X-ray Photoelectron Spectroscopic Probing of Nano-zero Valent Iron Assisted Nitrate Degradation

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Excess nitrate adversely contributes to groundwater pollution. However, nitrate remediation is not an easy task. Upon boiling it concentrates, and does not sorb, in significant amounts, onto soils or other surfaces. Metallic iron (Fe) is an attractive alternative for nitrate reduction compared to conventional treatment processes. In this research nano zero valent iron-reduced graphene oxide composite (nZVI-rGO) was synthesized using modified Hummers method. Polyphenols derived from natural tea leaves were used to reduce Fe^{2+}/Fe^{3+} into Fe. All X-ray photoelectron spectroscopic (XPS) measurements were carried out by an XPS (5000 VersaProbe II ULVAC-PHI Inc., Japan) system equipped with an X-ray source (monochromatic Al K_α 1486.7 eV X rays). These measurements were used to elucidate the surface sites and the oxidation states of nitrogen adhered to the surface of nZVI-rGO. At 5.6 pH, composite material reduce 70% of 0.8064 mM nitrates within an hour at 25℃. However, the mechanistic steps of nitrate reduction are inconclusive to date. The Fe-XPS signal was assigned to oxidized Fe signaling surface oxidation, and Fe(0) within the core-shell structure of nZVI-rGO. The N 1s transition indicates the aromatic N presence in polyphenols. After nitrate reduction, ammonia accounts for 95% of the nitrogen mass balance with N_2, NO and NO_2^- traces. The peak at 706.7 eV contributes to Fe(0) was disappeared and the intensity of the Fe(II) and Fe(III) peaks decreased. During the reduction, oxidized Fe^{2+}(aq) was converted into Fe_3O_4 via spontaneous electron transfer between the Fe^{2+} and the pre-existing surface Fe^{3+} oxides and enhanced the nitrate removal efficiencies. nZVI reduces nitrate into NO, which has a high electron density. This NO can easily trap free electrons and form negatively charged NO^-. The adsorbed NO^- to the cationic iron oxides sites of nZVI-rGO surface identified by N 1s transition peak at 401.7 eV. Further research is required for the identification of nitrogen-containing groups of natural green tea leaves polyphenols to confirm the surface sites of nitrogen.

Keywords: Nano-zero valent iron; Nitrate reduction; Polyphenols; Reduced graphene oxide; X-ray photoelectron spectroscopy