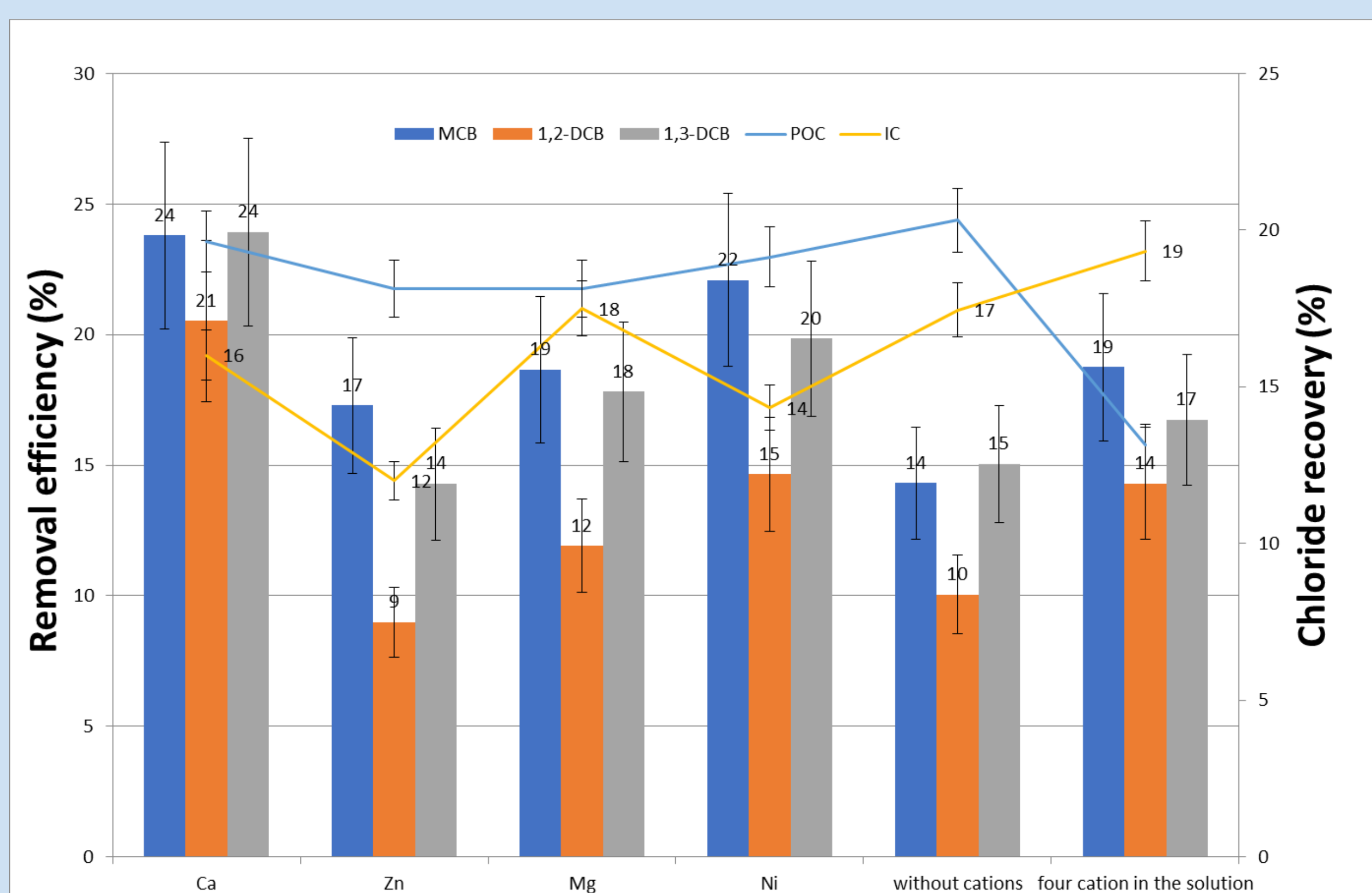


Fig. 4. Removal efficiency of chlorobenzene compounds, POC values and chloride concentrations after ferrate treatment applied at molar ratios of 1:1:5 and 1:4:5 (organic compounds: cation: iron) in absence or presence of one or four cations

### Treatment with ferrate solution

- At molar ratios of 1:1:5 the presence of Ca had a strong influence on the removal of CB compounds (Fig. 2.) and in addition the largest part of Ca remained in the solution phase (Fig. 3.).
- Zn, Mg and Ni had lower but nearly similar effect on the removal of CB compounds, however, considerable amounts of these elements could adsorbed on the Fe(OH)<sub>3</sub> precipitation.
- The 1,2-dichlorobenzene (DCB) was the less degradable compound.
- In absence of cations the CB removal was the lowest. It means the removal efficiency can be increased by addition of different cations and first of all Ca can be recommended for these purposes.
- The results of POC measurements harmonize with the HS/GS-MS data and the changes of chloride concentrations.

## Conclusions

Adsorption of CB compounds on Fe(OH)<sub>3</sub> precipitation does not play any role in the CB removal from groundwater based on the experiments with iron-chloride. Ferrate treatment resulted in 15-25% removal of CB compounds depending on the presence of different cations. Due to adsorption and co-precipitations of cations investigated on the Fe(OH)<sub>3</sub>, their removal amounted to 40-80% for Mg, Zn, and Ni, however, for Ca this value remained below 20%. The ferrate treatment resulted in approximately twice higher cation removal compared to the iron chloride treatment.

