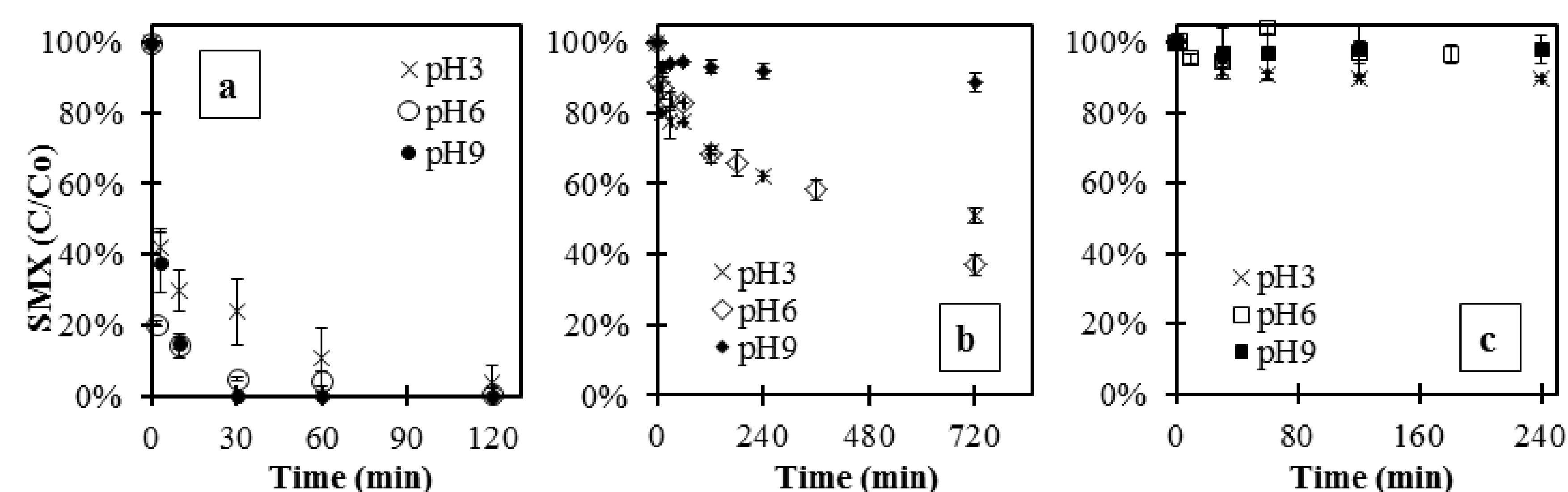


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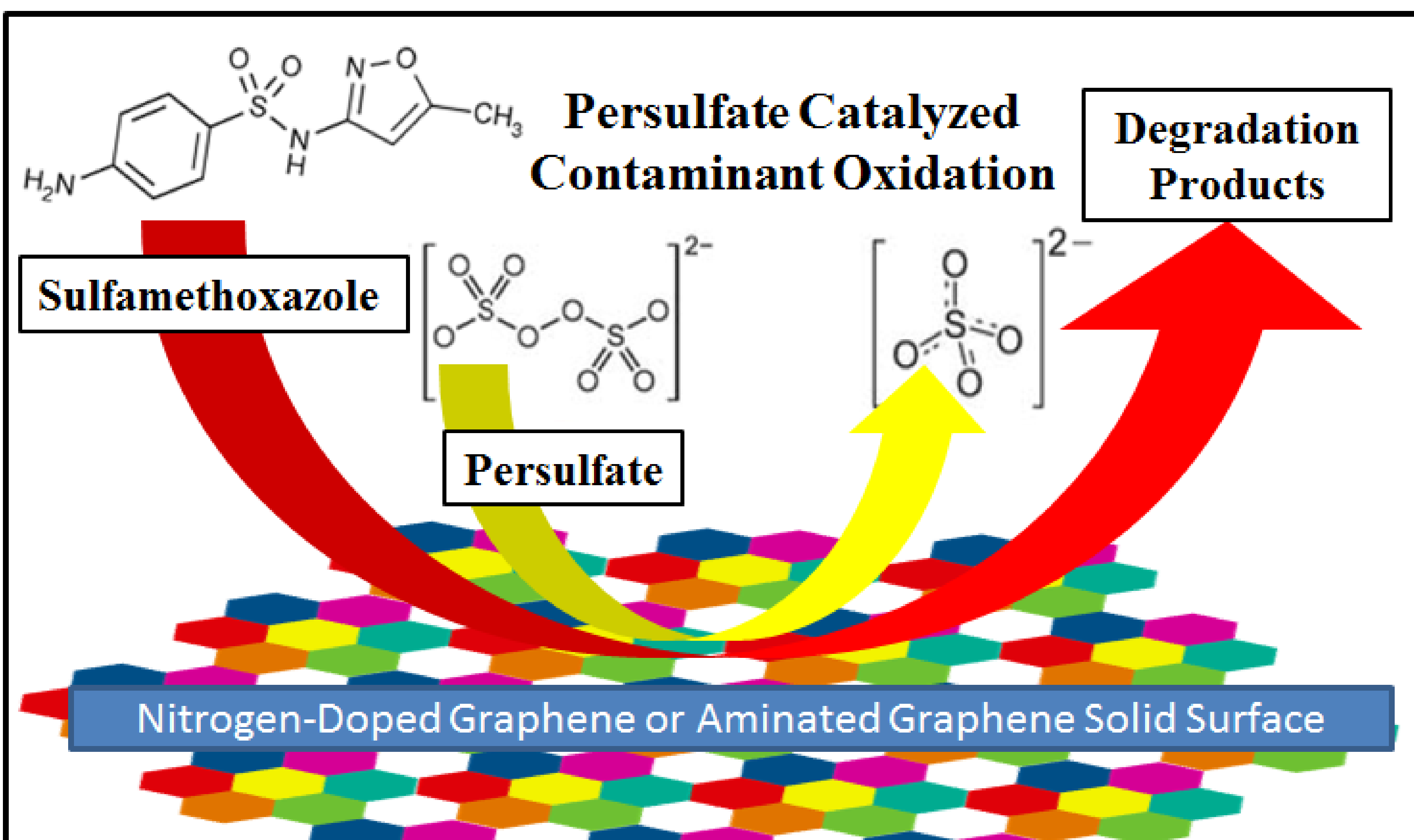
Poster #472-216

## Abstract

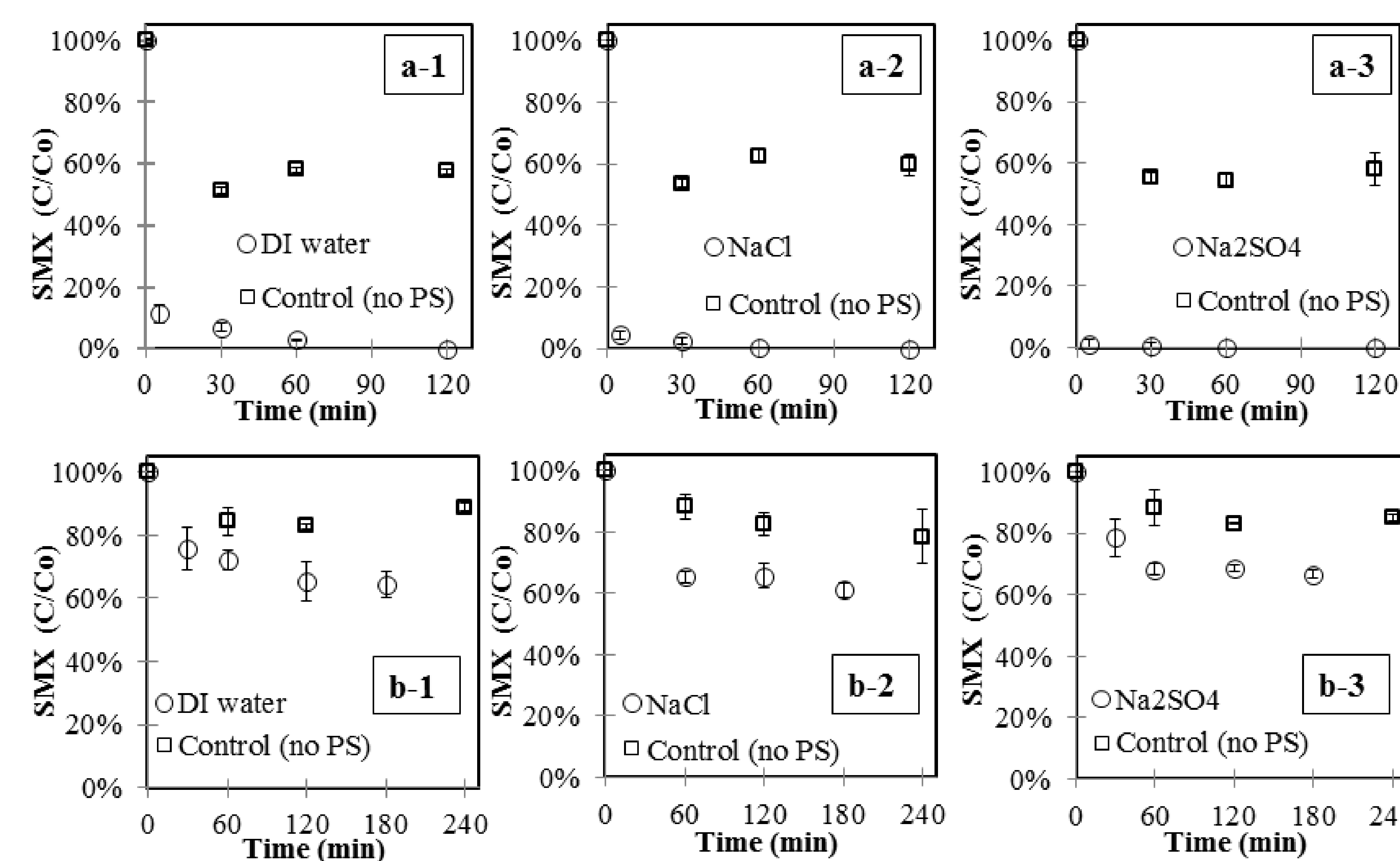
We evaluated three types of functionalized, graphene-based materials for activating persulfate (PS) and removing (i.e., sorption and oxidation) sulfamethoxazole (SMX) as a model emerging contaminant. Although advanced oxidative water treatment requires PS activation, activation requires energy or chemical 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 (NH<sub>2</sub>-GP) can effectively activate PS. Overall, PS activation by graphene oxide was not observed in this study. N-GP (50 mg L<sup>-1</sup>) can rapidly activate PS (1 mM) to remove >99.9% SMX within 3 hours, and NH<sub>2</sub>-GP (50 mg L<sup>-1</sup>) 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 NH<sub>2</sub>-GP. Increases in ionic strength (100 mM NaCl or Na<sub>2</sub>SO<sub>4</sub>) and addition of radical scavengers (500 mM ethanol) both had negligible impacts on SMX removal. With bicarbonate addition (100 mM), while the catalytic ability of N-GP remained unaltered, NH<sub>2</sub>-GP catalytic ability was inhibited completely. Humic acid (250 mg L<sup>-1</sup>) was partially effective in inhibiting SMX removal in both N-GP and NH<sub>2</sub>-GP systems. These results have implications for elucidating oxidant catalysis mechanisms, and they quantify the ability of functionalization of graphene with hetero-atom doping to effectively catalyze PS for water treatment of organic pollutants including emerging contaminants in soil and groundwater.



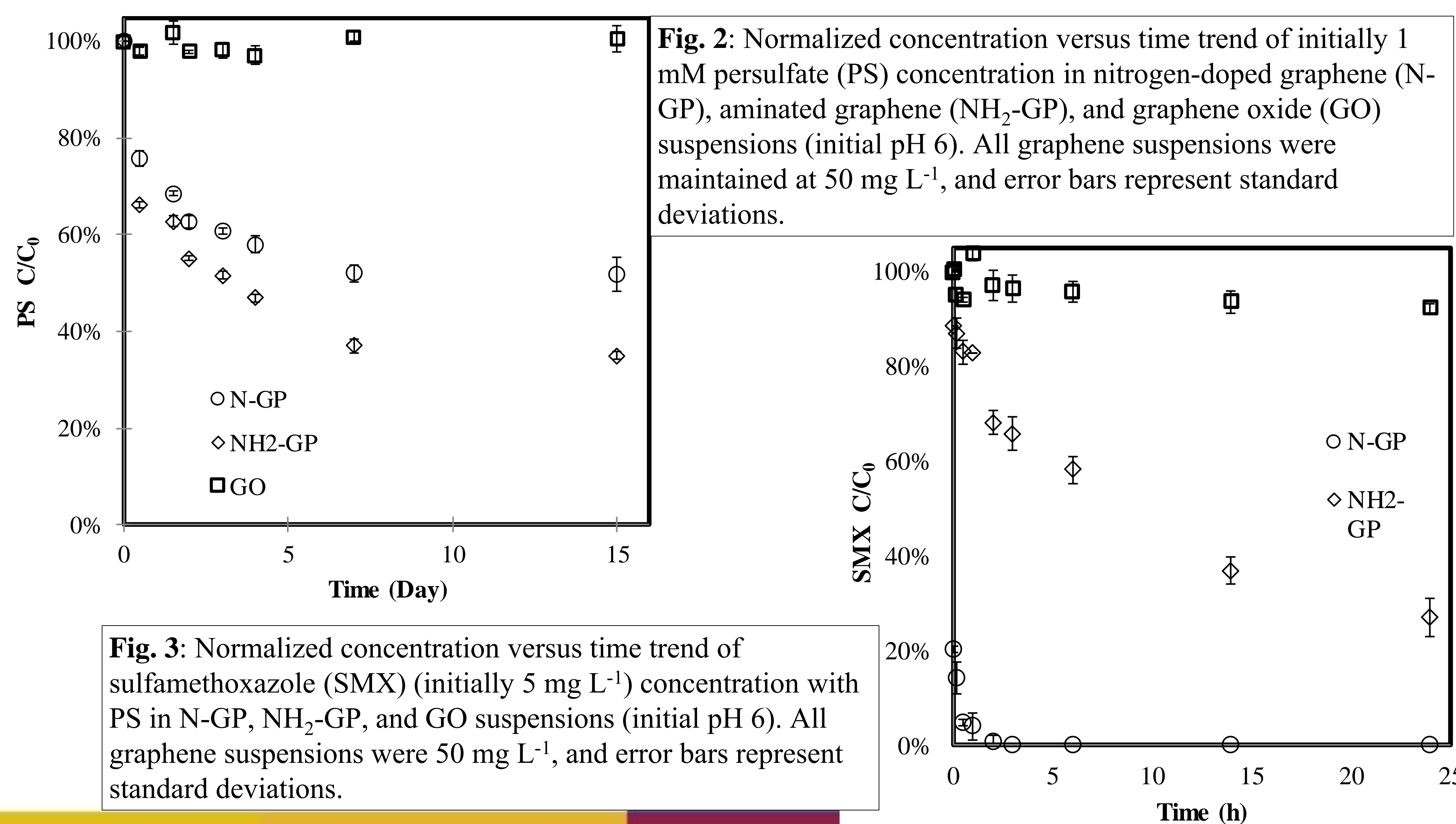
**Fig. 4:** Effect of solution chemistry (pH variability) on SMX (initially 5 mg L<sup>-1</sup>) removal kinetics by 1 mM PS in (a) N-GP, (b) NH<sub>2</sub>-GP, and (c) GO suspensions. All graphene suspensions were 50 mg L<sup>-1</sup>, and error bars represent standard deviations



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

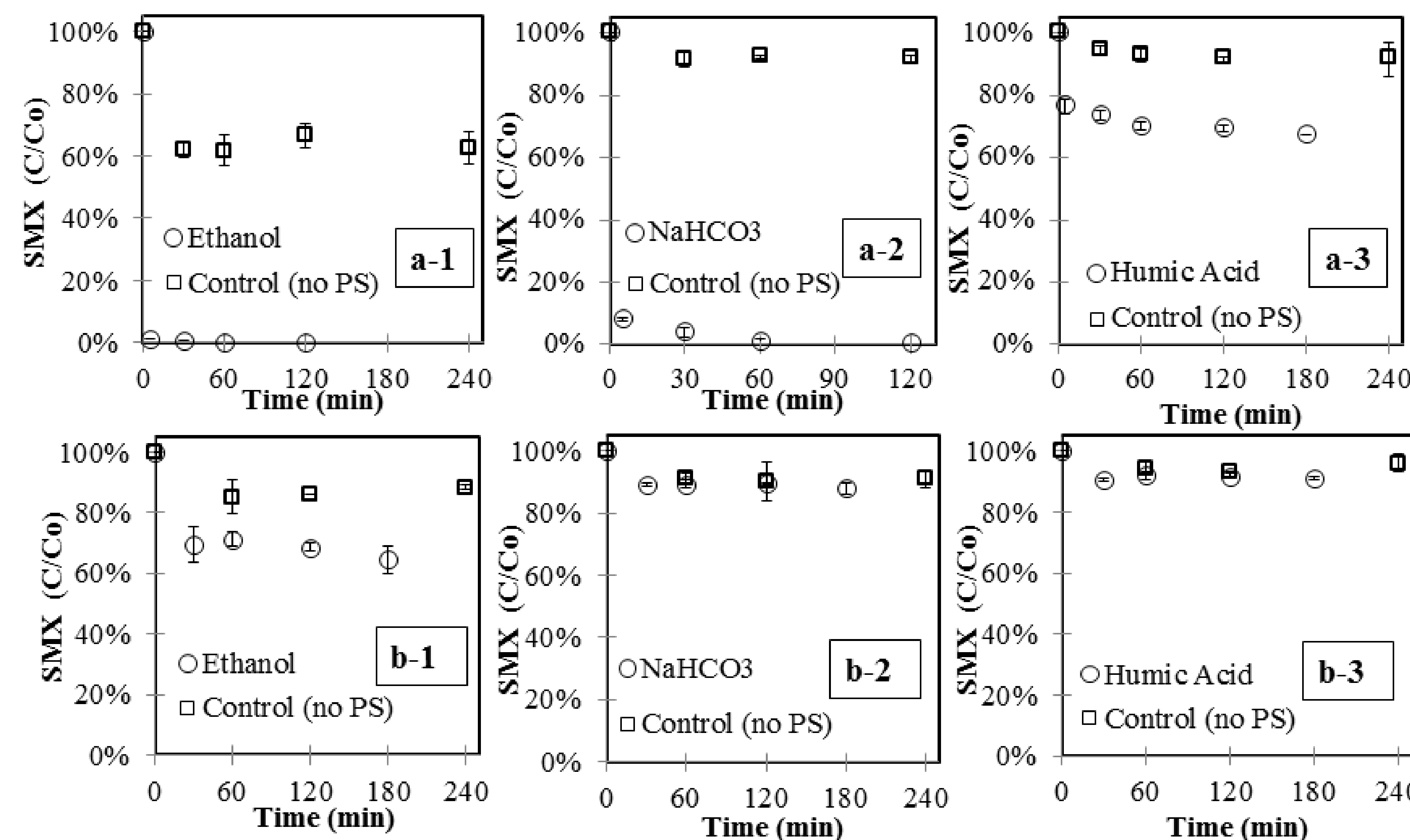


**Fig. 5:** Effect of solution chemistry (ion type and strength) on SMX (initially 5 mg L<sup>-1</sup>) removal kinetics by 1 mM PS in N-GP [(a-1) DI water control; (a-2) 100 mM NaCl; (a-3) 100 mM Na<sub>2</sub>SO<sub>4</sub> all in N-GP] and NH<sub>2</sub>-GP [(b-1) DI water control; (b-2) 100 mM NaCl; (b-3) 100 mM Na<sub>2</sub>SO<sub>4</sub> all in NH<sub>2</sub>-GP] suspensions (sorption experiments were without PS). All graphene suspensions were 50 mg L<sup>-1</sup>, and error bars represent standard deviations.



**Fig. 2:** Normalized concentration versus time trend of initially 1 mM persulfate (PS) concentration in nitrogen-doped graphene (N-GP), aminated graphene (NH<sub>2</sub>-GP), and graphene oxide (GO) suspensions (initial pH 6). All graphene suspensions were maintained at 50 mg L<sup>-1</sup>, and error bars represent standard deviations.

**Fig. 3:** Normalized concentration versus time trend of sulfamethoxazole (SMX) (initially 5 mg L<sup>-1</sup>) concentration with PS in N-GP, NH<sub>2</sub>-GP, and GO suspensions (initial pH 6). All graphene suspensions were 50 mg L<sup>-1</sup>, and error bars represent standard deviations.

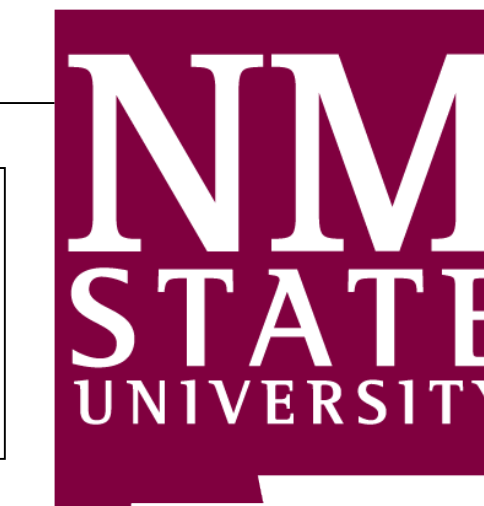


**Fig. 6:** Effect of oxidant consumers (500 mM ethanol, 100 mM bicarbonate, 250 mg L<sup>-1</sup> humic acid) on SMX (initially 5 mg L<sup>-1</sup>) removal kinetics by 1 mM PS in N-GP [(a-1) ethanol; (a-2) bicarbonate; (a-3) humic acid all in N-GP] and NH<sub>2</sub>-GP [(b-1) ethanol; (b-2) bicarbonate; (b-3) humic acid all in NH<sub>2</sub>-GP] suspensions (sorption experiments were without PS). All graphene suspensions were 50 mg L<sup>-1</sup>, and error bars represent standard deviations.

## Summary

- N-GP and NH<sub>2</sub>-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 NH<sub>2</sub>-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 NH<sub>2</sub>-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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