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Oxidative Aging of Polyvinyl Chloride (PVC) Microplastics: Implications for Vector Potential toward Methylene Blue

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INTRODUCTION & AIM

Microplastics (MPs), plastic particles smaller than 5 mm, are widespread pollutants in aquatic and terrestrial systems, originating from larger plastic fragmentation or direct manufacture. They persist in nature and pose risks by carrying harmful chemicals and affecting biological functions. Polyvinyl chloride (PVC) MPs represent a major fraction of this pollution, with their behavior changing through aging. This study compares pristine PVC (PVC-0D) and samples oxidatively aged with $KMnO_4$ at 70 °C for 3 days (PVC-3D) and 7 days (PVC-7D) to assess how oxidation alters their adsorption of methylene blue, highlighting the increased vector potential of aged MPs for organic pollutants and their environmental implications.

METHOD

Three PVC microplastic samples were prepared: pristine PVC (PVC-0D), and oxidatively aged samples in $KMnO_4$ at 70 °C for 3 days (PVC-3D) and 7 days (PVC-7D), without UV exposure, to simulate environmental weathering. XRD analyzed crystallinity changes, FTIR identified chemical modifications, TGA evaluated thermal stability, and zeta potential measured surface charge variations. Adsorption experiments with methylene blue were conducted, and data were fitted to pseudo-first-order and pseudo-second-order kinetic models, as well as Langmuir and Freundlich isotherms, to elucidate adsorption mechanisms and vector potential influenced by oxidative aging.

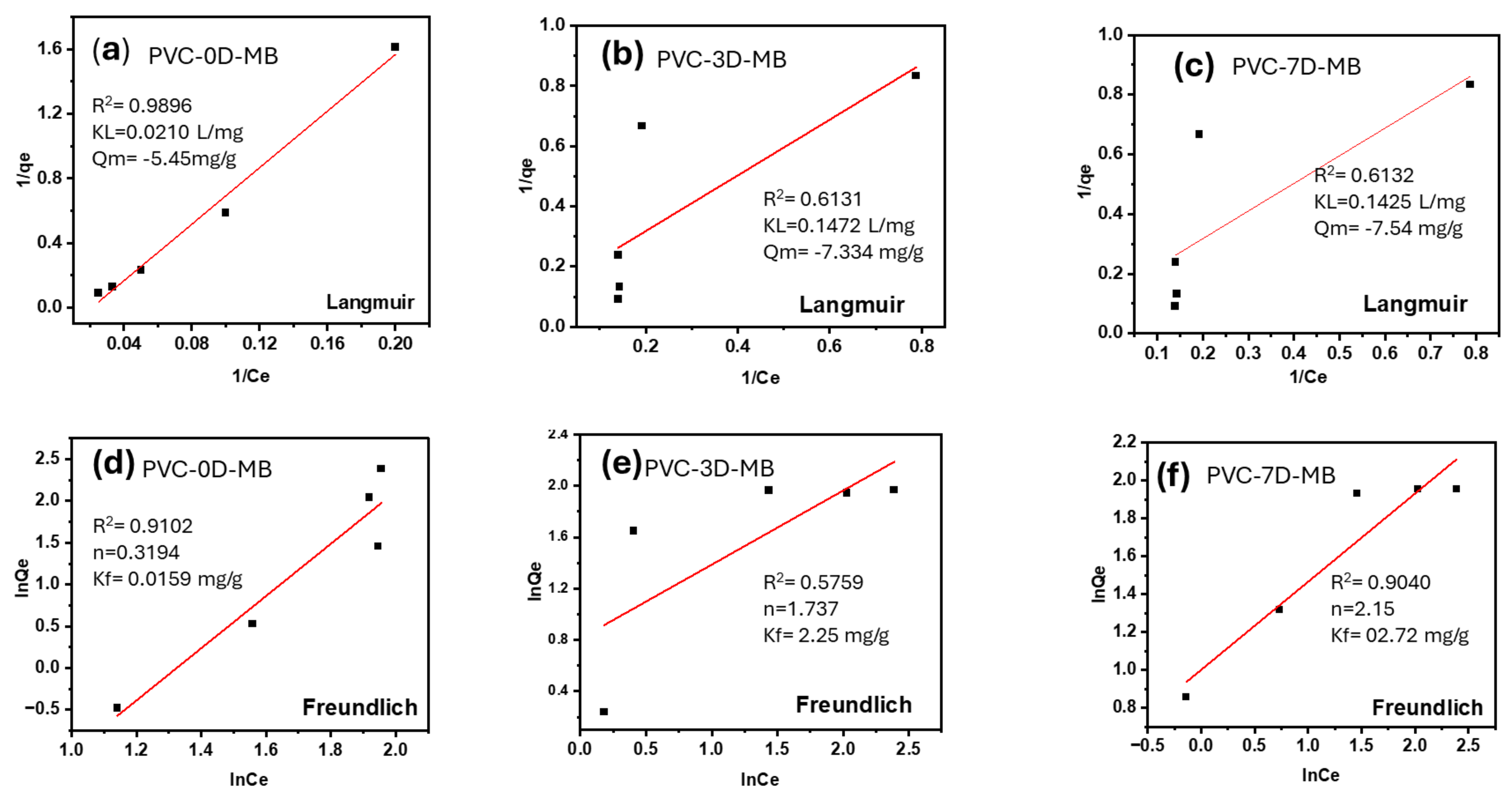

Figure 4. Isotherms fitting for pristine PVC and aged PVC for methylene blue adsorption

RESULTS & DISCUSSION

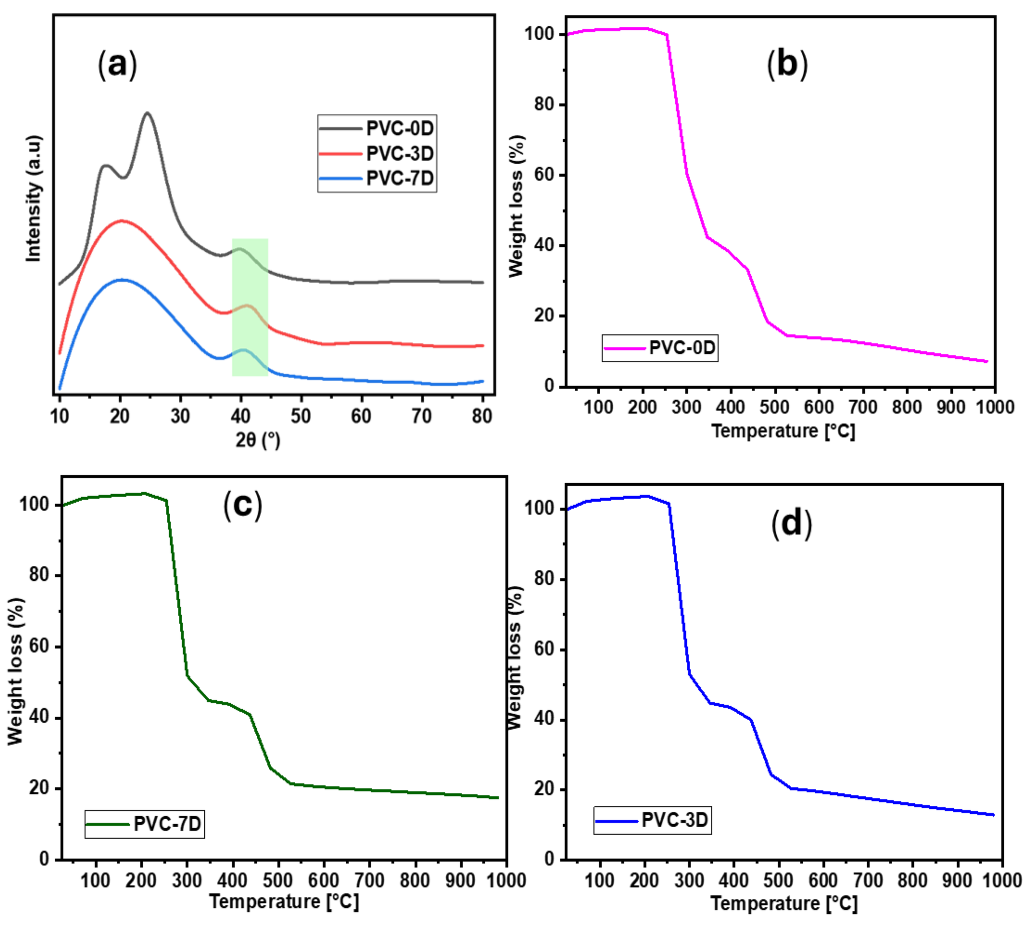

Figure 1a. XRD b-d. TGA

XRD Fig 1a: PVC-0D shows a broad peak at 2θ ≈ 16.5°–25°, typical of semicrystalline PVC. PVC-3D shifts slightly to ~17° with lower intensity, indicating partial amorphization. PVC-7D shows further intensity loss and broadening, confirming reduced crystallinity.

TGA Figs 1b–d:

PVC-0D shows high stability up to ~150 °C, with major degradation at ~270–370 °C and ~7% residue. PVC-3D begins degrading earlier (~250 °C) with ~95% mass loss, indicating reduced stability from oxidative attack. PVC-7D degrades fastest (~230 °C onset) and leaves ~3–4% residue, confirming progressive oxidation and weakened polymer bonds after aging. Oxidative aging decreases crystallinity and stability, enhancing surface reactivity and fragmentation, which increases PVC's potential to adsorb and transport organic pollutants

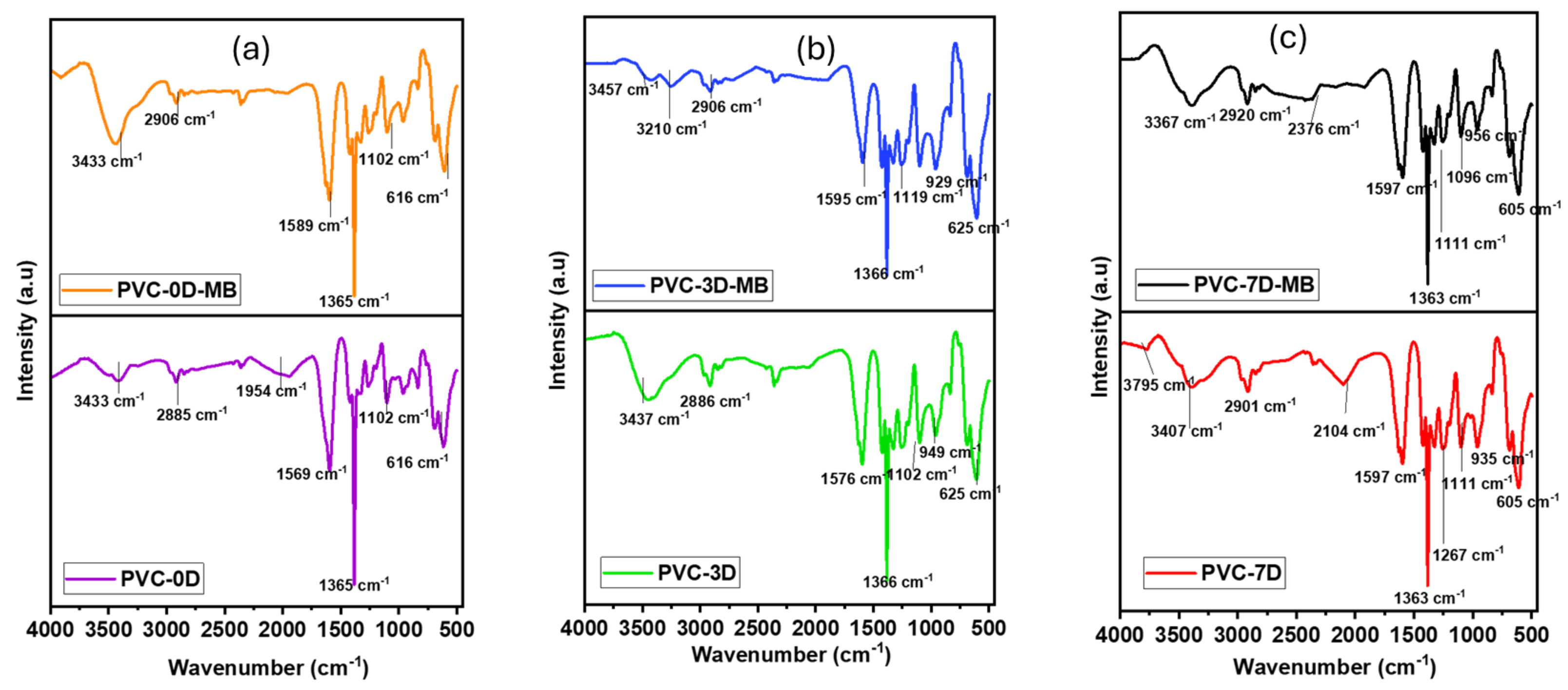

Figure 2. FTIR before and after adsorption of PVC with methylene blue

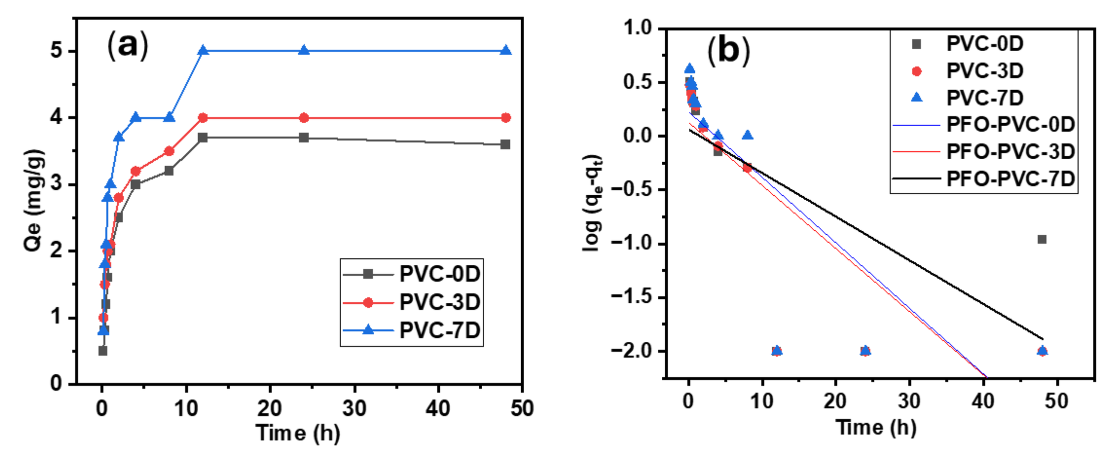

Figure 3a. Effect of time b. Pseudo first order & c. Pseudo-second order. Experimental conditions; Initial MB concentration of 20 mg/L, Adsorbent dosage of 1 g/L, and mixing speed of 180 rpm)

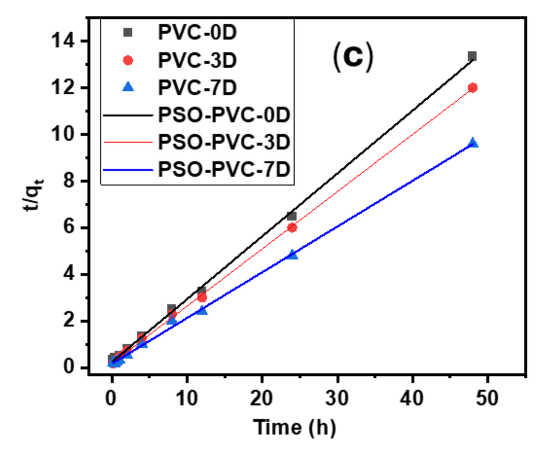

Table 1: Adsorption kinetic models and parameters of the adsorption of Methylene blue by PVC-0D, PVC-3D, & PVC-7D

Kinetic Models	Parameter	Unit	PVC-0D	PVC-3D	PVC-7D
Pseudo-First Order	R^2	–	0.4110	0.6899	0.6845
	k_1	min^{-1}	0.0934	1.353	0.1403
	q_e(pred)	$mg\ g^{-1}$	1.08	19.45	1.69
	q_e(exp)	$mg\ g^{-1}$	3.71	4.08	5.10
Pseudo-Second Order	R^2	–	0.9990	0.9995	0.9988
	k_2	$g\ mg^{-1}\ min^{-1}$	0.303	0.327	0.236
	q_e(pred)	$mg\ g^{-1}$	3.71	4.08	5.10
	q_e(exp)	$mg\ g^{-1}$	3.71	4.02	5.01

CONCLUSION

Aged PVC (PVC-7D) showed the highest methylene blue adsorption, followed by PVC-3D and PVC-0D, due to increased surface oxidation and porosity. The best fit with the Freundlich and pseudo-second order models indicates multilayer, chemisorption-driven adsorption on heterogeneous surfaces. Environmentally, aged PVC poses greater pollutant transport risks; monitoring and mitigation of aged MPs are strongly recommended.

REFERENCES

Shi, Y., Shi, L., Huang, H. *et al.* Analysis of aged microplastics: a review. *Environ Chem Lett* **22**, 1861–1888 (2024). https://doi-org.ezproxy.newcastle.edu.au/10.1007/s10311-024-01731-5