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A Comparative Sorption Study for Phenol & Tricholorophenol onto Polyethylene Type Microplastics

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Abstract

In freshwater systems, microplastics and organic contaminants are prevalent pollutants. Using kinetics and isotherm analyses, this research investigates the sorption of two organic compounds (Phenol and 2,3,6-Trichlorophenol) on pristine polyethylene (PE). The hydrophilic nature of phenol is hypothesized to have low affinity for PE, on the contrary, 2,3,6-TCP is expected to have higher affinity. The goal of this study is to compare the interactions between PE and two extensively used yet physio-chemically distinct chemicals. Experimental results show 2,3,6-TCP sorption is fast (teq=24hr) with qeq 180 µg/g, while phenol sorption is slow (teq=28days), with non-detectable capacity. PE sample, having medium to high density and crystallinity seems to result in longer equilibration times and lower sorption capacity when compared to other MPs studied in the literature.

Keywords: Microplastics; phenol; trichlorophenol; polyethylene; sorption

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1. INTRODUCTION

Microplastics (MPs) are plastic particles with a diameter less than 5 mm. Because of their widespread use, chemical stability, resistance to degradation, and simplicity of disposal, MPs have a long-life span in the environment and can be consumed by biota [1]. Although it is unclear if MP-sorbed organic contaminants (OCs) pose additional ecological harm to organisms through MP ingestion, they do raise concerns since they represent a potential entry route for trace OCs into the food chain. Given the variety of MP types/sizes and OCs available, it is vital to investigate interactions between MPs and OCs. Phenol and its derivatives are primarily used to make phenolic resins, utilized in plywood, construction, automobile, and appliance sectors [2]. Aim of this study was to comparatively evaluate sorption of two commonly used chemicals, phenol in its pure form and its trichlorinated form, onto microplastics.

2. METHODOLOGY

MPs used were obtained in powdered form from a local water tank manufacturer. Prior to use, MPs were sieved, washed in an ultrasonic bath for 30 mins and dried at 30°C. MPs were characterised as PE via FTIR analysis, have 0.935 g/cm^3 density and 49.4% crystallinity as obtained from DSC, with BET surface area

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0.1034 m^2/g. OECD guideline [3].was followed during sorption studies. Batch sorption experiments were carried out in triplicate using 40 mL amber glass vials with Teflon lined caps. Experiments on sorption kinetics, effect of solid: liquid (S/L) ratio (25 g/L), particle size (d_p) (0.250-0.500 mm) were carried out. Phenol was analyzed using USEPA method 9065, while 2,3,6-TCP was measured spectrophotometrically at 289nm. Laboratory control samples yielded ≤10% error.

3. RESULTS AND DISCUSSION

Phenol sorption kinetics was complicated with test and control reactors yielding almost identical concentration trends. The % change in phenol concentration in 28 days was 23.7% and it was 23.1% for the control (Figure 1). Prior to experiments, phenol solution was tested to be stable and theoretical calculation of volatile loss cannot account for the decrease in phenol concentration. Experiments were also performed with smaller particle size MPs (0.106-0.180 mm), with some difference between the two (23.3% for test and 20.2% for control), but not appreciable. These demonstrate that phenol has no discernible affinity for PE type MPs. Effect of pH on sorption was tested at pH=4 and 6, with similar results (results not shown). The acidity constant for phenol is much higher than these values (with a pKa around 10) so, both at both pHs, phenol was in its unionized form and did not show much affinity for PE.

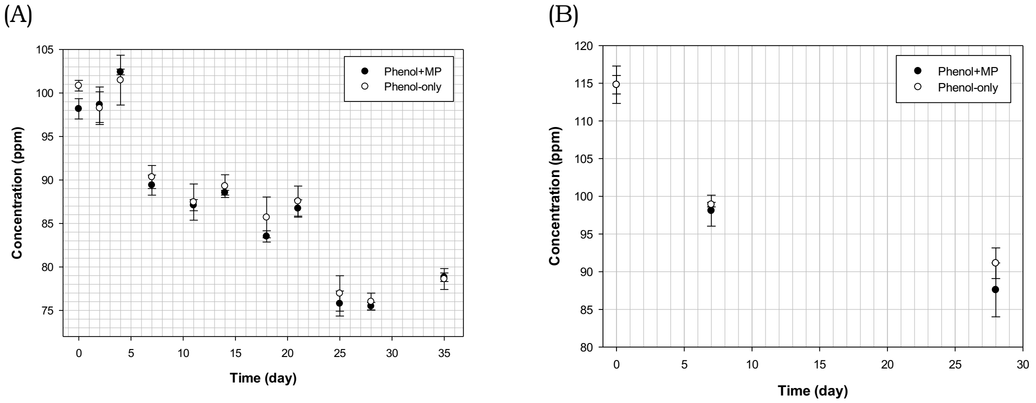

***Figure 1. (A)** Phenol sorption on PE with large particle size (dp=250-500 µm), **(B)** Phenol sorption on PE with small particle size (dp=106-180 µm).*

2,3,6-TCP sorption kinetics were comparably much faster, reaching equilibrium at about 24hrs (Figure 2). Approximately 40% of 2,3,6-TCP is sorbed by MPs by the 12th hour as can be seen in below figure, after which sorption slowed down, with total sorption at 47.9% in 96 hours. No sorption was detected this time in control reactors of 2,3,6-TCP sorption experiments.

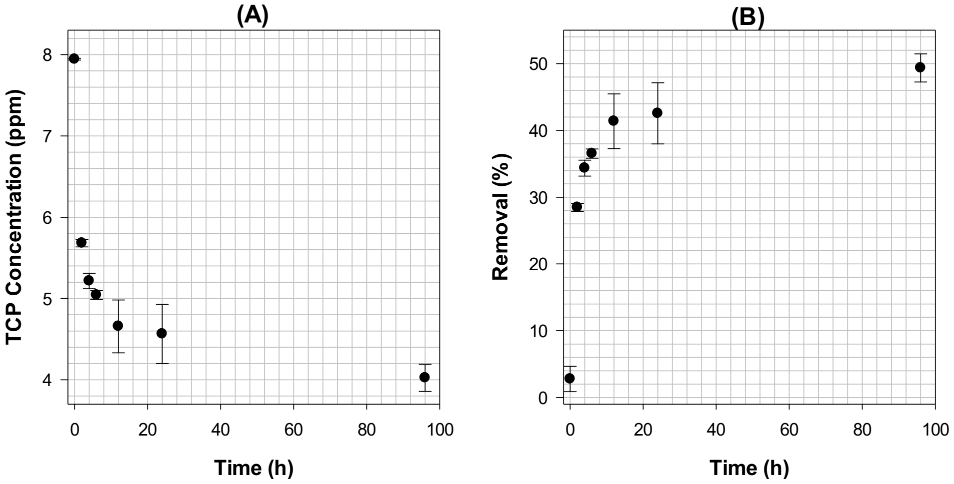

***Figure 2. (A)** 2,3,6-TCP sorption on PE **(B)** removal percentage of 2,3,6-TCP.*

Effect of pH on the sorption of 2,3,6-TCP was tested at pH=4 and 8. The pKa of 2,3,6-TCP is 5.8, therefore pH values of 4 and 8 were chosen to see both sides of the spectrum, and to see how 2,3,6-TCP sorbs onto MPs in its phenolate form. When the pH is adjusted to 4 there is a sorption of up to 72% onto the microplastics. When pH is at 8 there is a reduced affinity to sorb onto the microplastics which is 25% which is lower than when the pH is unadjusted (pH 6±1) around the pKa which is 5.9 the sorption is 58% as in the graph (Figure 3**)**. These results indicate that the anionic form has much lower affinity for MPs.

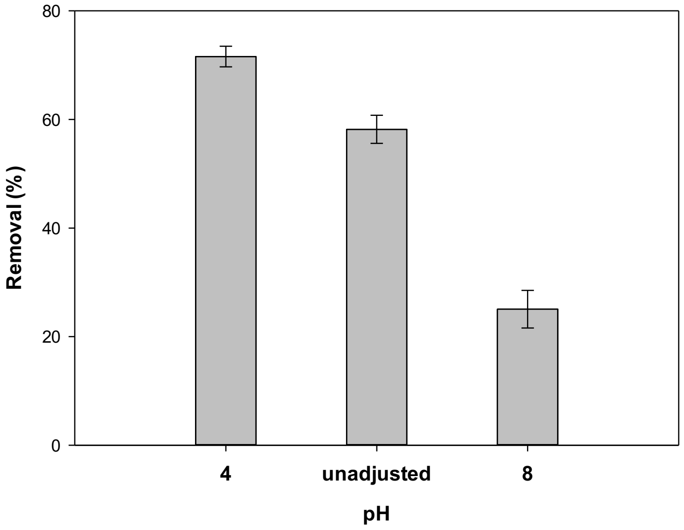

Figure 3 *Removal percentage of 2,3,6-TCP in pH 4, unadjusted pH and pH 8.*

Effect of particle size of the MPs on the sorption of 2,3,6-TCP was also investigated. Experiments were performed with smaller particle size MPs (0.106-0.180 mm), larger particle sizes (0.850-1 mm) and mixed particle size(<1mm). The results from the experiments showed that there is no significant effect on MPs particle size in the sorption of 2,3,6-TCP onto microplastics. For the smaller particle size there was 33% sorption for the larger particles there was 43% removal as shown in the graph (Figure 4).

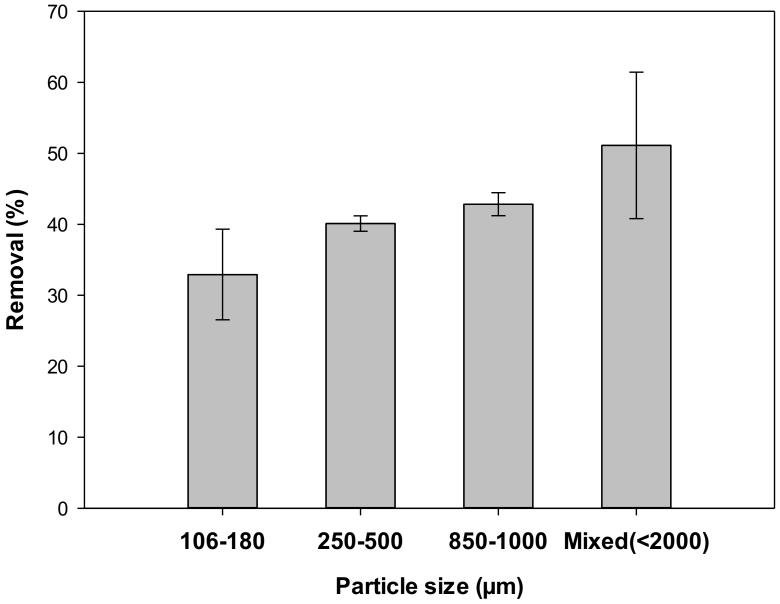

Figure 4 *Removal percentage of 2,3,6-TCP in different particle sizes.*

4. CONCLUSION

Phenol is a highly soluble organic compound (with aqueous solubility more than 90,000 ppm) having quite a low logK_{ow} of 1.44. It is expected for highly hydrophobic compounds to have a higher affinity for sorption as a means of escaping from the aqueous phase. Phenol being highly hydrophilic, as well as ionizable (with a pKa of 10), escaping tendency from water is expected to be low. 2,3,6-TCP, on the other hand, is a less soluble organic compound and with higher logK_{ow} of 3.77. Therefore, it is expected for highly hydrophobic compounds like 2,3,6-TCP to have a higher affinity for sorption as a means of escaping from the aqueous phase, that is why high sorption to MPs is observed. Effects of pH on phenol no discernible sorption could be observed in test reactors, when compared to control reactors, therefore change in pH was not significant in the sorption of phenol onto MPs. When it comes to 2,3,6-TCP there is a significant effect of pH on the sorption to MPs with the lower pH showing higher affinity for sorption. This change in characteristic is due to the dissociation of the two compounds. When phenol was undissociated, 2,3,6-TCP dissociated at the pHs tested, so results showed a variation. Particle size has no great effect on the sorption to MPs in phenol as well as 2,3,6-TCP.

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