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CHEMICAL REDUCTION OF NITRATE BY ZEROVALENT IRON NANOPARTICLES ADSORBED RADIATION GRAFTED COPOLYMER MATRIX

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INTRODUCTION

Nitrate contamination of global water resources due to globalization of modern agricultural practices is an emerging threat worldwide. Nitrate is potentially hazardous when present in drinking water at sufficiently high concentrations. Due to its high solubility nitrate may actually be the most widespread and priority contaminant in drinking water [1]. It acts as a precursor for several health hazards ranging from blue baby syndrome to gastric cancer. Treatment of nitrate containing water is challenging due to its stability. Since it neither forms insoluble minerals that could be removed as precipitates nor significantly adsorbs under aquifer conditions, reduction is the only possible way to fully remove nitrate contamination from ground water The nitrate molecule is a good electron acceptor and hence nZVI can play a major role due to its extremely small size and strong reduction capacity [2]. The results obtained in this work suggest that metallic-Fe can support chemical reduction of nitrate contaminated water. This research specifically focuses on the development of novel methodologies to reduce excess nitrate in drinking water utilizing nZVI stabilized radiation grafted copolymer matrix.

METHODOLOGY

Preparation of NWPE/PP-g-PAA

Figure 1: Schematic diagram for preparation of NWPE/PP-g-PAA

DG % = $[(W_g - W_o)/ W_o] \times 100$

DG Degree of grafting
W_o initial weight
W_g final weight after grafting

Stabilization of nZVI in NWPE/PP-g-PAA

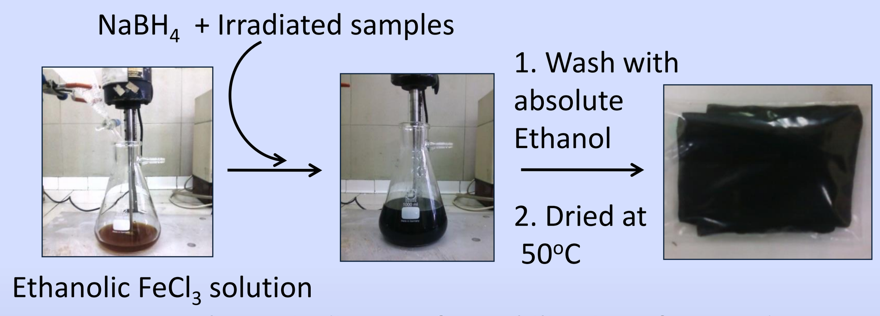


Figure 2: Schematic diagram for stabilization of nZVI-Ads-NWP

$$2FeCl_{3(aq)} + 6NaBH_{4(aq)} + 18H_2O_{(l)} \longrightarrow 2Fe^0_{(s)} + 6NaCl_{(aq)} + 6B(OH)_{3(aq)} + 21H_{2(g)}$$

0.723 M NO_3^- solution — 1.2 g/ L nZVI-Ads-NWP, 24 h

- Iron → Ion Chromatography: $4 Fe^0 + NO_3^- + 7 H_2O \longrightarrow 4 Fe^{2+} + NH_4^+ + 10 OH^-$
- Ammonia → NH_3 Electrode: $4 Fe^0 + NO_3^- + 10 H^+ \longrightarrow 4 Fe^{2+} + NH_4^+ + 3 H_2O$

RESULTS AND DISCUSSION

Effect of initial pH on nitrate reduction

At pH 3.0

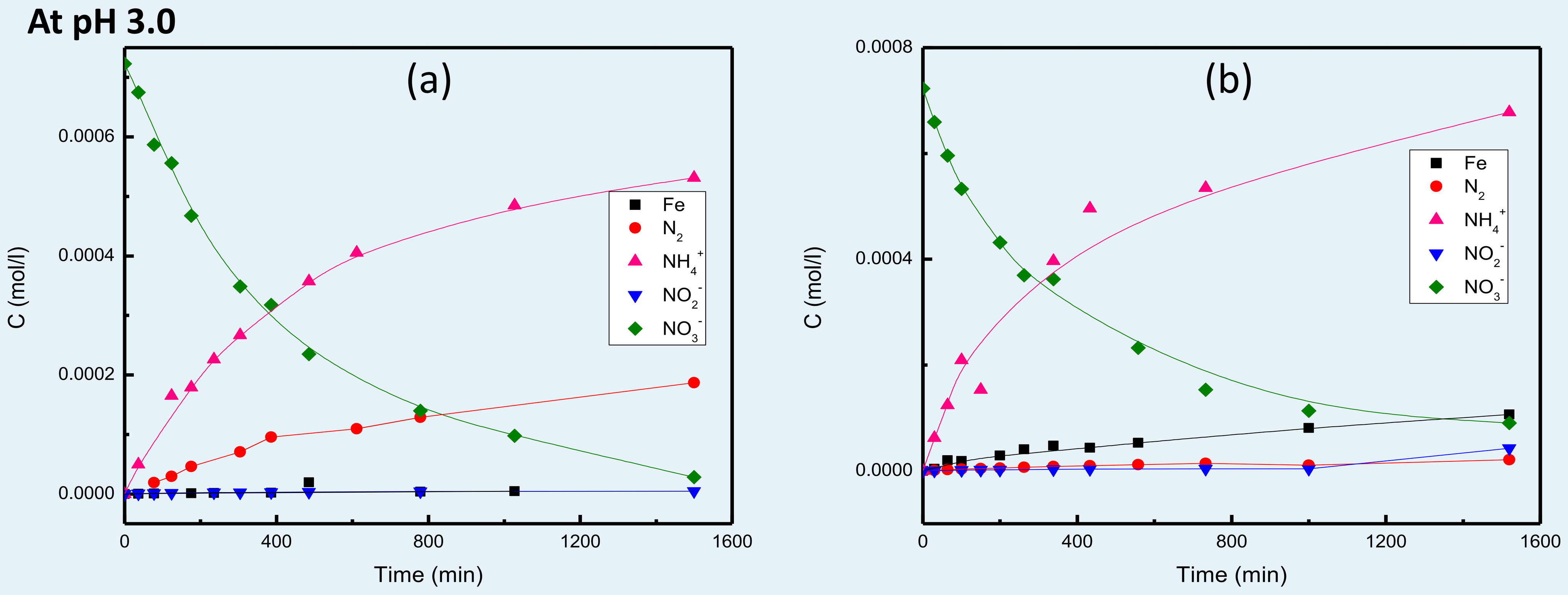


Figure 3: Effect of pH on nitrate removal at pH 3.0 for (a) nZVI-Ads-NWP (b) ZVI

Table 1: Percentage values for reduction of nitrate at different pH

Initial pH	nZVI-Ads-NWP	ZVI
3.0	96.07	78.29
4.0	87.50	73.67
5.0	79.55	39.49

- According to characterization data, the surface of nZVI contains ferrous hydroxide and other protective layers due to core-shell structure [3].
- At low pH values, these protective layers can be readily dissolved exposing pure iron particles for efficient chemical reduction of NO_3^- [4].

Modelling : 1 – pK BSM approach

Aim: To develop a surface complexation model for bond formation between nZVI and carboxylic group on the grafted surface.

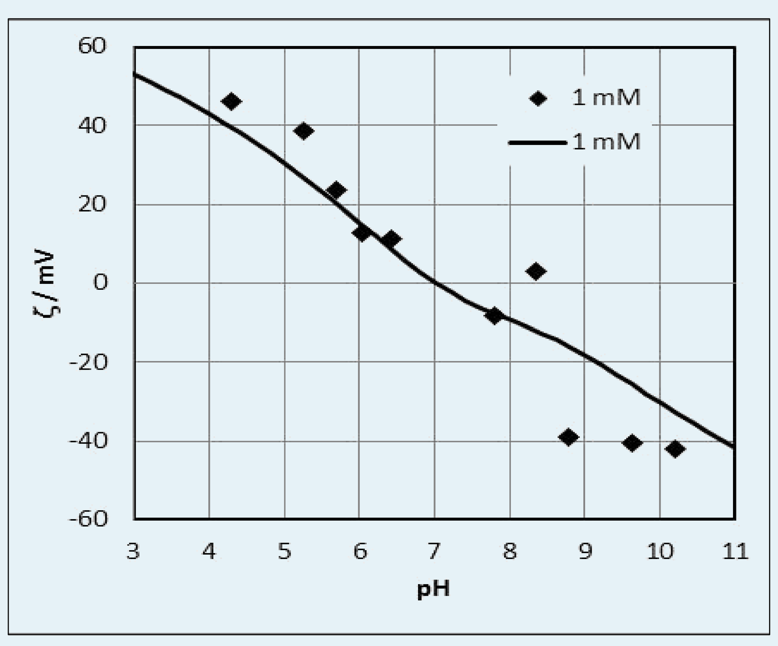


Figure 4: Variations of zeta potential as a function of pH

1-pK BSM: only one reaction can describe protonation/ deprotonation of surface according to:

$$\equiv MOH_2^{0.5+} \longleftrightarrow \equiv MOH^{0.5-} + H^+$$

Surface site protonation according to 1-pK approach.

Data fitting:
FTTEQL2 – equilibrium calculations
UCODE – parameter optimizations

Interpretation of nitrate reduction kinetics by nZVI

Suggestion: Eley-Rideal like mechanism as supported by FTIR data

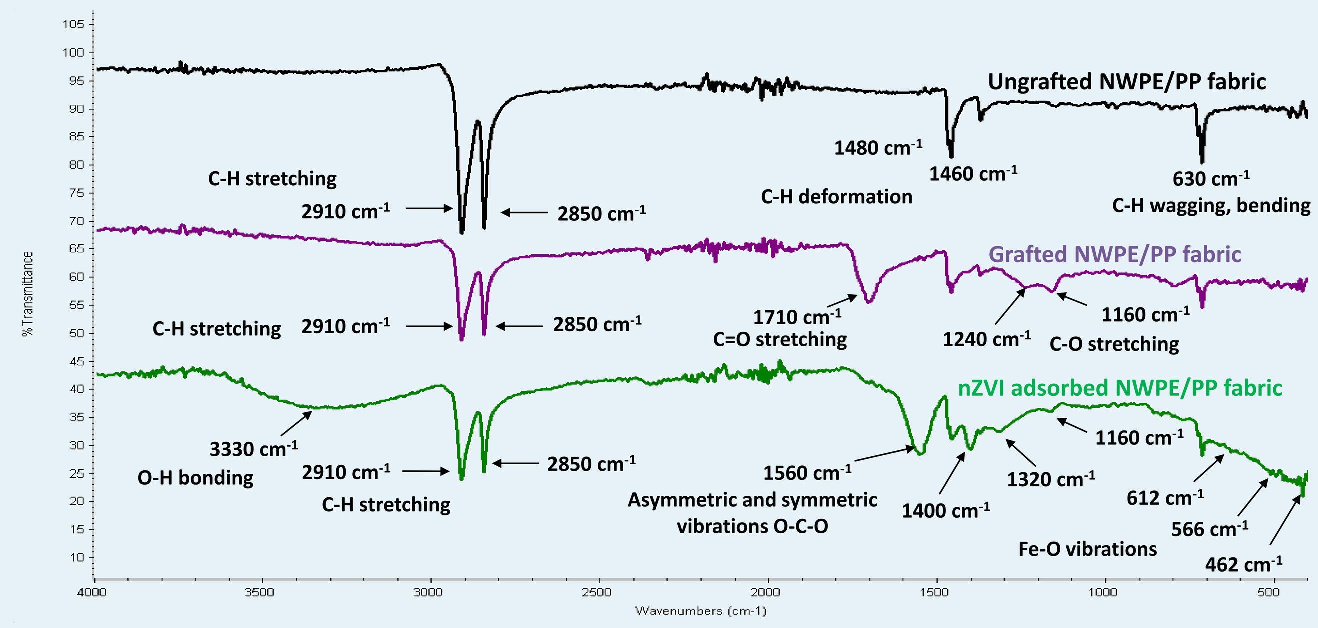


Figure 5: ATR-FTIR spectra of ungrafted NWPE/PP, NWPE/PP-g-PAA, nZVI-Ads-NWP fabric

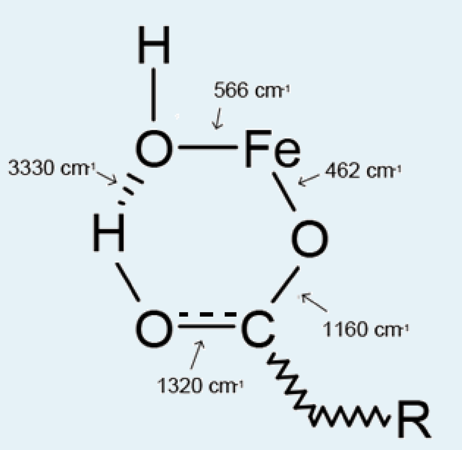


Figure 6: Predicted monodendate surface complex between nZVI sites and –COOH

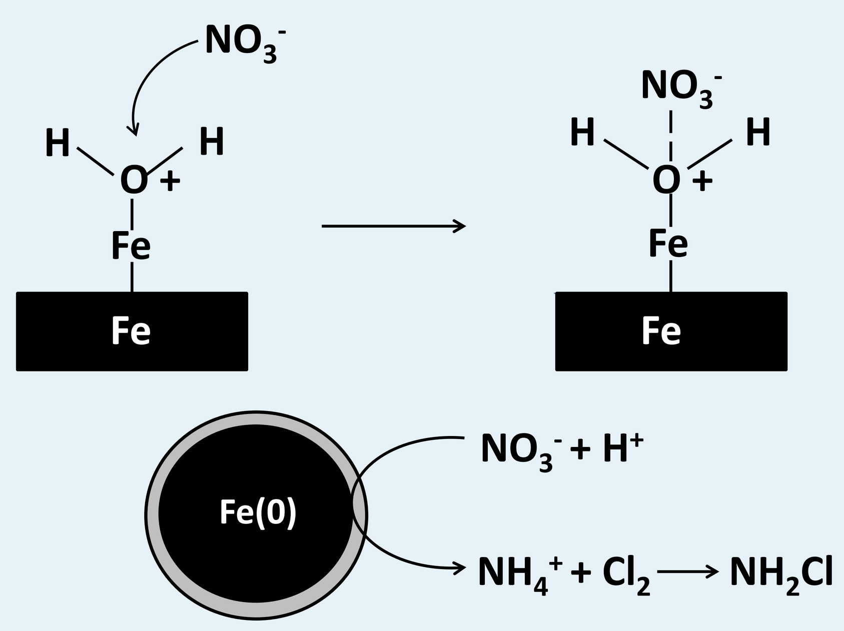
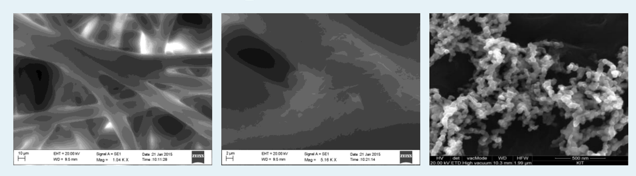


Figure 7: Interpreted Eley-Rideal like mechanism for reduction kinetics of nitrate by nZVI

Characterization [3]

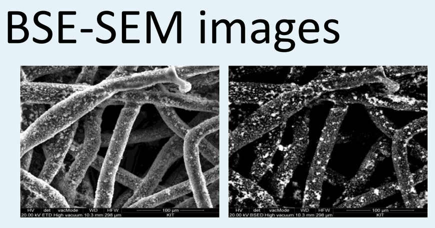
SEM Images

SE-SEM images



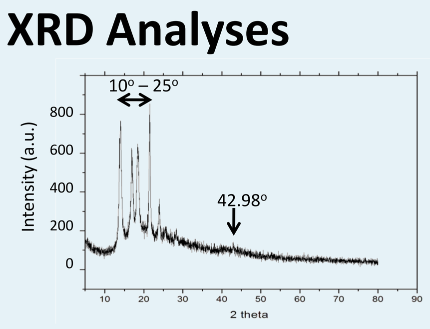
- Increase in diameter
- Protrusion
- Well anchored onto grafted surface in the form of chain like aggregated nanospheres

BSE-SEM images



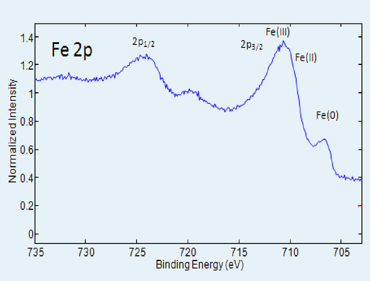
- Bright areas - high electron density - metallic iron
- Grey areas - low density - magnetite

XRD Analyses



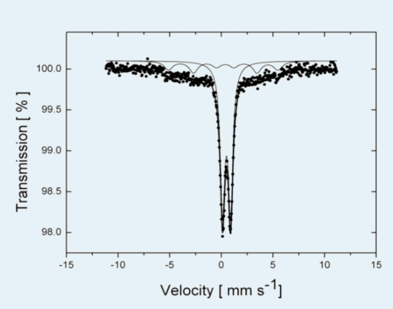
- 2θ of 10° – 25°: crystallinity of polymer matrix part
- 2θ of 42.98°: presence of zero-valent iron (α-Fe)

XPS Analyses



- 706.5 eV denotes $Fe2p_{3/2}$ implies presence of Fe^0 at core of nZVI
- 710 and 719.6 eV elemental line and satellite shake-up characteristic for Fe(III)

Mössbauer Analysis



- Major paramagnetic doublet represents phase composition of iron oxide shell
- Minor broad magnetic sextet corresponds to phase compositions of iron core
- Small contribution of sextet to total spectrum due to refinements of structure to nm level

CONCLUSION

Nitrate reduction by nZVI is an acid-driven surface mediated process. nZVI water interface is characterized by 1-pK Basic Stern Layer Model (BSM) and an Eley-Rideal like mechanism can be used to describe nitrate reduction kinetics. In accordance with green technology, such nZVI-Ads-NWP has a great potential in improving the nitrate reduction process required in drinking water industry.

REFERENCES

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