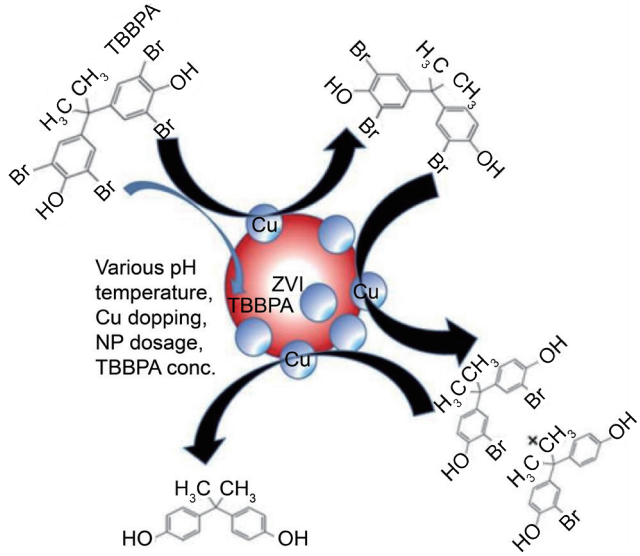
Nano-Iron Rapidly Degrades Toxic Pollutants

Nanoscale bimetallic zerovalent iron particles rapidly degrade halogenated contaminants in water.



Known and emerging persistent organic pollutants (POPs) have garnered attention due to their presence in environmental matrices and their adverse health and ecological effects; this is primarily true for POPs with halides, such as pentachlorophenol (PCP), polybrominated diphenyl ethers (PBDEs), and tetrabromobisphenol A (TBBPA). Yang-Hsin Shih and his collaborators (National Taiwan University) developed several nanomaterials and investigated the ability of specific microbes to effectively degrade POPs and several emerging organic contaminants.[1,2] PBDEs and TBBPA are applied to polymeric materials in the production of brominated flame retardants (BFRs). Studies have reported PBDE contamination in several sites in Taiwan; furthermore, crops growing in contaminated soil uptake PBDEs. This novel study utilized the debromination mechanism and absorptive capacity of nanoscale zerovalent iron (NZVI) to rapidly remove PBDEs. However, NZVI cannot dechlorinate PCP. The modification of the NZVI surface with a second metal enhances the reactivity of particles, causing them to behave as electron transferrers. Pd and Fe nanoparticles (NPs) effectively remove PCP. For common cations, the enhancement of Cu^{2+} and Ni^{2+} ions was achieved by doping the reduced forms of Cu and Ni on the Pd and Fe surfaces using X-ray Near Edge Spectrometry (XANES) analysis. Ni–Fe and Cu–Fe NPs were later developed to enhance PCP removal.[3,4] For Cu–Fe bimetallic nanoparticles (Cu–Fe BNPs), the TBBPA removal rate and debromination efficiency increased with higher Cu doping content, higher temperature, and lower pH. One study analyzed the complete debromination pathway and the time evolution of intermediate byproducts at different pH values.[4] Cu–Fe BNPs can be used more than six times and thus serve as stable and reusable catalysts. Genotoxic test results of the treated solution indicated no notable hazardous potential. Moreover, the Fenton reaction can be employed to degrade byproducts using additional H_2O_2.

Spectra obtained from an analysis of the particles with X-ray diffraction at 2θ = 44.1° and 43° at **TLS 13A1** revealed zerovalent states of Fe and Cu, respectively (**Fig. 1(a)**).[4] After the reaction, the researchers discovered peaks of FeO_x instead of Fe^0. Shih's team used XANES at **TLS 17C1** to further analyze the particles.[4] The normalized Fe K-edge spectra of the bimetallic nanoparticles (**Fig. 1(b)**) revealed an obvious absorbance feature from 7112 to 7115 eV, which also corresponds with zerovalent Fe. Cu transferred electrons from Fe to pollutants to promote dehalogenation. Cu–Fe BNPs with a Cu content of 4% had the best reactivity.

Cu–Fe BNPs are promising as a means to treat BFRs. Furthermore, compared with several surfactants, cetyl trimethylammonium bromide (CTAB) was observed to markedly enhance the removal of PCP with Ni–Fe NPs.[3] The small particle size of Ni–Fe CTAB and the electrostatic interaction between electronegative phenolate groups of PCP and electropositive Ni–Fe CTABs increased the

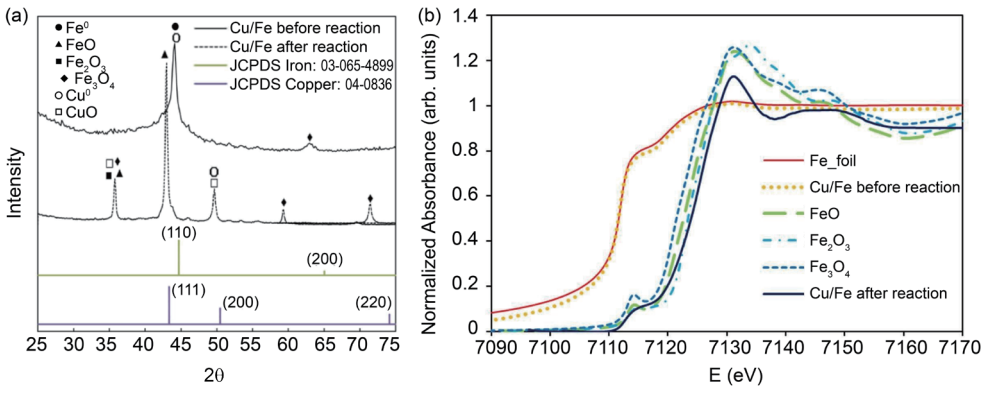


Fig. 1: (a) XRD pattern of Cu–Fe BNPs before and after reaction (b) Fe K-edge XANES spectra of Cu–Fe BNPs before and after reaction. [Reproduced from Ref. 4]

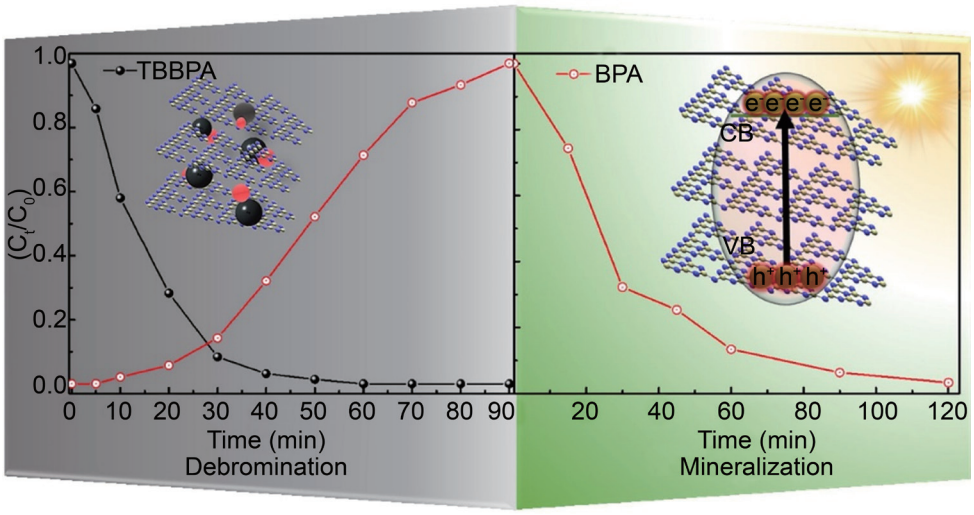


Fig. 2: Sequential debromination of TBBPA in the absence of light and BPA mineralization under solar light irradiation using exfoliated graphitic carbon nitride. [Reproduced from Ref. 6]

absorption of PCP onto Ni–Fe surfaces by CTAB and accelerated the reduction of PCP. In addition, the combination of CTAB with the bulky, soft surface of Ni–Fe NPs enabled enhanced electron transfer from the zerovalent Fe core. Short-chain organic acids were also evaluated to avoid the use of metal. Oxalic acid (OA) enhanced PCP degradation by NZVI compared with other short-chain organic acids. OA yielded the highest efficiency of PCP dechlorination by NZVI due to its strong complexation and pH buffering properties. This environmentally safe treatment strategy does away with the need for doping with secondary metals and facilitates the decontamination of POPs. This study also synthesized TiO_2 nanotubes to effectively degrade antibiotic sulfamethoxazole by photoelectrocatalysis. This team of researchers recently synthesized graphitic carbon nitride (g-C_3N_4) with Fe–Cu NPs and graphene quantum dots (GQDs)/g-C_3N_4 nanocomposites; both are ecologically sound materials for organic pollutant degradation—namely, for TBBPA and its byproduct bisphenol A.[5,6] **Figure 2** illustrates a potential solution for complete TBBPA degradation by g-C_3N_4. (Reported by Yun-Cheng Mei and Kai Wang, National Taiwan University)

This report features the work of Yang-Hsin Shih and his collaborators published in J. Hazard. Mater. ***432****, 128630 (2022).*

TLS 13A1 X-ray Scattering
TLS 17C1 EXAFS

- XRD, XANES
- Chemistry, Physics, Materials Science, Environmental Science

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