The role of abiotic and biotic aging in the removal of microplastics in the coagulation process

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INTRODUCTION & AIM

Although coagulation is a well-known and widely used technique for removing suspended particles, there are no detailed data on its effectiveness in microplastic (MP) elimination. The research available on the removal of MPs by coagulation is at a preliminary stage and there is no research available on the mechanism and effectiveness of removal and the factors that increase the efficiency of elimination. A significant limitation of the research conducted so far on the coagulation process relative to MP elimination is the removal of only one type of MP, while in the environment, there is a mixture of particles differing primarily in composition but also in size and shape. The second limitation is ignoring the fact that microplastic particles present in environmental conditions are transformed/aged under the influence of abiotic and biotic factors. These particles then change not only their appearance, size/mass, or density but also their surface and chemical composition. These changes may have both positive and negative effects on the efficiency of microplastics elimination in the coagulation process.

The main goal of this research was to analyze the impact of biotic and abiotic aging of polyethylene on the effectiveness of coagulation. The impact of mechanical stress, thermal oxidation, chemical treatment, and colonization by microorganisms were examined.

MATERIALS AND METHODS

PE characteristic

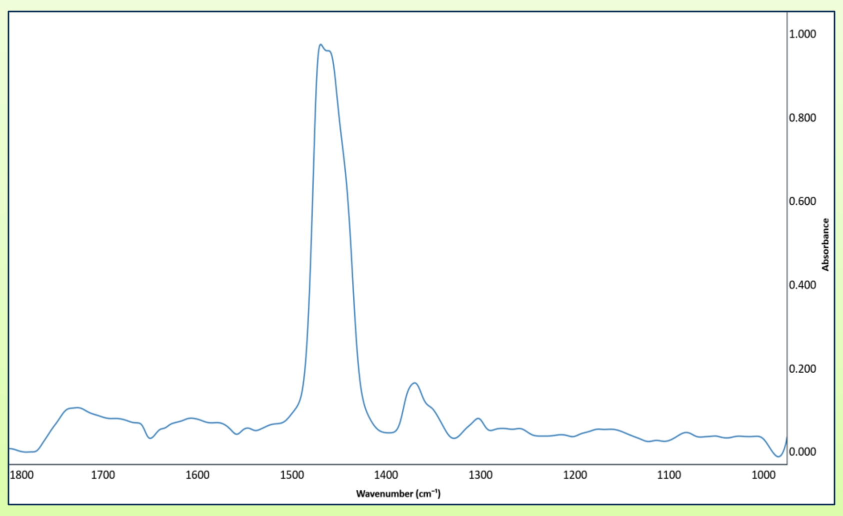

Table 1. Characteristics of PE

Microplastic	Size [µm]	Density in 25°C [g/mL]	CAS number
Polyethylene PE	34-50	0.94	9002-88-4

Coagulation process

- Stuart flocculator with 6 rotators (SW6) was used for coagulation experiments.
- Each tap water sample volume was 500 mL. The doses of PE was 0.1 g/L. The coagulant dose ($AlCl_3 \cdot 6H_2O$) used in this study was 0.05 g/L.
- The mixing speed was maintained at 300 rpm/min for 1 min, then 50 rpm/min for 15 min, with a subsequent sedimentation of 45 min.
- After sedimentation, the supernatant was collected to calculate the removal efficiency of microplastics.

Table 2. Characteristics of tap water

Parameters	Unit	Average value
Color	mg/L	<5
Turbidity	NTU	<0.20
pH	-	7.70
Conductivity	µS/cm	647
NO_3^-	mg/L	6.3
NO_2^-	mg/L	<0.05
Cl^-	mg/L	38
SO_4^{2-}	mg/L	36
Total organic carbon	mg/L	1.50
Total hardness	mg $CaCO_3$/L	260

Aging processes

Aging process	Experimental setups
Mechanical stress	Stress by shaking MPs (5 g) in water (20 mL) during 15, 30 and 60 days Stress by shaking MPs (5 g) in water (20 mL) with sand (0.5 g) during 15, 30 and 60 days
Thermal oxidation	Incubation of MPs in water (20 mL) at 5, 25 and 60 °C during 15, 30 and 60 days
Chemical treatment	Immersion of MPs (2.5 g) in different reagents (20 mL of 0.1M HCl, 0.1M NaOH, CH_3OH, 30% H_2O_2, 0.1M $KMnO_4$, 0.1 M $Na_2S_2O_8$)
Biotic aging	Incubation of PE (1g) with Bacillus strains during 7, 15 and 30 days
Mechanical stress + biotic aging	Stress by shaking MPs (5 g) in water (20 mL) during 15 days + 7 days biotic aging

Microplastic analysis

- All supernatants collected from each experiment were filtered through pre-weighed Whatman filters.
- The residuals flocs on the surface of the MPs were eliminated using an HCl solution. The MPs-containing filters were dried for 18 hours at 60°C.
- MPs-containing membrane were weighted after they cooled to room temperature.
- The total removal efficiency of microplastics removal was calculated by the following formula:

$$E=\frac{m0-mt}{m0}*100\%\ ,$$

where E is the removal efficiency of microplastics during coagulation (%), m_0 is the mass of microplastics in the solution at the beginning of coagulation process (g), m_t is the mass of microplastics in the supernatant after coagulation process (g).

Dried microplastic samples were suspended in ethanol and deposited on infrared reflective glass slides (7.5 cm × 2.5 cm, MirrIR, Kevley Technologies, USA). The glass slides were analyzed in transflection by automated LDIR Imaging (with Quantum Cascade Laser, Agilent 8700). The following parameters of the microplastics were determined: diameter range and mean diameter, area, perimeter, circularity, and solidity.

RESULTS & DISCUSSION

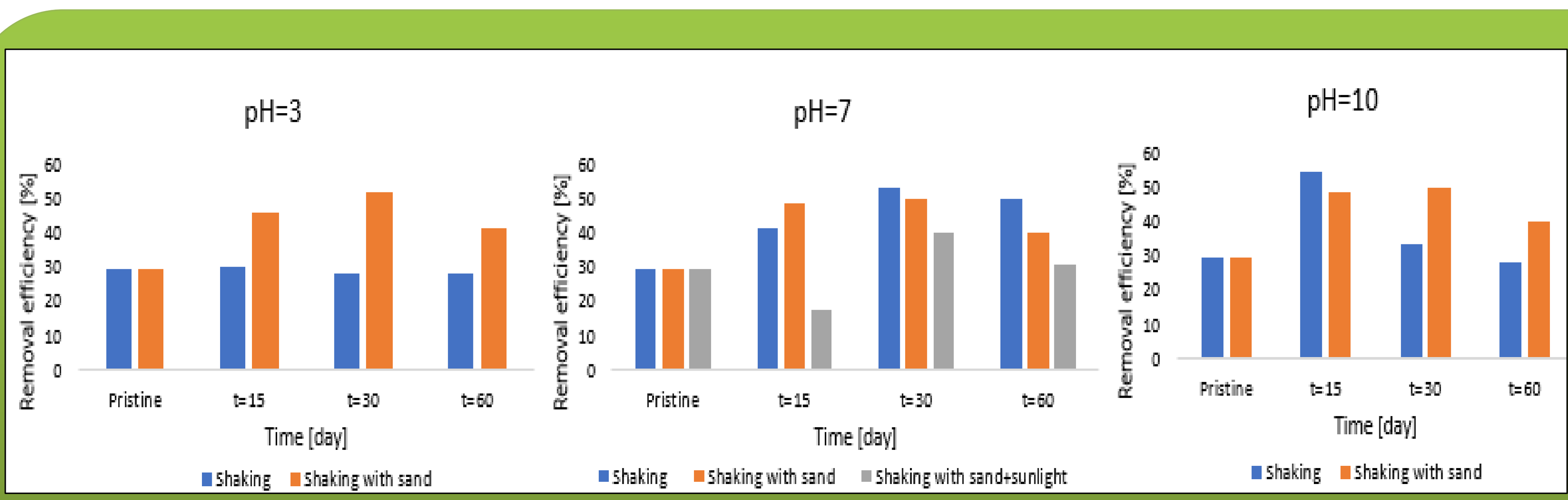

Fig. 1. Impact of mechanical stress and pH value on PE elimination

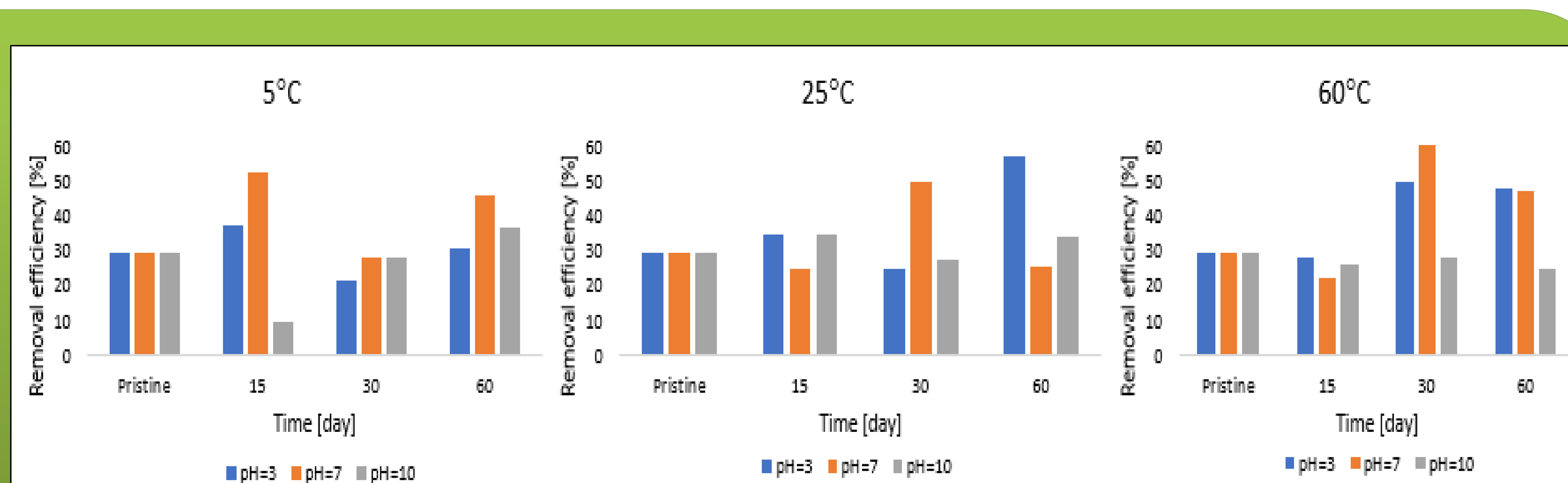

Fig. 2. Impact of thermal oxidation and pH value on PE elimination

Table 3. Impact of chemical treatment and time on PE elimination

Temperature [°C]	Time [day]	HCl (0.1M)	NaOH (0.1M)	CH_3OH	H_2O_2 (30%)	$KMnO_4$ (0.1M)	$Na_2S_2O_8$ (0.1M)
		PE elimination [%]					
5	1	64.2	49.6	37.6	34	44.6	17.6
	7	33.8	69.6	43.8	2	65.6	47.4
	14	34.2	53.2	9.6	19.4	62.8	37.6
	28	33.4	53.2	11.8	25.8	65	39.6
25	1	62.6	51	25.6	14.8	32.2	23.8
	7	58.6	44.2	25.2	37	40.6	44
	14	49.8	76	41.4	37.2	51.8	68.8
	28	46.4	56.2	34.8	26.8	39.8	37.6
60	1	31	44	8	22.8	63	23
	7	48.2	48	5.8	23.6	61.8	60.4
	14	49.9	78	13.6	12.2	71	61.6
	28	43.8	**80.2**	7.4	21.6	64	48.4

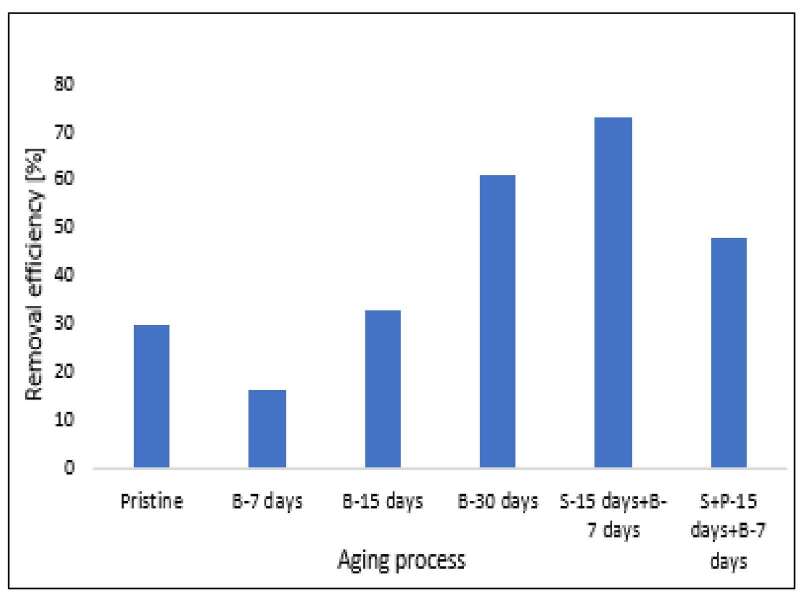

Fig. 3. Impact of biotic aging on PE elimination

CONCLUSION

- We investigated the removal ratio of PE MPs under various experimental condition, explored the effects of different aging treatments of PE on coagulation performances.
- Both positive and negative effects of aging on the efficacy of coagulation in eliminating PE have been observed.
- A noticeable increase in the MPs elimination rate was observed when PE was aged by (1) shaking (pH=7 and pH=10) without access to sunlight; (2) biotic aging above 15 days, (3) chemical treatment with HCl, NaOH, $KMnO_4$, $Na_2S_2O_8$.
- The highest PE removal efficiency was obtained during PE incubation in NaOH solution at a temperature of 60°C for 28 days.
- The presented results refer to preliminary studies. Further studies will concern the analysis of changes in the physicochemical and structural properties of microplastic particles as a result of ageing.

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