Metal-Free Catalysis of Persulfate Activation and Organic-Pollutant Degradation by Nitrogen-Doped Graphene and Aminated Graphene

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Abstract
We evaluated three types of functionalized, graphene-based materials for activating persulfate (PS) and removing (i.e., sorption and oxidation) sulfamethoxazole (SMX) as a model emerging contaminant. Although advanced oxidative water treatment requires PS activation, activation requires energy or chemical inputs, and toxic substances are contained in many catalysts. Graphene-based materials were examined herein as an alternative to metal-based catalysts. Results show that nitrogen-doped graphene (N-GP) and aminated graphene (NH2-GP) can effectively activate PS. Overall, PS activation by graphene oxide was not observed in this study. N-GP (50 mg L\(^{-1}\)) can rapidly activate PS (1 mM) to remove >99.9% SMX within 3 hours, and NH2-GP (50 mg L\(^{-1}\)) activated PS (1 mM) can also remove 50% SMX within 10 hours. SMX sorption and total removal was greater for N-GP, which suggests oxidation was enhanced by increasing proximity to PS activation sites. Increasing pH enhanced the N-GP catalytic ability, and >99.9% SMX removal time decreased from 3 hours to 1 hour when pH increased from 3 to 9. However, the PS catalytic ability was inhibited at pH 9 for NH2-GP. Increases in ionic strength (100 mM NaCl or NaSO\(_4\)) and addition of radical scavengers (500 mM ethanol) both had negligible impacts on SMX removal. With bicarbonate addition (100 mg L\(^{-1}\)) both had negligible impacts on SMX removal. With bicarbonate addition (100 mg L\(^{-1}\)) both had negligible impacts on SMX removal. With bicarbonate addition (100 mg L\(^{-1}\)).

Fig. 1: Conceptual model of functionalized graphene oxide activation (carbocatalysis) of persulfate and oxidative transformation of contaminants of emerging concern in soils and groundwater.

Fig. 2: Normalized concentration versus time trend of initially 1 mM persulfate (PS) concentration in nitrogen-doped graphene (N-GP), aminated graphene (NH2-GP), and graphene oxide (GO) suspensions (initial pH 6). All graphene suspensions were maintained at 50 mg L\(^{-1}\), and error bars represent standard deviations.

Fig. 3: Normalized concentration versus time trend of sulfamethoxazole (SMX) (initially 5 mg L\(^{-1}\)) concentration with PS in N-GP, NH2-GP, GO suspensions (initial pH 6). All graphene suspensions were 50 mg L\(^{-1}\), and error bars represent standard deviations.

Summary
- N-GP and NH2-GP effectively activate PS and sorb SMX, which resulted in enhanced SMX overall removal through coupled sorption and oxidative transformation (GO did not activate PS).
- The activation ability of NH2-GP can be limited under some aquatic chemistry conditions including occurrence of high pH and presence of HA and bicarbonate ions.
- The N-GP system was less affected by solution chemistry impacts, compared to the NH2-GP system, making it more widely applicable for PS activation.
- Compared to other PS activation methods (e.g., toxic metal-based, heat, or base) that require reagent or energy inputs to continue throughout treatment time periods, graphene-based activation is a promising metal-free alternative, which is a non-toxic PS catalytic process requiring no additional chemical or energy inputs.

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Fig. 4: Effect of solution chemistry (pH variability) on SMX (initially 5 mg L\(^{-1}\)) removal kinetics by 1 mM PS in (a) N-GP, (b) NH2-GP, and (c) GO suspensions. All graphene suspensions were 50 mg L\(^{-1}\), and error bars represent standard deviations.

Fig. 5: Effect of solution chemistry (ion type and strength) on SMX (initially 5 mg L\(^{-1}\)) removal kinetics by 1 mM PS in N-GP [(a) DI water control; (b) 100 mM NaCl; (c) 100 mM NaSO\(_4\)] and NH2-GP [(b) DI water control; (b) 100 mM NaCl; (b) 100 mM NaSO\(_4\)] all in N-GP] suspensions (sorption experiments were without PS). All graphene suspensions were 50 mg L\(^{-1}\), and error bars represent standard deviations.

Fig. 6: Effect of oxidant consumers (500 mM ethanol, 100 mM bicarbonate, 250 mg L\(^{-1}\) humic acid) on SMX (initially 5 mg L\(^{-1}\)) removal kinetics by 1 mM PS in N-GP [(a) ethanol; (b) bicarbonate; (b) humic acid all in N-GP] and NH2-GP [(b) ethanol; (b) bicarbonate; (b) humic acid all in NH2-GP] suspensions (sorption experiments were without PS). All graphene suspensions were 50 mg L\(^{-1}\), and error bars represent standard deviations.