

Influence of catalyst zeta potential on the activation of persulfate

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The effect of the zeta potential of nano zero-valent iron (nZVI) and carbocatalyst on the activation of persulfate was investigated. The oxidation experiments were performed on three different compounds, with variously modified nZVI and three distinct carbocatalysts. From the obtained results, an evident linear correlation between nanoparticles' zeta potential and reaction rate constants of these three compounds oxidation may be observed. This phenomenon is not mechanism-specific and occurs for the radical and non-radical processes. The present work indicates the critical influence of the surface charge of nZVI and carbocatalysts on the persulfate catalytic activation.

Klíčová slova: catalyst, nZVI, persulfate, pollutants, oxidation

Úvod

Nanotechnology has attracted increasing interest in various research areas due to the versatility of nanomaterials [1]. Among environmental applications, nanotechnologies are frequently used in water treatment [2].

One of the nanomaterials often used in environmental applications is zero-valent iron (ZVI). This is considered a moderately strong reducing agent, which may be used to eliminate several contaminants in groundwater [3]. Zero-valent iron nanoparticles (nZVI) are manufactured by different methods but mainly by chemical reduction of iron(III). The modification of nZVI particles plays a crucial role in improving their properties, from which the most common practice is surface coating and emulsification.

nZVI may be used for direct treatment of a wide range of pollutants, and has recently been applied for the activation of peroxydisulfate (PDS, persulfate) and hydrogen peroxide. The catalytic activation of these oxidants aims to produce more reactive hydroxyl and sulfate radicals, which are responsible for the degradation of contaminants. They can be used to treat water contaminated by e.g. chlorinated ethenes, micropollutants, hexachlorocyclohexanes, and many others. Persulfates may be directly catalyzed on the surface of nZVI to form free radicals.

Zeta potential is a parameter describing charge of the nanoparticles. While the zeta potential may be used for the general evaluation of nanoparticle stability, we hypothesize that it can be used for better understanding and enhancing the catalytic processes

To the best of our knowledge, this is the first work that evaluates the influence of zeta potential on the improvement of the catalytic activation of PDS by metal nanoparticles. The present work investigates the effect of changing the zeta potential of nZVI by stabilization using two different polymers with opposite charges, i.e., positive - chitosan (CS) and negative - polyacrylic acid (PAA). Such coated nanoparticles were used as PDS activators to oxidize three different compounds in a broad pH spectrum. As further confirmation, different carbonaceous materials were tested to confirm the role of surface charge for the activation of PDS.

Metodika

The activation of PDS was performed with three different surface-modified nZVI and three different carbonaceous materials. Three different pollutants were tested to understand the correlation between the catalyst zeta potential and the PDS radical production rate. While the sulfamethoxazole (SMX) oxidation test was performed at pH 3.0 and 5.0, the methyl orange (MO) oxidation experiment (for nZVI) was performed in a near-neutral pH (and in various pH values for the carbonaceous materials), and 4-nitrophenolate at pH 11. The reaction kinetics were fitted using the pseudo-first-order kinetic model. All the surface-modified nZVI were created in such way that the variances in size, morphology and ZVI content would be minimal. Therefore, the differences in rate constants could practically be assigned solely to the different surface properties of the nZVI.

Výsledky a diskuze

Fig. 1a shows the evolution of the zeta potential as a function of pH for the three different nZVI samples.

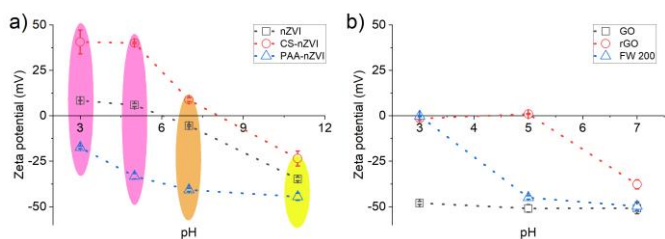


Fig. 1 Zeta potentials of a) nZVI, CS-nZVI and PAA-nZVI at different pH values. The pink, orange, and yellow ellipses mark the pH range used for the SMX, MO and 4-NP oxidation experiments, respectively; b) zeta potentials of GO, rGO and FW 200 at different pH values. The lines were drawn to guide the eye of the reader.

All three curves have the typical S-shape for the higher pH to more negative values due to the presence of hydroxide ions, which neutralize the positive charges of the nanoparticles. In the case of nZVI modified by PAA, the zeta potential has a negative value in the whole pH range (-17 ± 1 mV at pH 3.0, -33 ± 1 mV and at pH 5.0, -41 ± 1 at pH 7.0, -45 ± 2 mV at pH 11.0). The other two nZVI samples (pristine nZVI and CS-nZVI) behave in a similar way. In a low pH range (pH 3.0 and 5.0), the zeta potential values are positive (around 40 mV for CS-nZVI in both pH values; 8 mV for pH 3.0, and 6 mV for pH 5.0 for nZVI); at a neutral pH, the value is around zero (9 ± 1 mV for CS-nZVI and -5 ± 1 mV for nZVI); and for a higher pH, it is negative (-35 ± 1 mV for nZVI, -23 ± 4 mV for CS-nZVI, respectively). The addition of CS did not change the character of the curve but increased the absolute value of the zeta potential. Zeta potential of carbonaceous materials is reported in **Fig 1b**. Significant differences in the profile of the zeta potential between the nZVI species confirmed the success of the nanoparticle modifications and enabled the PDS activation tests to be performed. The removal of three different pollutants at different pH values (namely SMX at pH 3.0-5.0, MO at 7.0 and 4-NP at 11.0) was tested to understand the correlation between the catalyst zeta potential and the PDS radical production rate. Apparent rate constants (k_{app}) of the pseudo-first-order reaction are proportional to the nZVI zeta potential (**Fig. 2a**). Namely, the highest is for PDS activated by CS-nZVI at pH 5.0 ($\zeta = +40$ mV, CS-nZVI had almost identical zeta potential at pH 3.0 and 5.0), then by PAA-nZVI at pH 3.0 ($\zeta = -17$ mV) and the lowest is for pH 5.0 ($\zeta = -33$ mV). Similarly, MO was used as a model compound at a neutral pH. Similar to the trend shown in previous tests, MO removal and corresponding rate constants (**Fig. 2b**) are higher for the more positive zeta

potential values of nZVI (for nZVI $\zeta = -5$ mV, for CS-nZVI $\zeta = 9$ mV, and for PAA-nZVI $\zeta = -41$ mV).

The rate constant again correlated linearly with the zeta potential. The correlation between the zeta

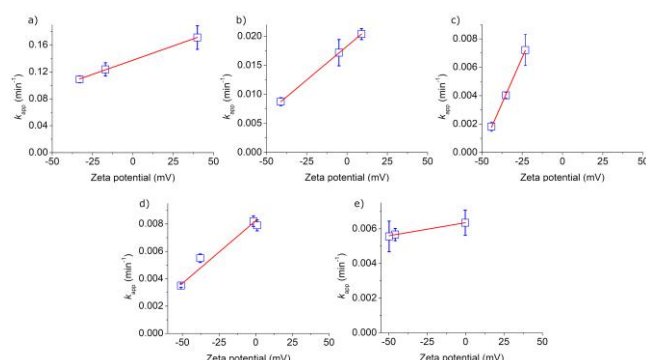


Fig. 2 The correlation between the zeta potential values of the nZVI and k_{app} of a) SMX b) MO, c) 4-NP oxidation, d) correlation between the zeta potential values of the GO/rGO and k_{app} of MO oxidation, and e) correlation between the zeta potential values of the FW 200 and k_{app} of MO oxidation (all reaction conditions are listed in the methodology section).

potential of nZVI and rate constants of oxidation was also investigated at a high pH (pH = 11.0). Similarly, as the zeta potential increased, a higher reaction rate constant was recorded (**Fig. 2c**). The less negative zeta potential of the catalyst resulted in a better activation of persulfate.

Závěr

To the best of our knowledge, the present article reports the close correlation between the zeta potential values of catalysts and the k_{app} of the oxidation of several organic compounds for the first time; and provides insights in the understanding of the heterogeneous activation of PDS.

Poděkování

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Reference

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