

Microplastics-Assisted Hexavalent Chromium Transportation in Soapy Water Environments

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Abstract - The sorption medium plays a vital role in vector transport of microplastics bound metal ions. The influence of soapy water on transportation of microplastics bound Cr(VI) and sorption mechanisms are still not clear. Therefore, in the present study the performance of pristine and aged polyethylene (PE) microplastics to adsorb Cr(VI) in soapy water was compared with NaNO₃ and humic acid (HA) mixed water. The influence of pH, contact time, and concentration of Cr(VI) on the sorption performances of PE microplastics have also been tested. Soapy water exhibited a greater adsorption performance than NaNO₃ and HA mediums. The highest adsorption of Cr(VI) occurred at an acidic pH range from 2.0 to 2.5 without depending on the sorption medium. Hydrophobic and electrostatic interactions predominantly played a vital role in binding of Cr(VI) in soapy water onto PE microplastics through surface complexation. Adsorption kinetic data for pristine PE microplastics was well fitted with the non-linear pseudo-second-order kinetic model, thereby indicating that the chemisorption-based surface adsorption is the rate-limiting process. Sorption kinetic data of aged PE microplastics were fitted well for fractional power and intra-particle-diffusion models suggesting that the adsorption was assisted through diffusion-controlled adsorption that depends on sorption time. Isotherm data fitted with Hill model implicit a cooperative adsorption process. Microplastics bound Cr(VI) largely released from the surface at basic pH conditions implying the sorption of Cr(VI) is influenced primarily by the pH. Hence, soapy water could be a potential sorption medium for microplastics bound Cr(VI) ions influencing the migration of Cr(VI).

Keywords: *Polyethylene microplastics, sorption medium, vector transport, chemisorption, cooperative adsorption*

I. INTRODUCTION

Chromium (Cr) can be introduced as one of the major potentially toxic elements which can commonly exist in the environment. Industrial metallurgy, coal combustion, and pesticides are the major anthropogenic sources of the environmental existence of Cr(VI) in groundwater [1]. Hydrophobicity, surface area, and charge of the microplastic surfaces greatly influence the adsorption of pollutants in water through hydrophobic and electrostatic interactions [2]. Domestic wastewater is mixed with soap, shampoo, and other detergents and ends up in surface water systems. Microplastics bound the vector transportation of Cr(VI) in the presence of soap water have not been studied yet. Nevertheless, polyethylene (PE) microplastics showed a notable adsorption performance for Cr(VI) in surfactant rich water indicating the

role of surfactants in the vector transport of Cr(VI) [3]. Hence, it is important to reveal the interactions and mechanisms behind the Cr(VI) adsorption onto microplastics with soap-enriched sorption medium. The present study investigates the adsorption behaviour of Cr(VI) onto PE microplastics in soap water comparing to organic and ionic species-rich water. Further, implications for the soap water boosted adsorption of Cr(VI) onto both pristine and naturally aged PE microplastics are revealed concerning the sorption isotherm and kinetic profiles.

II. MATERIALS AND METHODS

A 1 g L⁻¹ of pristine microplastic dosage was used in the entire experiment. All samples were shaken at a speed of 150 rpm at 25 °C. The samples were filtered through 0.22 µm PTFE filters. The pH edge experiment was conducted with an initial concentration of 5 mg L⁻¹ of Cr(VI) in water and the solution pH was adjusted to a range of 2.0–9.0. The effect of NaNO₃ (0.1 M), humic acid (HA) (1.5 mg L⁻¹), and soapy water (commercial dish wash in water 0.4% V/V) on Cr(VI) adsorption were examined by repeating the pH edge experiment at the same range (i.e., pH 2.0–9.0). By calculating the adsorption capacity of each batch, the best pH and the solution medium for Cr(VI) adsorption were selected. Both kinetic and isotherm experiments were performed at pH 2.0–2.5 in the presence of soapy water (0.4% V/V). The kinetic experiment was conducted for 7 days and the initial concentration for Cr(VI) was 5 mg L⁻¹. First sample was withdrawn after 12 h and then each vial was withdrawn at 24 h of time interval. Adsorption isotherm experiments were carried out with Cr(VI) concentrations ranging from 1 to 25 mg L⁻¹ for 168 h. The same procedure was performed for the aged PE microplastics. The control experiment was conducted only without microplastics. The kinetic data were modelled with pseudo-second-order, Elovich, fractional power, and intra-particle diffusion kinetic models while isotherm data were modelled with Hill, Freundlich, and Langmuir isotherm models. The optimized parameters for the adsorption were determined using Origin statistical computer software (version 8.0).

III. RESULTS AND DISCUSSION

The adsorption of Cr(VI) showed a gradual increase with decreasing pH, reaching the maximum adsorption at pH 2.0–2.5. In the lower pH range Cr(VI) ions are present in the forms of HCrO_4^- , H_2CrO_4 , and $\text{Cr}_2\text{O}_7^{2-}$ whereas the HCrO_4^- is the predominant ionic form. Since pH_{pzc} of microplastics are around pH 4.0, at the pH range of 2.0–2.5, the surface of microplastics is positively charged. The protonated surface of microplastics enriches the affinity of HCrO_4^- ions towards itself and binds through electrostatic interactions. The decreased adsorption efficiencies with further increase in the pH from 2.0 might be due to the drop of H^+ ions in the sorption medium and thereby increased negative charge density at the surfaces of microplastics. Repulsive effects between HCrO_4^- and negatively charged adsorbent surface and competitive effects between HCrO_4^- and adding OH^- ions for occupying available adsorption sites cooperatively decrease the adsorption of Cr(VI). Due to the remarkable adsorption performances of both pristine and aged PE microplastics at acidic pH (pH 2.0–2.5) without depending on the sorption medium, pH 2.0 was chosen as the optimum pH condition.

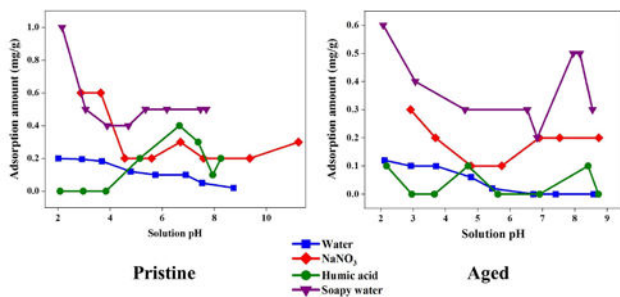


Fig. 1. Adsorption performances of pristine and aged PE microplastics in the presence of different sorption mediums

Adsorption performance of Cr(VI) onto both pristine and aged PE microplastics in the presence of soap water was more notable than the performance in the presence of NaNO_3 or HA likely indicating soap water medium accelerates the adsorption of Cr(VI) than the sorption mediums consist of ionic and organic species (Figure 1). Sorption performance in the presence of 0.1 M NaNO_3 was second highest whereas the microplastics in an aqueous solution mixed with HA showed the least Cr(VI) adsorption. Presence of NO_3^- ions affects the binding affinity of HCrO_4^- towards protonated microplastics surface making competency to each other. Besides, Na^+ and HA reduce the mobility of HCrO_4^- in the sorption medium hindering sorption sites. Anionic surfactant (Sodium dodecyl sulfate) can influence the adsorption process of Cr(VI) onto PE microplastics [3]. Hence, surfactants consisting of the sorption medium might be supported the adsorption of Cr(VI) onto the surfaces of PE microplastics. Consequently, hydrophobic and electrostatic interactions predominately play a vital role in the binding mechanism of Cr(VI) onto PE microplastics through surface complexation. Chromium ion sorption onto pristine PE microplastics reached equilibrium slightly within 168 h (7 days). Adsorption kinetic data for pristine PE microplastics was well fitted with the non-linear pseudo-second-order kinetic

model indicating that surface adsorption is the rate-limiting process that involves monolayer chemisorption (Table 1). Nevertheless, Cr(VI) onto aged microplastics did not reach a sorption equilibrium. Sorption kinetics for aged microplastics was well described by the fractional power and intra-particle-diffusion models (Table 1). Accordingly, Cr(VI) adsorption onto aged PE microplastics was assisted through diffusion-controlled adsorption which depends on sorption time (Table 1). Adsorption processes were well fitted with the Hill isotherm model. Resultant Hill cooperativity coefficients (n_H) for pristine and aged PE microplastics for the present study indicate the positively cooperative binding of Cr(VI). Consequently, once one Cr(VI) ion occupies a site and adsorbs onto the surface of microplastics, the binding affinity to occupy more Cr(VI) ions enhances spontaneously.

Table 1: Modeling data for kinetic and isotherm experiments

| Kinetic data | | | | |
|--|------------------------------|--|-------|-------|
| Pseudo-second order $q_t = (k_1 t q_c^2) / (1 + (k_1 q_c t))$ | k_1 | q_c | R^2 | |
| Pristine PE + Surfactant | 0.003 | 1.595 | 0.989 | |
| Fractional power $q_t = K t^v$ | K (mg g^{-1}) | v (h^{-1}) | R^2 | |
| Aged PE + Surfactant | 0.089 | 0.462 | 0.963 | |
| Intra-particle diffusion $q_t = k t^{1/2}$ | R^2 | k ($\text{mg g}^{-1} \text{s}^{-1/2}$) | | |
| Aged PE + Surfactant | 0.959 | 0.076 | | |
| Isotherm data | | | | |
| Hill $Q_e = (Q_H (k_H C_e)^{n_H}) / (1 + (k_H C_e)^{n_H})$ | Q_H (mg g^{-1}) | k_H (L mg^{-1}) | n_H | R^2 |
| Pristine PE + Surfactant | 1.296 | 0.142 | 4.564 | 0.988 |
| Aged PE + Surfactant | 1.541 | 0.092 | 5.081 | 0.973 |

IV. CONCLUSIONS

Influence of the sorption medium for adsorption of Cr(VI) ions onto pristine and aged PE microplastics was studied. Soapy water was the most potential sorption medium at acidic pH range from 2.0 to 2.5 compared to water, NaNO_3 , and HA mediums. Pristine PE microplastics underwent monolayer chemisorption whereas aged PE microplastics underwent diffusion-controlled cooperative adsorption which depended on sorption time. Hydrophobic and electrostatic interactions predominately play a vital role in the binding mechanism of Cr(VI) in soapy water onto PE microplastics through surface complexation.

References

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