

Decontamination of TNT, RDX, and HMX High-Explosive Groundwaters by Zero-Valent Iron Nanoparticles

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Currently, soils and groundwaters were polluted by explosives-contaminated wastewaters discharged from military factory worldwide. These high-explosives are toxic to human beings and very difficult to be removed from the environment. Therefore, a highly efficient and clean method was developed utilizing zero-valent iron nanoparticles (ZVINs) to reduce the explosives-contaminated wastewaters. In this research, HPLC, LC/MS, and GC/MS were used to determine the efficiency of degradation, kinetic model, thermal model, activation energy, and reaction pathways. Moreover, the properties of ZVINs after degradation were also analyzed by FE-SEM, TEM, XRD, ESCA, BET, and XANES/EXAFS techniques.

Experimentally, ZVINs with a diameter of 50-80 nm and specific surface area of 42.58 m²/g were measured by FE-SEM and BET. The ZVINs had a strong characteristic peak at $2\theta = 44.6^\circ$ investigated by XRD patterns. In the degrading experiments, 100 ppm TNT, 35 ppm RDX and 5 ppm HMX were degraded at room temperature ($25 \pm 1^\circ\text{C}$) completely with 0.1 g ZVINs within 1 h. The experimental results were placed into a simple Langmuir-Hinshelwood equation ($\ln(C_0/C_a) = kt$) and the r^2 were all upon 0.995. However, the degradation statistics corresponded to the pseudo first order kinetics. The thermodynamics study was carried on three different high-explosives under 25-35°C and the activation energies of TNT, RDX and HMX were calculated to 9.74, 10.08 and 12.46 kcal/mol by Arrhenius equation, respectively.

In reductive degradation processing, the ZVINs were chemically reduced and sheet-typed nanopowders were found. Meanwhile, the surface of Fe, FeO, Fe₃O₄, and Fe₂O₃ species were also measured by ESCA and the crystalline structures were similar with Fe₃O₄ and Fe₂O₃ species identified by XRD patterns. In addition, the valence of ZVINs after degradation was 8/3 shown in XANES spectra. The coordination number of Fe atom was close to 4 and the bond distance of Fe-O was about $1.94 \pm 0.01 \text{ \AA}$ determined by EXAFS analysis.

Keywords: Zero-valent iron nanoparticle, High-energy explosives, TNT, RDX, HMX, Reductive degradation, XANES/EXAFS.

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