



Emerging Pollutants: Protecting Water Quality for the Health of People and the Environment

Interaction of the pesticide fipronil and its biodegradation products with polyethylene microplastics in ultrapure and river water

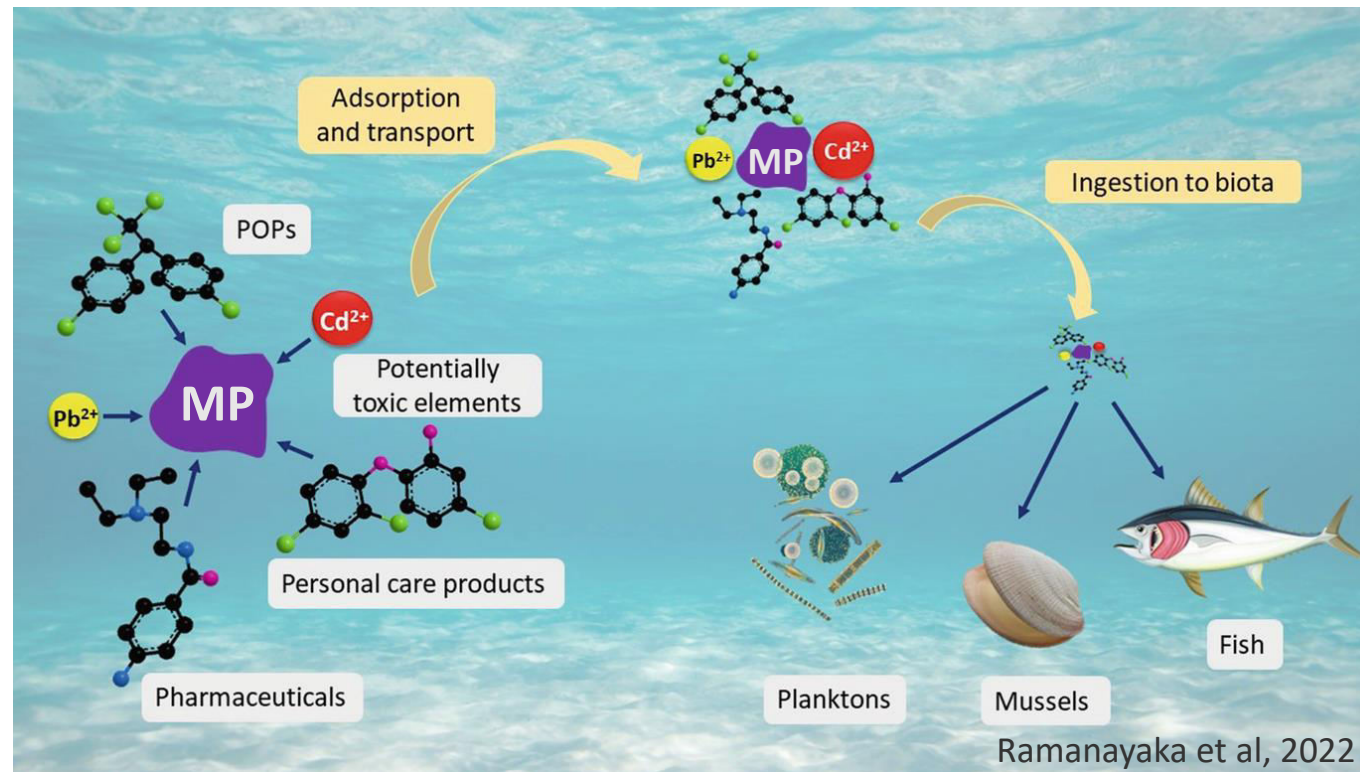
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Microplastics in Aquatic Environments

- Microplastics (MPs) have a high surface area to volume ratio, potentially sorbing different types of contaminants.

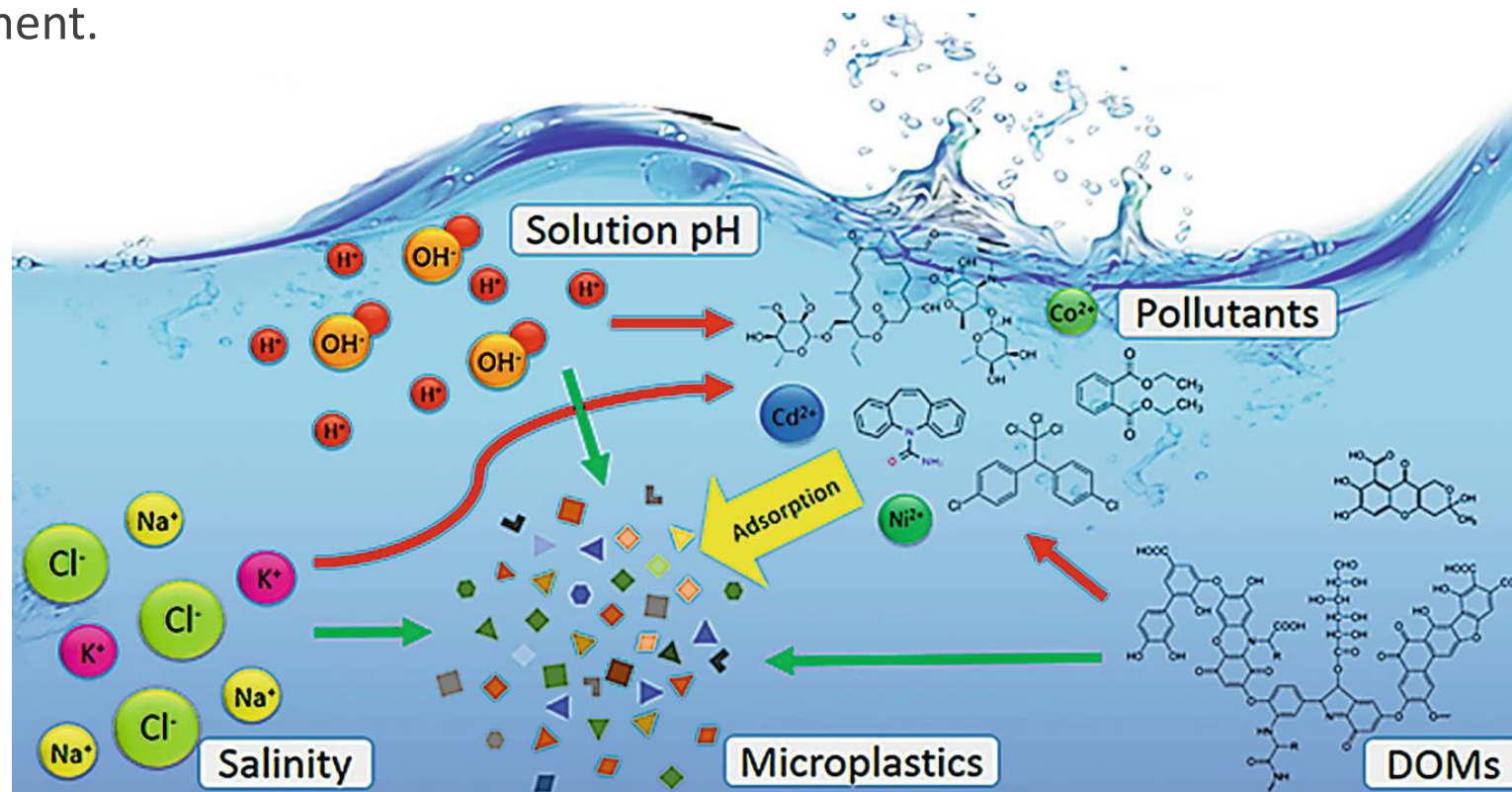


Ramanayaka et al, 2022

https://doi.org/10.1007/978-3-030-39041-9_50

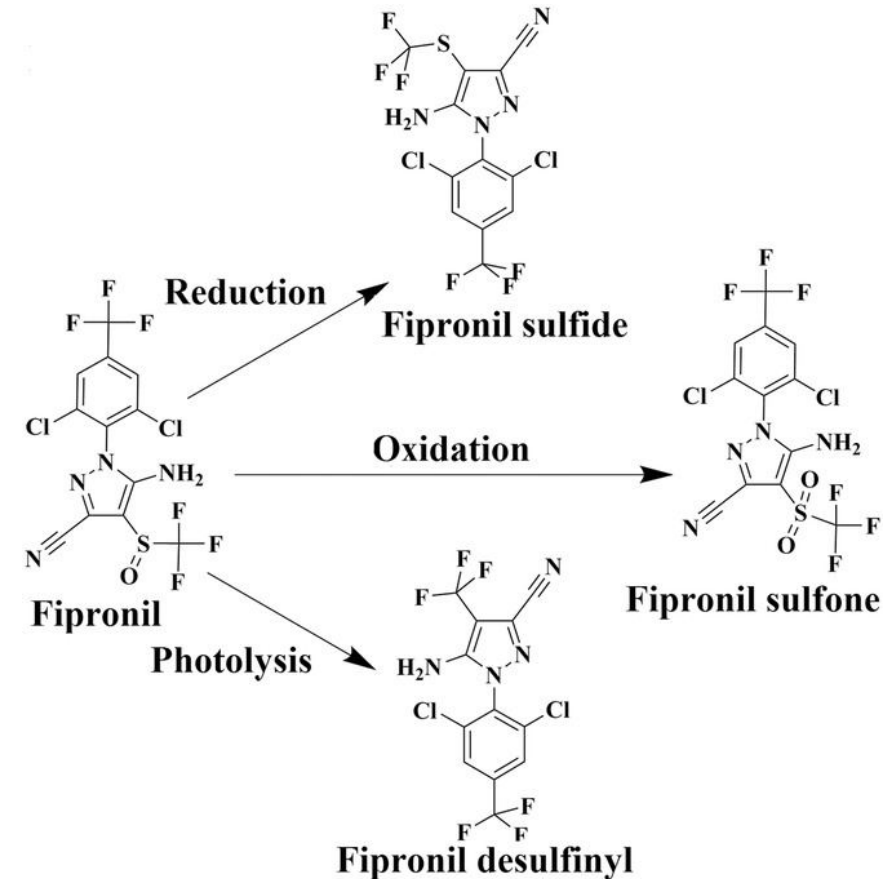
Sorption of Contaminants onto Microplastics

- Sorption processes depend on the characteristics of the microplastics, the contaminants, and the environment.

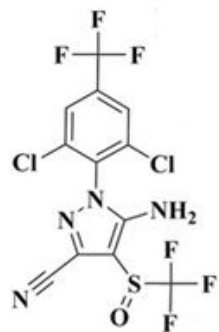


Pesticides in Aquatic Environments

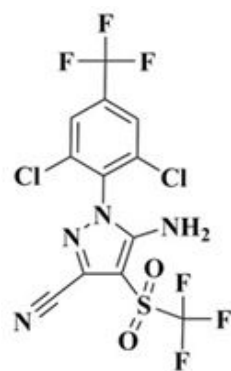
- Fipronil is a broad-spectrum insecticide. Its use in agriculture has been prohibited by the European Commission, but it is still widely used in Brazil.
- Fipronil undergoes biotic and abiotic transformations in aquatic environments.
- The transformation products fipronil sulfide, fipronil sulfone, and fipronil desulfinyl have been considered more toxic and persistent than fipronil (Qu et al, 2016).
- Fipronil and its transformation products have high K_{ow} .



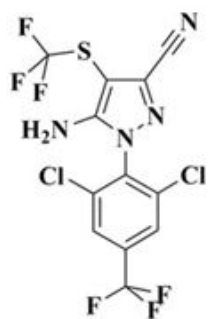
Sorption of Fipronil, Fipronil Sulfone, and Fipronil Sulfide onto Polyethylene MPs



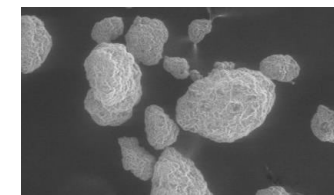
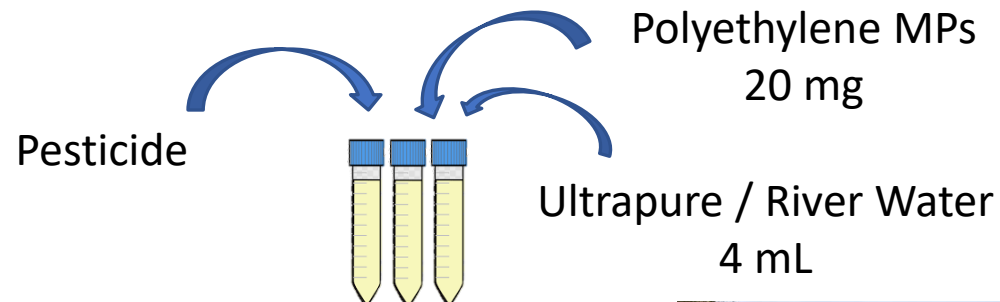
Fipronil



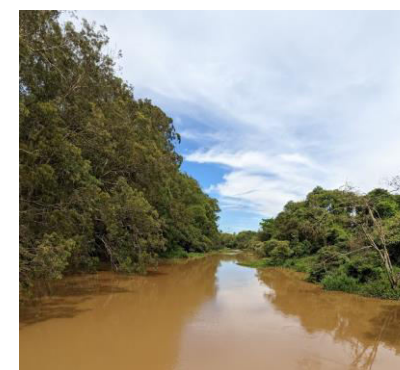
Fipronil sulfone



Fipronil sulfide



Average particle size: 106 μm

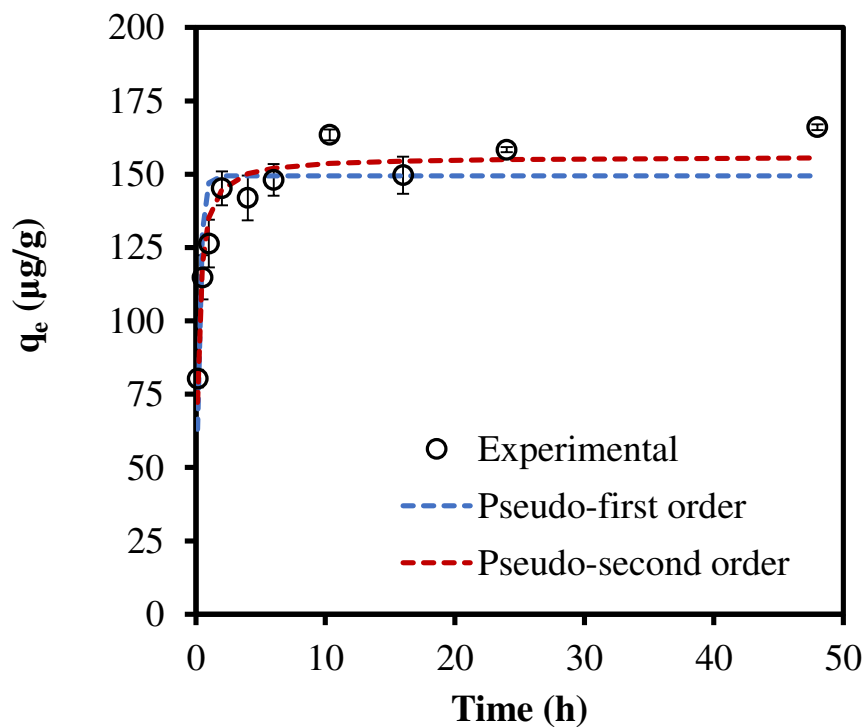


Atibaia River – Campinas, SP

Total Carbon: 14.1 mg/L
Total Organic Carbon: 9.1 mg/L
pH: 5.94
Conductivity: 137.4 $\mu\text{S/cm}$

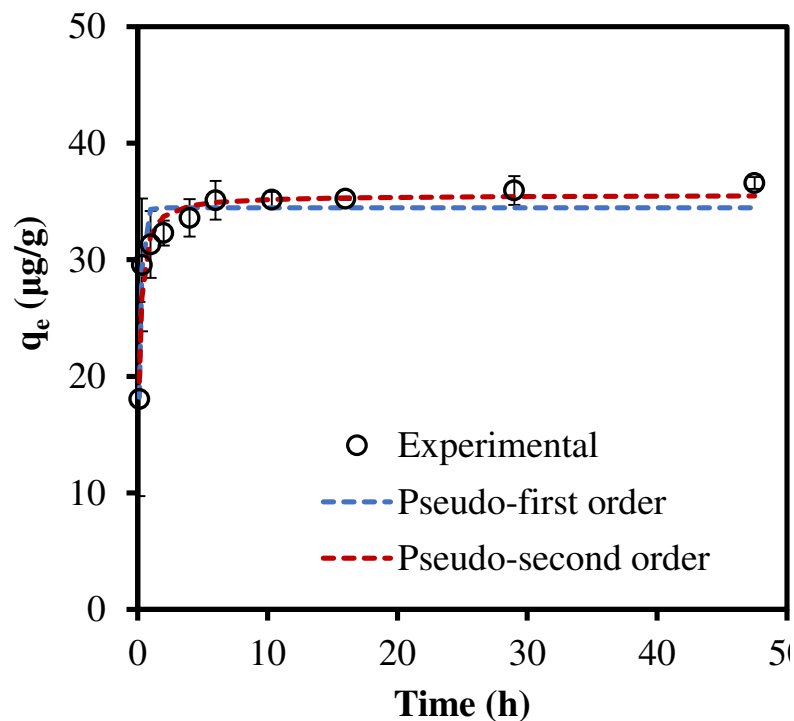
Kinetics in Ultrapure Water

Fipronil ($C_0 = 1000 \mu\text{g/L}$)



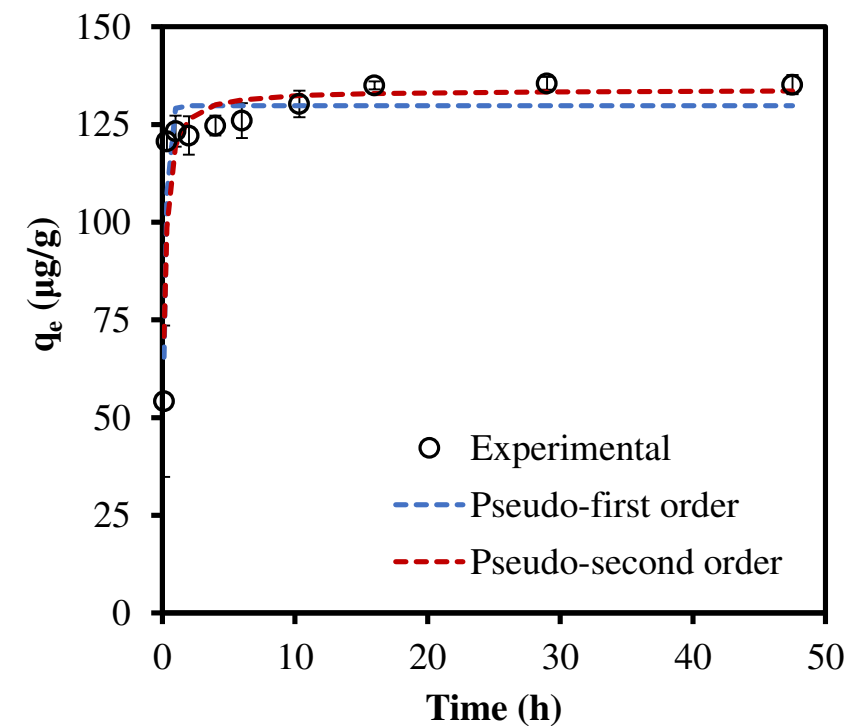
Pseudo-second order: $R^2 = 0.921$

Fipronil Sulfone ($C_0 = 250 \mu\text{g/L}$)



Pseudo-second order: $R^2 = 0.927$

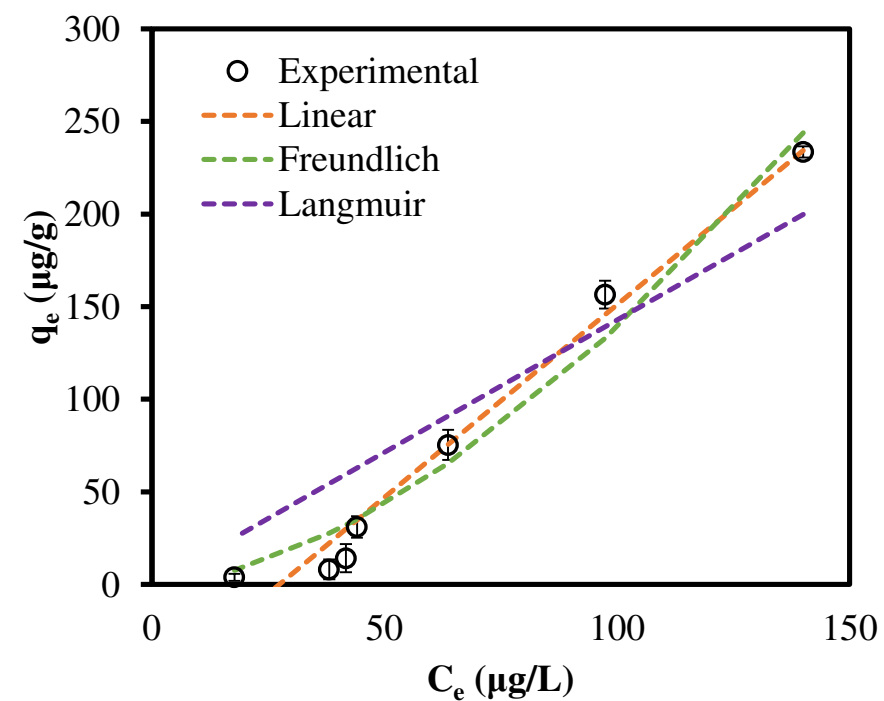
Fipronil Sulfide ($C_0 = 800 \mu\text{g/L}$)



Pseudo-first order: $R^2 = 0.955$

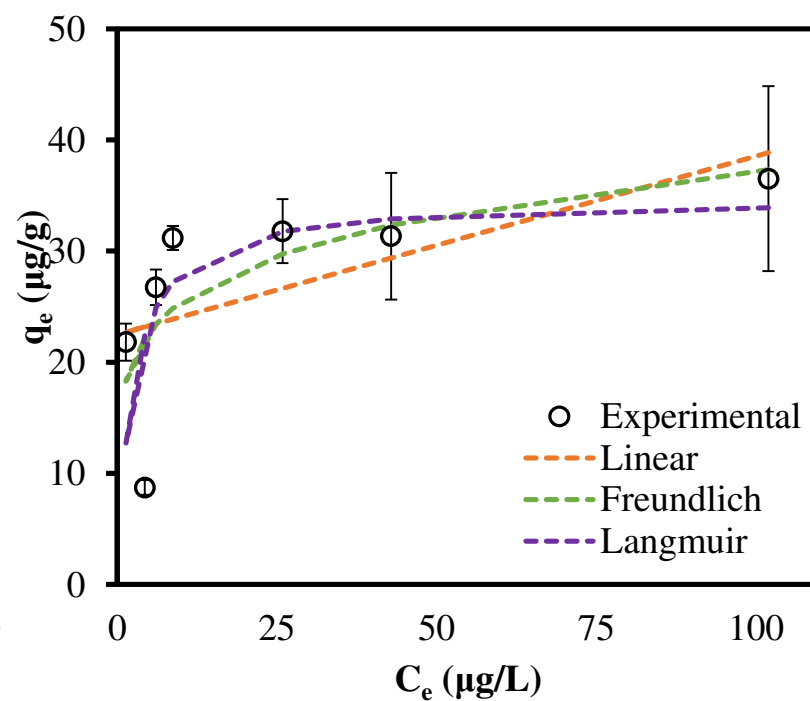
Isotherms in Ultrapure Water

Fipronil (48 h)



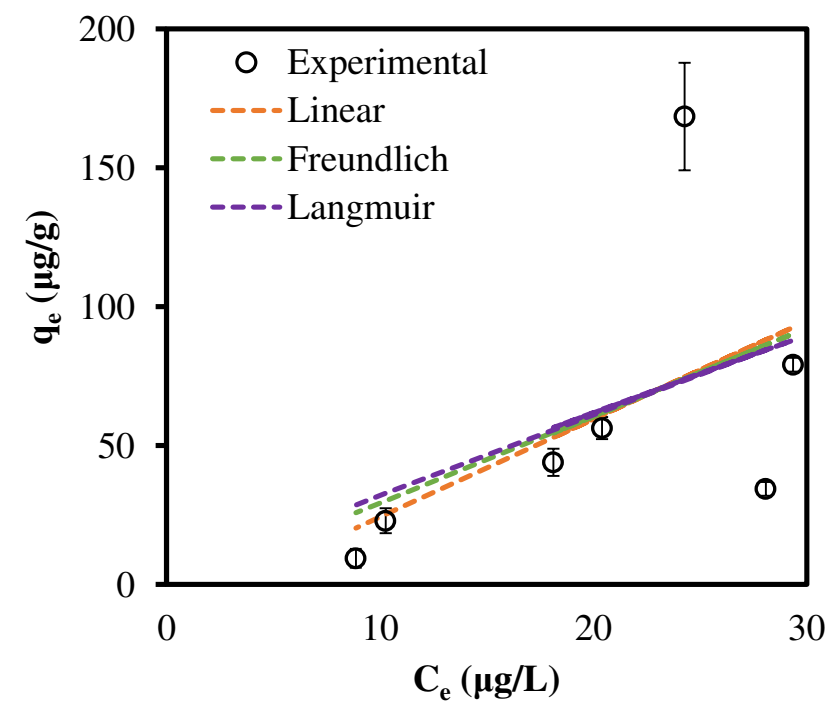
Linear: $R^2 = 0.971$

Fipronil Sulfone (48 h)



Freundlich: $R^2 = 0.512$

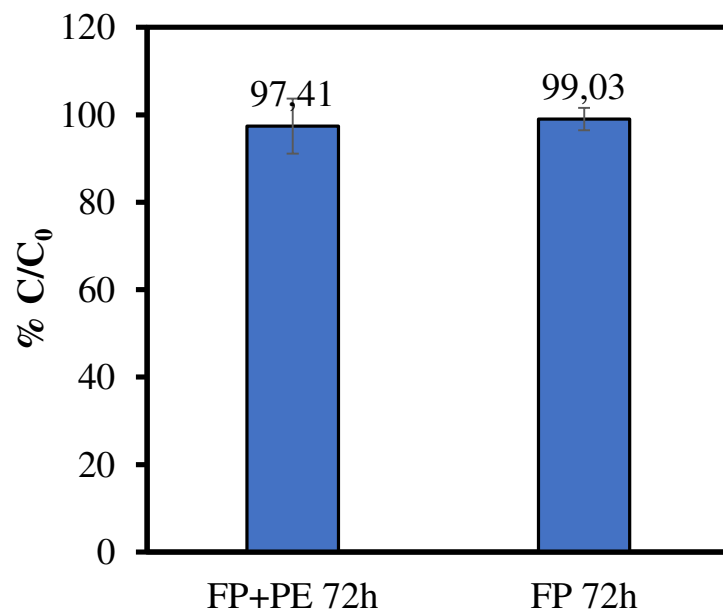
Fipronil Sulfide (48 h)



Langmuir: $R^2 = 0.283$

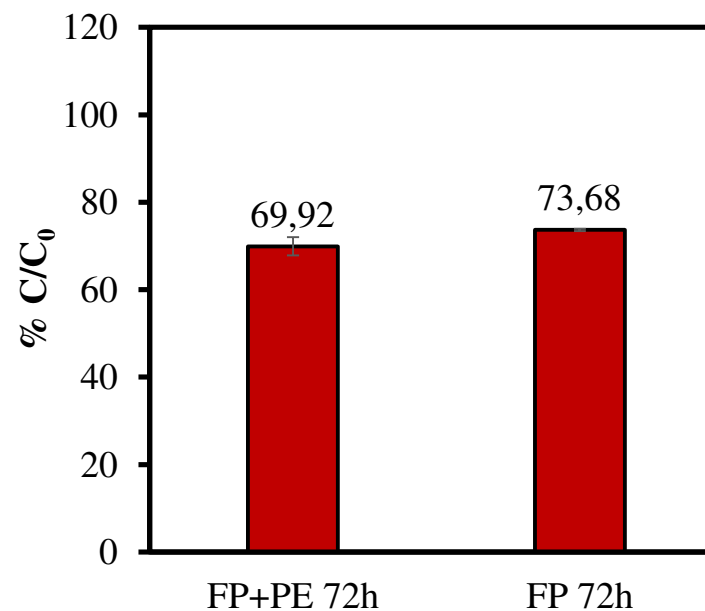
Pesticide Removal in Water from the Atibaia River

Fipronil (48 h)



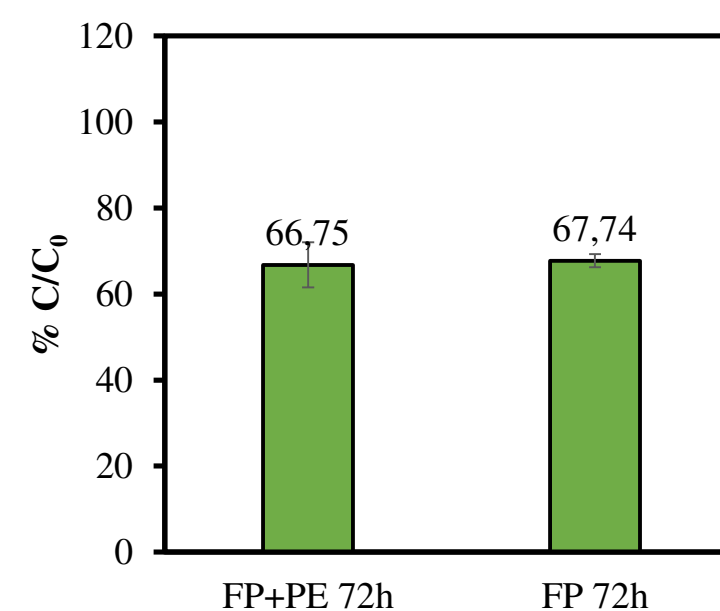
C/C₀ ultrapure water: 14%

Fipronil Sulfone (48 h)



C/C₀ ultrapure water: 14%

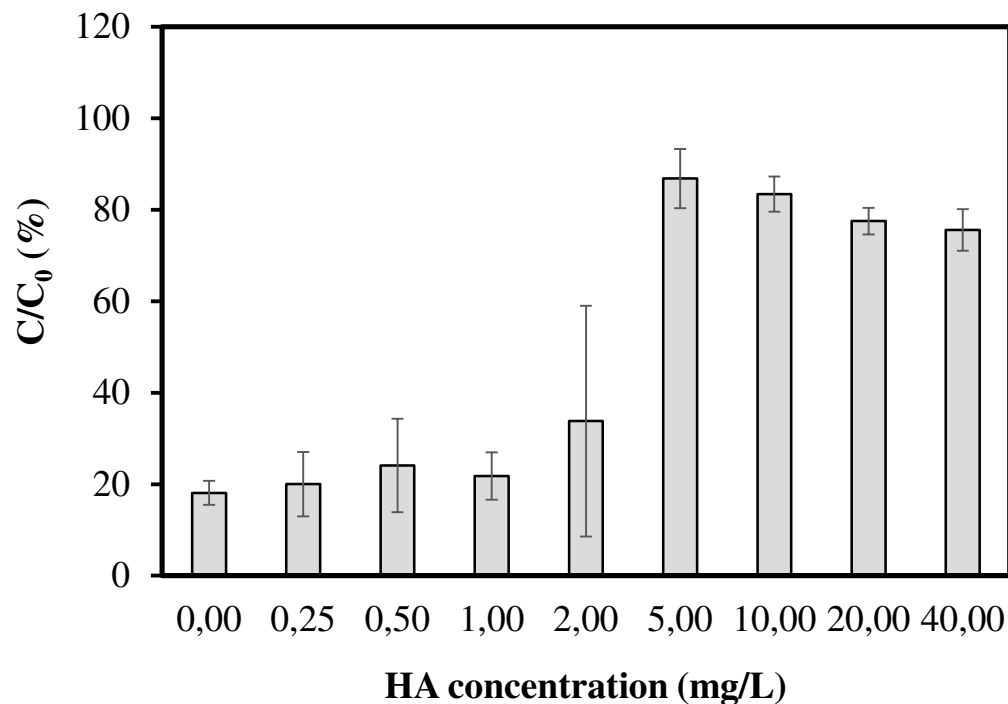
Fipronil Sulfide (48 h)



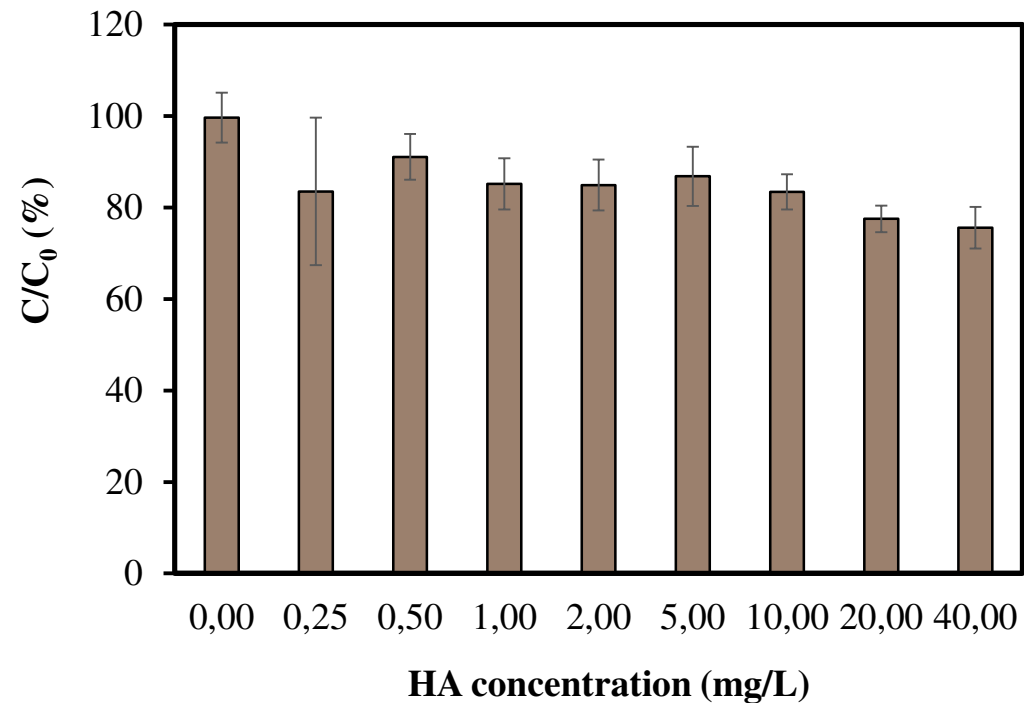
C/C₀ ultrapure water: 24%

Fipronil Removal in Ultrapure Water with Humic Acids

Fipronil + Humic Acids + PE (72h)



Fipronil + Humic Acids (72h)



High concentrations of HAs (≥ 5 mg/L) decreased PE MPs sorption capacity.

Conclusions

- Fipronil, fipronil sulfone and fipronil sulfide were highly sorbed by polyethylene microplastics in ultrapure water (86, 86, and 76%, respectively).
- Significant decrease in the sorption capacity was observed for the three compounds in water from the Atibaia river with or without microplastics.
- The presence of high concentrations (≥ 5 mg/L) of dissolved organic carbon in the form of humic acids also decreased the sorption capacity of polyethylene microplastics.
- Further studies are needed to evaluate the sorption of fipronil and its transformation products onto microplastics in different matrices and the toxic effects on aquatic organisms.

Thank you!

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