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Hybrid composites of nano-sized zero valent iron and covalent organic polymers for groundwater contaminant degradation

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Abstract:
Zero valent iron is commonly used in a variety of treatment technologies (e.g. permeable reactive barriers), though recently a heavier focus has been placed on nano-sized zero valent iron (nZVI). Having superior reductive properties and large surface areas, nZVI is ideal for the degradation of chemicals such as azo dyes and trichloroethylene (TCE). However, stabilization and immobilization of nZVI is a key parameter in its effectiveness as a chemical degradation agent for both *in-situ* and *ex-situ* applications. Most importantly, this inhibits unwanted iron oxidation from the environment and prevents particle agglomeration; but also still allows for contaminant diffusion into the composite matrix, leading to degradation. In this study, the effect of various covalent organic polymers (COPs) as effective supporting materials for nZVI for optimal pollutant degradation was assessed. These COPs demonstrate promising results for the ability to adsorb and remove carbon dioxide, yielding the notion that they are capable of groundwater contaminant removal. Composites of nZVI impregnated within COPs of high surface areas exhibit effective ability to degrade azo dyes, up to 95%, over a 30-minute reaction period. Dye decolorization results were designated a precursor for effectiveness of pollutant decontamination; pollutants ranging in chlorinated organics, heavy metals, and various other groundwater contaminants.

Using transmission electron microscopy (TEM), dimensional extrapolation of composite widths were on average approximately 6nm, with extremes at 2.5nm and 24nm. Composite lengths exhibited much more variance, and although the average was approximately 110nm, many lengths were observed as low as 50-70nm and as high as 260-280nm ranges.

BET surface areas of the polymers were as small as 1.8m^2/g using COP47, and as large as 600m^2/g using COP19. Degradation of acid black I exhibited very fast kinetics within the first 2.5 minutes, with a strong plateau effect thereafter for 30 minutes, plotted in Figure 1. Ultimately, dye removal rates were as high as 95% in COP19 and as low as 42% in COP48. Removal efficiency was determined to be a function of the BET surface area, as well as individual properties of the core/linker molecular make-up of each COP. The parallel control experiment with nZVI and COPs clearly indicated the azo dye removal mechanism by COP-nZVI-composite, the synergistic effect of adsorption onto COPs and reduction by impregnated nZVI. This translates well for treatment of many groundwater pollutants, with similar trends in abilities of each composite to degrade pollutants.

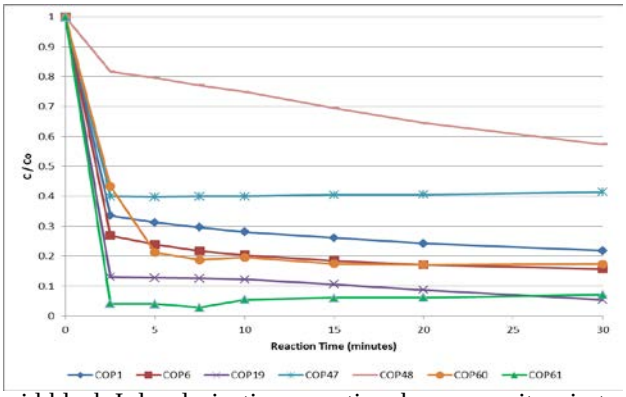

Figure 1 Reaction kinetics of acid black I decolorization over time by composites, in terms of peak absorbance values, using UV-Vis spectrometry; initial peak absorbance (λ_{max} = 618nm) at 60µM was approx. 3.14.

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