Environmental Effects on the Fate and Co-Transport of Pesticides and Microplastics in Soils Irrigated with Wastewater

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Abstract In this paper we report results from a series of kinetics and isotherms experiments under different conditions (salinity, organic carbon, and temperature) that were conducted in order to determine the equilibrium time and the sorption response of typical biodegradable microplastics in comparison to non-degradable microplastics to three common pesticides present in wastewater. Moreover, we investigated the molecular mechanisms involved in this sorption via characterization using Fourier Transform Infrared Spectroscopy and Nuclear Magnetic Resonance. Finally, we also present results from soil column experiments designed to facilitate understanding the key and fundamental processes of MPs transport in saturated soil influenced by aging and sorption under various scenarios.

Keywords: Microplastics, pesticides, sorption, groundwater, transport in soils

1. Introduction

Microplastic pollution in soils and groundwater is an emergent research area since excessive plastic debris is being released directly into the terrestrial environment. In recognition of its importance several critical reviews addressing this thematic area have been published in recent years (Yu and Flury, 2020; Liu et al., 2020; O'Kelly et al., 2021; Ren et al., 2021a; Viaroli et al., 2022). Microplastics (MPs) have significant effects on the biological and ecosystem functions of soils. Sources for MPs soil pollution include land spreading of sewage sludge and biowaste composts application in agricultural fertilizers, in addition to wastewater used in irrigation and landfill leachates. In particular, wastewater is a major source of MPs and an assortment of contaminants. Quite often untreated or minimally treated wastewater is released and seeps into soil and eventually reaches groundwater. Although MPs are considered chemically inert, could be rendered vectors for emerging contaminants (e.g., antibiotics, pesticides) given their sorption capacity due to their very high surface area. MPs have been shown to extend the survival and dispersal of pathogens resulting in increased travel distances, which in turn affect the safety of groundwater drinking supplies (Gao et al., 2021). Moreover, the organic compounds absorbed into MPs could act as substrates for microbial growth/enrichment on MPs and consequently change operation parameters in wastewater treatment facilities and/or their transport behavior in soils.

MPs can be aged via mechanical abrasion, photo- and thermally-initiated oxidative degradation, hetero aggregation, and bioturbation resulting in changes in their physicochemical properties. An increase in MPs surface roughness and oxygen-containing groups and a decrease in size could enhance the sorption and mobility of MPs in the soil and groundwater environment (Ren et al., 2021b). However, the interactions among ageing, sorption, and transport of MPs in the terrestrial system have yet to be thoroughly researched. Furthermore, the sorption ability of degradable MPs for conventional organic contaminants and emerging pollutants compared to nondegradable MPs has yet to be extensively studied.

In this study we report a series of kinetics experiments and isotherms under different conditions (e.g., pH, salinity, organic carbon, and temperature) that were conducted in order to determine the equilibrium time and the response of biodegradable microplastics (BMPs) as opposed to conventional microplastics (CMPs) to three widely used pesticides, based on which Polanyi theory used for nanomaterials is investigated and benchmarked to classic macro-scale isotherms models. This study also aims to understand the key and fundamental processes of MPs transport in saturated soil influenced by aging and sorption under various scenarios, and climatic conditions.

2. Materials and Methods

2.1. Types of MPs and pesticides tested

Standards of pesticides (Atrazine, Metolachlor, and Prometon) (purity 98.0%), and several MPs (polycaprolactone (PCL), polyhydroxyalkanoates (PHA), polyhydroxybutyrate (PHB), polylactic acid (PLA) and polyvinyl chloride (PVC) (Sigma-Aldrich) were used in this study. Wastewater samples were taken from the University of Connecticut Wastewater Treatment Plant.

The residual concentration of pesticides was measured using HPLC with a C18 column.

2.2. Batch sorption experiments

20 mg of MPs and 10 mL of background solution containing 0.01 M CaCl2 were added to 40 mL glass vials. A specified volume of pesticide stock solution was spiked (v/v 02% acetone) into each vial to get the desired initial concentrations. Sorption kinetics experiments were performed for given time intervals with an initial pesticide concentration of 80 µg/l. Sorption isotherm experiments were conducted with a series of initial concentrations of each pesticide in the range 30-300 µg/l. The experiments lasted for 72 h and were run in duplicate. Isotherms for pH, TOC, salinity, and temperature effects were also investigated. However, due to page limitations not all results are presented herein.

2.1. Adsorption modeling

The sorption kinetics data were fitted with two classic models, namely pseudo-first order and pseudo-second order (PSO) equations. To understand the rate-limit step of adsorption and surface energy distribution, kinetics data were also fitted to intraparticle and Elovich models. The sorption isotherms were fitted with the most common Langmuir and Freundlich isotherms and were compared to the Polanyi adsorption isotherm potential theory. The validity of sorption models was evaluated based on the goodness-of-fit parameter (R^2) and Chi-square analysis.

2.2. Soil column experiments

Our experiments have followed a procedure similar to that reported in Gui et al. (2022). We have chosen Polylactic acid (PLA) as a BMPs representative in order to investigate the transport of biodegradable microplastics in a saturated soil column under different conditions, followed by a model that informs about the transport properties. The MPs transport experiment was conducted in a column with an inner diameter of 1.8 cm. Soil with an average particle size of 985 µm was packed into the column with a filling height of 8 cm with both ends of the soil column capped with 80 µm pore size nylon membranes and porous stone of 45 µm pore size as supporting materials. The soil column was then saturated with ultrapure water for 4 h to stabilize the colloids that may exist on the surface of the medium particles. A conservative tracer (KBr) was flashed through the column to determine the hydrodynamic conditions. After that, the column was continuously saturated with 10 mM KCl background electrolyte solution for 2 h. Then 875 mL of 28 mg/L Niel-red stained PLA MPs suspension was pumped upward at a flow rate of 0.9 mL/min. The effluent was collected, then filtered, and suspended particle concentrations of MPs were processed using microscopy Fluorescence to determine effluent concentration.

3. Results and Discussion

Kinetics sorption data were best fitted by the PSO model (R^2: 0.999), and the sorption equilibrium was achieved within 3 days. This reveals the time needed for microplastics to absorb pesticides from wastewater and concentrate them on their surface. Furthermore, the intra-particle model exhibited a very good fit (R^2: 0.98), indicating that particle diffusion was involved in controlling the process and the internal film diffusion is the rate-limiting step for adsorption (Figure 1). The maximum adsorption capacity ranged 84-120 µg/L for PVC, 64-98µg/L for PHB, 90-145µg/L for PLA, 50-85 µg/L for PHA, and 100-130 µg/L for PCL. Because linear isotherms deviate from experimental data, the Polanyi adsorption potential theory to adsorption from solution on microplastics was also tested and showed reasonably good fit (R^2=0.93).

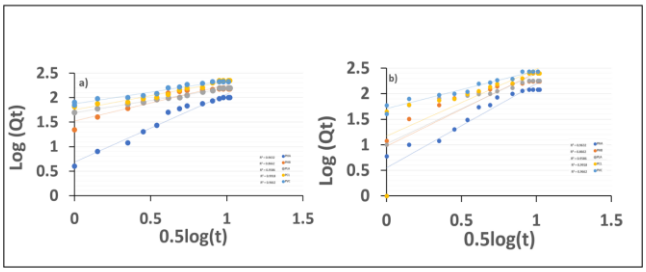

Figure 1. Intra particle diffusion order sorption kinetics of (a) atrazine and (b) prometon for PLA, PHA, PHB, PCL and PVC MPs (Initial concentration 80µg/L, solution pH 7.0, Temperature 25° C)

Environmental conditions can play a vital role in the sorption process as they can change the surface chemistry. Samples collected at different time were tested in order to investigate the effects of environmental factors (pH, salinity, TOC, and temperature) on the sorption behavior. Herbicide sorption on PLA was generally not affected by salinity, pH, or dissolved organic matter. However, salinity and TOC matter significantly decreased sorption on the rest of the MPs (Figure 2).

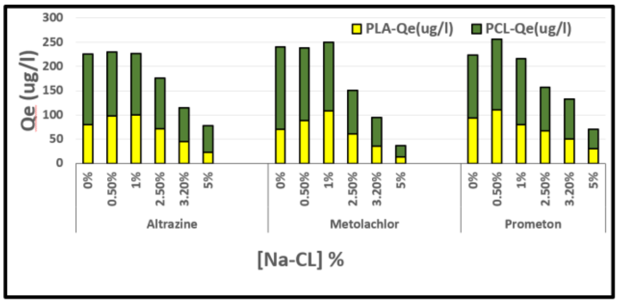

Figure 2. Effect of salinity on the adsorption of herbicides on a) PLA and b) PCL

The effects of salinity on sorption may change depending on the types of organic pollutants and the nature of the microplastics considered. As a sorbent for the three herbicides, PLA exhibited good stability under the salinity of various solutions. A possible explanation for this is that the salting-out effect was too weak to affect the strong sorption capacity of PLA significantly. In comparison, salinity negatively affected the herbicide's sorption by PCL. Suppressive effects might have occurred because sorption included cation exchange.

We have investigated the effect of MPs size on their transport in soils by deploying three sizes of MPs (350, 250, and 100 µm) in the soil column. The breakthrough curves (BTCs) indicated that the smaller microplastics are likely to be more mobile. Therefore, 100 µm was chosen for subsequent experiments, which involved aged biodegradable PLA MPs that were synthesized via mechanical abrasion using IKA mill tube C. In this case BTC showed a concentration of 13 mg/L, indicating that aged MPs can migrate farther; this may be due to the smaller size and rough surface, which was confirmed from microscopic images. However, the BTC results show a non-monotonic behavior, which is a result of soil pore blockage (Figure 3).

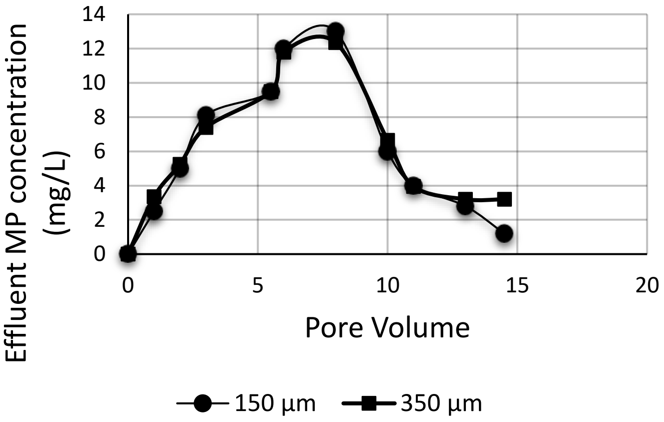

Figure 3. The microplastic breakthrough curve in soil column experiments for 350 and 150 µm MPs

Chu et al. (2019) reported a similar behavior and concluded that models based on the classic convection-diffusion (advection-dispersion) are not well suited to study this phenomenon. We have also investigated co-transport of MPs and contaminants. Atrazine was sorbed to microplastics and the column experiment was repeated. The atrazine input concentration was 150 µg/L, the flow rate was 0.9 ml/min, the ionic strength was 0.01 mM KCL, and the pH was 7. As microplastics travel in the column they collide with soil grains and this increases the desorption of pesticides molecules from the MPs surface, and in combination with solution chemistry, the desorbed molecules exhibit chemisorption to the sand particles. We have found that microplastics can increase the mobility of contaminants which may lead to potent water table contamination (Figure 4a).

At the conclusion of the transport experiments (8 h), the columns were transferred and stored for 24 h at -95° C. Afterwards; the columns were dissected at 2 cm intervals, the four sections were processed, the data were normalised to obtain MPs-atrazine profile as a function of depth (Figure 4b). The smaller size microplastics have higher surface area per unit volume and thus absorb more pesticides per unit mass of microplastics. Therefore, as the microplastics travel through the soil column, the atrazine that is adsorbed onto their surface is released into the soil, resulting in a higher concentration of atrazine per unit depth of ground for the smaller microplastics when compared to the larger ones.

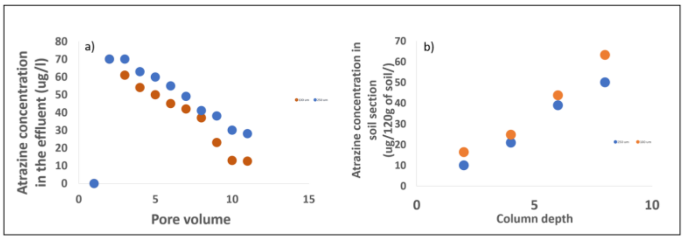

Figure 4. Atrazine concentration a) in the effluent, and b) as a function of column depth; inflow is at depth zero

4. Conclusions and Future Work

In this paper we reported results from a series of kinetics and isotherms experiments in order to determine the equilibrium time and the sorption response of typical biodegradable microplastics in comparison to non-degradable microplastics to three common pesticides present in wastewater. The validity of sorption models was evaluated based on R^2 and Chi-square analysis. Herbicide sorption on PLA was generally not affected by salinity, pH, or dissolved organic matter. However, salinity and TOC matter significantly decreased sorption on the rest of the MPs.

We also presented results from soil column experiments designed to facilitate understanding the key and fundamental processes of MPs transport in saturated soil influenced by aging and sorption under various scenarios. Soil column BTC showed that aged MPs can migrate farther; this may be due to the smaller size and rough surface, which was confirmed from microscopic images. However, the BTC results showed a non-monotonic behavior, which is a result of soil pore blockage. Finally, we have found that microplastics can increase the mobility of contaminants which may lead to potent water table contamination.

In future work, we will investigate the effect of different experimental conditions (pH, ionic strength, organic fraction and Fe fraction) on PLA transport by examining BTCs and their surface properties. Luo et al. (2020) have identified a positive correlation between Kd and both organic content and Fe presence. We hypothesise that the surface charge will change following a functional group change, which will drastically impact the PLA aggregation and sorption to soil particles. The results will be implemented in a model that simulates the transport in a 1D soil column, similar to the work of Ryu et al. (2021) and employing multi-physics software (e.g., COMSOL). İn addition, we will investigate the molecular interactions between MPs and pesticides and MPs with soil particles to unfold the mechanism behind the sorption and aggregation of MPs to pesticides/sand grains regarding different media conditions.

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