The potential of microplastics as adsorbents of sodium dodecyl benzene sulfonate and chromium in an aqueous environment

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Graphical Abstract
Highlights

- Adsorption behavior of SDBS and Cr(VI) on microplastics (MPs) is investigated.
- Adsorption capability is evaluated using two types of MPs such as PET and PS.
- Changes in crystallinity and morphology of MPs are assessed in relation to adsorption.
- Models are proposed for adsorption of target pollutants onto MPs.
Abstract

Considering the omnipresence of microplastics (MPs) in aquatic environments, their potential as carriers for diverse waterborne pollutants has been recognized. In this work, various aspects of the adsorptive behavior of two ionic components, sodium dodecyl benzene sulfonate (SDBS) and Cr(VI), are explored using two types of MPs as model adsorbents, namely poly(ethylene terephthalate) (PET) and polystyrene (PS). The influence of key variables (pH, particle size, and dose of the MPs) on adsorption is evaluated systematically. The maximum adsorption capacity values of SDBS on PET and PS are estimated to be 4.80 and 4.65 mg·g⁻¹, respectively, while those of Cr(VI) ions are significantly lower at 0.080 and 0.072 mg·g⁻¹. The influence of pH and MP particle size on the adsorptive equilibrium of SDBS is best described by a Freundlich isotherm, while the behavior of Cr(VI) is best accounted for by a Langmuir isotherm that takes into account associative adsorption across at least two active surface sites.

Keywords: Microplastics; SDBS; Cr(VI); Carrying mechanism; Adsorption modeling
1. Introduction

The environmental and health impacts of plastic pollution have been recognized as a global environmental challenge (Boots et al., 2019; Kanhai et al., 2020; Vignieri and S., 2016). The environmental significance of microplastics (MPs) has been explored in a number of respects, including spatiotemporal distribution (Corcoran et al., 2020; Ouyang et al., 2020; Wang et al., 2020b), biotoxicity (Dong et al., 2020b; Guo et al., 2020; Sorensen et al., 2020; Wang et al., 2020a), separation/identification (Gong and Xie, 2020; Kanyathare et al., 2020), and as adsorbents/carriers of pollutants (Almeida et al., 2020; Dong et al., 2020a; Holmes et al., 2020; Liao and Yang, 2020; Liu et al., 2020; Tang et al., 2020; Zhang et al., 2020b). MPs can be classified into two types, primary and secondary. The former are engineered small particles for targeted applications, while the latter are the natural outcome of environmental (or mechanical) degradation of larger plastics (Cole et al., 2011). Primary MPs are used in household goods, air-spray media, personal care products (e.g., facial cleansers, toothpaste, and exfoliated sanding paste), and drug carriers in medicine (Cole et al., 2011; Gregory, 1996; Lei et al., 2017).

Approximately 6% of liquid skin-cleaning products sold commercially in the European Union, Switzerland, and Norway reportedly contain MPs, 93% of which was polyethylene (PE) (Browne et al., 2011; Fendall and Sewell, 2009; Gouin et al., 2015).

Both primary and secondary MPs are discharged into a variety of aquatic and terrestrial environments and biota, causing severe environmental problems (Alimi et al., 2018; Hidalgo-Ruz et al., 2012). The size of the MPs makes them available for ingestion by a wide range of organisms. In addition to direct harm, their adverse effects can be multiplied through a
number of indirect routes, such as vectors for toxic chemicals or microbial components (Hu et al., 2019; Jiang, 2018; Wang et al., 2018). Multiple reports have confirmed that MPs can carry a variety of contaminants into the environment (Brennecke et al., 2016; Kalcikova et al., 2017; Liu et al., 2018).

Pollutants bound on MPs reportedly exert a significant influence on the immune system of marine mussels (Pittura et al., 2018). Other studies have determined that ingestion of toxic chemicals adsorbed on MPs by marine fish results in oxidative stress, liver inflammation, and other pathological reactions (Rochman et al., 2013). Likewise, MPs have been reported to adsorb and carry a wide variety of pollutants such as pesticides (Fang et al., 2019), perfluoroalkyl substances (Llorca et al., 2018), and heavy metals (Brennecke et al., 2016). The toxic effects can be enhanced as these MPs migrate through the food web in marine ecosystems (Jinhui et al., 2019).

To date, numerous research efforts have been devoted to the adsorption potential of MPs against diverse pollutants (e.g., metal ions or surfactant molecules) and associated impacts. It has been demonstrated that a list of MPs, including polyvinyl chloride (PVC), polypropylene (PP), polyamides (PA), and polyformaldehyde (POM), can adsorb diverse metals (e.g., lead, copper, chromium, and cadmium) that typically exist concurrently in the same aqueous solution (Gao et al., 2019). Chromium is well known for its highly carcinogenic and teratogenic effects, the potential for which depends on valence state (Yang et al., 2019). More specifically, the toxicity of Cr(VI) is approximately 500 to 1000 times greater than that of Cr(III) (Mo et al., 2015).
In the presence of sodium dodecyl benzene sulfonate (SDBS), MPs form stable emulsions that can exert more toxic effects in many aquatic organisms (Messina et al., 2014; Shao et al., 2019). Some metals in cationic or oxyanionic forms, such as $\text{HCrO}_4^-$ and $\text{CrO}_4^{2-}$, can be adsorbed on MPs (Holmes et al., 2014). In our previous study, SDBS promoted adsorption of Cr(VI) by PE MPs (Zhang et al., 2020b). However, the individual interactions between MPs and each of these pollutants remain poorly understood. Information on the capturing/vectoring potential of pollutants and their associated mechanisms is rare.

To establish an effective strategy to control MPs and associated problems, it is important to develop better knowledge of the potential of MPs for adsorption of diverse pollutants and the governing mechanisms. We investigated the adsorption behavior of two ionic pollutants, SDBS and Cr(VI), using two types of MPs (PET and PS). The results of our study were used to explore the factors and processes controlling such mechanisms. This research provides new insights on interactions between MPs and key pollutant species in aqueous systems. The overall results are expected to help build a strategic platform to efficiently control MP-based pollution and associated environmental problems.

2. Materials and methods

2.1 Materials

Beads composed of PET and PS were purchased from Far Eastern Industry (Shanghai) Ltd. and Thai Petrochemical Ind Co., Ltd. (Thailand), respectively. The beads were milled using a high-speed rotary pulverizer (FW-80, Beijing Ever Bright Medical Instrument Co. Ltd.) to
produce MPs, which were then divided into different particle-size ranges using standard sieves (0.088, 0.105, 0.15, 0.20, 0.30, and 0.45 mm).

Anionic surfactant SDBS (CH₃(CH₂)₁₁C₆H₄SO₃Na, purity ≥90%) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd, Tianjin, China. Samples of K₂Cr₂O₇ with a purity of 99.8% were purchased from Tianjin Kaitong Chemical Reagent Co., Ltd, Tianjin, China. The other chemicals used in the experiment were of analytical grade, as shown in Table S1 in Supporting Information (SI). The concentrations of SDBS and Cr(VI) ions were determined using an ultraviolet-visible light (UV-Vis) spectrophotometer (UV 759CRT, Shanghai Youke Instrument Co., Ltd, Shanghai, China). Details of the solution preparation and characterization methods are provided in SI.

2.2 Adsorption experiments

Detailed information on the equipment used for the adsorption experiments is provided schematically in Fig. S2. First, a target mass of MPs particles was placed into a 100 mL Erlenmeyer flask, and 25.0 mL of SDBS or Cr(VI) was added to the solution. The flasks were sealed using a rubber plunge and placed in a thermostatic water-bath oscillator at a constant temperature of 298 K (SGA-C, Jiangsu Zhongda Instrument Technology Co., Ltd.). After stirring at 60 rpm for 12 h, the MPs were separated using syringe filters with a membrane pore size of 0.45 μm. Final concentrations of SDBS and Cr(VI) were determined using UV-Vis spectrophotometry.

The adsorption experiments were carried out independently across a range of variables for MPs (e.g., particle size and mass) and pH values of each solution sample containing SDBS and
Effect of MP particle sizes

To study the effect of MP particle sizes, approximately 0.1 g of PET or PS with several particle-size ranges (e.g., 0.088–0.105, 0.105–0.150, 0.15–0.20, 0.2–0.3, and 0.30–0.45 mm) were added into a conical flask (Exps. 1 and 4). The concentrations of the SDBS and Cr(VI) solutions used in this study were 40 and 20 mg-L\(^{-1}\), respectively. The contact time and temperature were 12 h and 298 K, respectively.

Effect of pH

The effects of pH on adsorption of SDBS by MPs were investigated by controlling pH in a range of 2.0 to 11.0 using dilute H\(_2\)SO\(_4\) or NaOH solutions (in Exp 2). This test was carried out using an MP dose of 0.1 g for 12 h at 298 K. In contrast, adsorption experiments against Cr(VI) were conducted at a fixed pH of 8 because the effect of pH is not as prominent on chromium as it is on SDBS.

Effect of MP dose

The effect of MP dose on the adsorption capacity of Cr(VI) was determined using seven masses of PET or PS MPs (0.03, 0.06, 0.09, 0.12, 0.15, 0.18, and 0.21 g) in a Cr(VI) solution of 20 mg-L\(^{-1}\) in Exp. 3.

The adsorption capacity AC (mg-g\(^{-1}\)) was calculated using Eq. (1):
The adsorption ratio (AR) for SDBS and Cr(VI) ions was calculated by Eq. (2):

\[
AR = \frac{C_0 - C_{eq}}{C_0} \cdot 100
\]  

(2)

As adsorption capacity is sensitive to initial concentration of pollutant, the concept of partition coefficient (PC), expressed in L g\(^{-1}\), was derived to describe the adsorption capacity on a more objective basis, using Eq. (3) (Vikrant and Kim, 2019; Zhang et al., 2020a):

\[
PC = \frac{AC}{C_{eq}}
\]  

(3)

### 2.3 Model equations

The predominance diagram for Cr(VI), shown in Fig. S8, suggests that only the CrO\(_4^{2-}\) composition of Cr(VI) is possible at pH 8 and concentration 20 mg/L (3.85 \(10^{-4}\) M). The corresponding equilibrium adsorption concentration for Cr(VI) can be described by a Langmuir adsorption isotherm, where the given ion associatively adsorbs using two active sites. This gives rise to Eq. (4), where \(K_{eq}, C_{liq},\) and \(q_{tot}\) are the equilibrium coefficient (L mg\(^{-1}\)), the liquid concentration at equilibrium (mg L\(^{-1}\)), and the total number of active sites for adsorption (mg g\(^{-1}\)), respectively:

\[
q_e = K_{eq} \cdot C_{eq} \cdot \left( \frac{-1 + \sqrt{1 + 8K_{eq}C_{eq} \cdot q_{tot}}}{4K_{eq}C_{eq}} \right)^2
\]  

(4)

In high equilibrium liquid concentrations, the expression for the isotherm can be rewritten as Eq. (5):
The total number of active surface adsorption sites can be assumed to be proportional to the area of MP particles; for spherical particles, the area-to-volume ratio is proportional to the inverse of diameter. Equation (6) combines these two observations and relates MP mass to experimental MP concentration and volume, as described in section 2.2:

\[ q_{\text{tot}} \propto A \rightarrow q_{\text{tot}} \propto \frac{m}{\rho \cdot d} \rightarrow q_{\text{tot}} = B \cdot \frac{6}{\rho \cdot d} = B' \cdot \frac{m}{d} = B' \cdot \frac{C_{\text{MP}} V}{d} \]  

Combining Eqs. (5) and (6), the Cr(VI) adsorption capacity is modeled by Eq. (7) with an additional exponent m, which takes into account particle-diameter dependency, possible surface roughness, and imperfectly spherical particles:

\[ q_e = \frac{B' \cdot C_{\text{MP}} V}{2 \cdot d^m} \]  

The selected concentration of SDBS (40 mg/L = 40\times10^{-3}/348.48 gives 1.15 \times 10^{-4} M) is well below the reported critical micelle concentration of 2.73 \times 10^{-3} to 2.92 \times 10^{-3} M (Dubey, 2011; Sood and Aggarwal, 2018)). As such, the presence of only singular SDBS molecules must be considered.

In this work, the adsorption behavior of SDBS is described by the Freundlich isotherm, as shown in Eq. (8). This isotherm considers physical adsorption, which can exceed monolayer coverage, which is typically described by Langmuir adsorption isotherms. Because SDBS adsorbates are long hydrophobic molecules with a carbon-chain length of \sim 12 \AA{} (relative to the 2.3 \AA{} atomic radius of CrO_4^{2-}), the concept of one or two active sites might not be sufficient to derive the correct interpretation.
The Freundlich isotherm tacitly includes the number of active sites for adsorption in its $m_{\text{MP}}$ term so that the same dependency, based on particle diameter, can be adopted, as displayed in Eq. (6). As pH increased, zeta potential decreased, as shown in Fig. S3, and the particles became more negatively charged. This gave rise to a smaller maximal adsorption capacity, as the SDBS ions were also negative, with a correspondingly smaller adsorption equilibrium coefficient. The product of $B'$, which is directly proportional to the total number of possible adsorption sites, and the equilibrium coefficient can be a function of pH, as seen in Eq. (9), with substitution (10):

$$m_{\text{ads}} = B'^n \cdot \left( \frac{C_{\text{eq}}}{d^m} \right)^{1/n} \cdot \frac{C_{\text{MP}} V}{d^m} \cdot \exp(-\alpha \cdot pH)$$  \hspace{1cm} (9)

$$B'^n = K'_{\text{eq}} \cdot B'$$  \hspace{1cm} (10)

To predict the adsorption capacity of MPs against Cr(VI) and SDBS, the average value for each particle-size range of MP was adopted in Eq. (7) and (9), respectively. A generalized reduced gradient algorithm was used to estimate the parameters in non-linear models using Eqs. (7) and (9) (de Levie, 1999).

### 2.4 Material characterization

The morphology of the two MPs was determined using focused ion beam scanning electron microscopy (SEM, Zeiss/Auriga FIB SEM). The zeta potential of PET and PS MPs in aqueous solution was determined using a microelectrophoresis apparatus (JS94H, Shanghai Zhongchen Digital Equipment Co., Ltd, Shanghai, China). The particle size of MPs was estimated by laser particle-size distribution (BT-9300, Bettersize Instruments Ltd, Dandong, Liaoning, China). Phase analysis was conducted using an X-ray diffractometer (XRD, with Cu Kα radiation, λ = 9
3. Results and Discussion

3.1 MP characterization

Fig. 1(a) and (d) depict the appearance of the as-received PET and PS MPs. The beads were round with a smooth surface. After milling, the resulting MPs particles had a stone-like shape, with particles ranging in size from 0.088 to 0.45 mm. The high-resolution scanning SEM images in Fig. 1(c) and (f) show the presence of cracks, grooves, and angular protrusions on the surface of the MP particles, which can provide extra active sites for adsorption. An XRD analysis was used to study the crystallinity of the MPs. Many crystallization peaks are evident on the PET spectra, as in Fig 5(c), and can be attributed to the semi-crystalline structure of the polymer (Hadjizadeh et al., 2011). The PS spectrum, as shown in Fig. 5(d), shows wide humps rather than peaks, indicating the lower crystallinity of PS relative to that of PET (Veisi et al., 2018).

3.2 Adsorption of SDBS by PET and PS

3.2.1 Effect of MP particle size on the adsorption capacity of SDBS

The adsorption capacity of SDBS by both PET and PS MPs increased gradually with decreasing particle size, as shown in Fig. 2(a) and (b). The adsorption capacity of SDBS on PET (0.81 mg·g⁻¹) was 2.5 times greater than that on PS (0.29 mg·g⁻¹) at a particle-size range of 0.30 to 0.45 mm. As particle size decreased to a range of 0.105–0.088 mm, the adsorption capacities of PET and PS increased to 1.17 and 0.65 mg·g⁻¹, respectively. This is consistent with the
distributions of hydrodynamic diameters of PET and PS in the solutions, as shown in Fig. 3(c) and (d). There was no apparent aggregation of the particles in the solutions, and no difference in diameter was evident between the solid-state and hydrodynamic stages.

The change of adsorption capacity of the two MPs coincided with the change in distribution of hydrodynamic diameters. For example, we assigned PET particles into two size groups: group “A” covered three sub-ranges of 0.15 to 0.20 mm, 0.20 to 0.30 mm, and 0.30 to 0.45 mm; and group “B” covered two sub-ranges of 0.088 to 0.105 mm and 0.105 to 0.15 mm. The differences in adsorption capacity of MP of different particle sizes in group A were less evident than those in group B. It is possible that the adsorption capacity of MPs was affected by particle size, which was reflected in the adsorption isotherm expressions (7) and (9). The relationship between hydrodynamic diameter distribution and adsorption capacity was similar between PS and PET, as mentioned above. The difference in hydrodynamic diameter distribution between two groups of PS ranging in size from 0.20 to 0.45 mm (group C) was less significant than those of the three groups with sizes ranging from 0.088 to 0.20 mm (group D). The adsorption capacity of MPs of different particle sizes in group C was much smaller than that in group D.

The adsorption capacity of PET was dominant over that of PS when the particles were smaller than 0.3 mm in diameter. The relative dominance of PET over PS can be explored further in relation to the factors governing their aggregation and adsorption in a water environment (e.g., zeta potential and hydrophobicity) (Li et al., 2018). The influence of zeta potential on particle aggregation behavior might be negligible because PET and PS MPs had similar values in deionized water at all pH values (Fig. S3). MPs undergo aggregation upon release into aquatic
environments, which is a critical factor that determines their environmental fate and ecological risks (Besseling et al., 2017; Carr et al., 2016). Aggregation increases the hydrophobicity of the particles while causing them to float on the surface of the solution. It is probable that most PET MPs can be suspended or sink in the water column after adsorbing SDBS (Paria and Khilar, 2004). As a result, PET could have a higher adsorption capacity than PS, as the former would have more contact with the solution.

The SEM images (Fig. 3) illustrate the negligible changes in morphology of the MPs during the adsorption process. The lack of visible swelling on the surface of PET or PS MPs can be attributed to the limited adsorption capacity of SDBS and its small molecular size. An XPS analysis carried out to assess the chemical states of carbon, sulfur, and oxygen elements on PET and PS MPs confirmed the adsorption of SDBS in the form of the S 2p peak in the XPS wide-scan spectra of both MPs, as in Fig. 4(a) and (b). Figure 4(c), which depicts a high-resolution scan of the S 2p region, shows that peaks at 167.8 eV and 168.9 eV correspond to S 2p$_{3/2}$ and S 2p$_{1/2}$, respectively. The intensity ratios of the S 2p$_{3/2}$ and S 2p$_{1/2}$ on the PET and PS spectra are close to 1.38:1, which is near the typical value of SDBS. The S 2p peak strength of PET was higher than that of PS, which is consistent with the adsorption data in that PET adsorbs more SDBS. Results of both the survey and the high-resolution scan of the O 1s peak in Fig. 4(c) and (d), (SI) support the presence of oxygen in sulfonate functional groups (-SO$_3$-), while further confirming that SDBS should be adsorbed on the surface of MPs.

3.2.2 Effect of pH on adsorption of SDBS
Figures 5(a) and (b) show the effect of pH on adsorption of SDBS by PET and PS MPs. The adsorption capacity for SDBS by both MPs decreased significantly with increase in pH. The adsorption capacity (or rate) of SDBS by MPs in acidic solution was higher than in alkaline solution. The adsorption capacities of SDBS by PET and PS MPs were 4.80 and 4.65 mg·g⁻¹ at pH 2.0 (after 12 h of shaking), respectively. In contrast, their capacities at pH 5 were reduced to 1.33 and 1.04 mg·g⁻¹, respectively. These values were maintained (e.g., 1 to 1.2 mg·g⁻¹) at pH 5 to 10. The capacity dropped to almost zero at pH 11. The adsorption of SDBS by PS MPs was lower than that by PET in acidic solution while slightly higher in alkaline environments. The zeta potential on the surface of the MPs changed from positive to negative (roughly from +18 mV to −54) at a pH from 2.0 to 11, which can be explained by the decrease in concentration of protons and their replacement by negatively charged anions at higher pH.

As an anionic surfactant, SDBS can be attached to an MP surface by attraction forces at a lower pH. As repulsive forces become more dominant at higher pH (> 5), adsorption of SDBS should decrease with increasing pH. Figures 5(e)–(i) show the proposed adsorption mechanism between SDBS and PET/PS MPs (e.g., ion-pair adsorption, ion exchange adsorption, dispersive force adsorption, and hydrophobic interaction adsorption), which should be explored further. The lower adsorption capacity on PET at higher pH can be explained by the surface charge properties and changes in zeta potential, as shown in Fig. S3.

3.3 Adsorption of Cr(VI) by PET and PS

3.3.1 Effect of MP dose on the adsorption capacity of Cr(VI)
The adsorption behavior of Cr(VI) on the surface of PET and PS MPs is plotted in terms of capacity and adsorption rate in Fig. 6(a)–(b). With increasing dose of PET/PS, the adsorption capacities of Cr(VI) increased such that the maximum adsorption capacities were 0.08 and 0.04 mg·g⁻¹ at 4.8 g·L⁻¹ PET and 3.6 g·L⁻¹ PS, respectively. The adsorption capacity of Cr(VI) decreased at higher doses of MPs (PET > 4.8 g·L⁻¹ and PS > 3.6 g·L⁻¹). This can be ascribed to the greater aggregation and adherence to air bubbles at increasing concentrations of MPs (Nogueira et al., 2020). The adsorption rate of Cr(VI) by MPs followed almost the same trend as adsorption capacity. The adsorption rate maintained constant values of 2.0% and 0.7% at high doses of PET and PS MPs, respectively (as detailed in SI S4). No visible change appeared in MP morphology before and after adsorption, as shown in Fig. 6(c)–(j), which also indicated no aggressive reaction between Cr(VI) and MPs in aqueous solution. The absence of new peaks in the XRD spectra suggests that the adsorbed materials were below the detection limit.

Generally, the adsorption capacity/rate of Cr(VI) was higher on PET than on PS, reflecting its slightly reduced hydrophobicity against the latter (Borcia et al., 2014). Reduced hydrophobicity decreased the surface tension of PET MPs in aqueous solution, facilitating adsorption of Cr(VI) on PET relative to PS, as can be observed in Fig. 7. The contact surface with MPs (PET/PS) was larger for SDBS than for Cr(VI). The hydrophobic particles (MPs) produced stable suspension more easily in SDBS solution than in Cr(VI) solution. Thus, the adsorption capacity of SDBS by MPs should be much larger than that of Cr(VI).

3.3.2 Effect of particle size of MPs on the adsorption capacity of Cr(VI)
The adsorption capacities of PET/PS MPs against Cr(VI) were compared across a range of particles sizes, as seen in Fig. 8(a)–(b). The adsorption capacity of Cr(VI) in aqueous solution increased gradually with decreasing MP particle size. Typically, the adsorption capacities of Cr(VI) by PET and PS were 0.019 and 0.016 mg·g⁻¹, respectively, at a particle-size range of 0.45 to 0.30 mm. After decreasing the particle size to between 0.105 and 0.088 mm, their adsorption capacities increased noticeably to 0.047 and 0.072 mg·g⁻¹, respectively. The effect of particle size on the adsorption capacity of Cr(VI) was more apparent in PS than in PET. Except for large particles (0.45 to 0.30 mm), the adsorption capacity of Cr(VI) on PS was higher than on PET. Grinding the plastic beads to the MP level increased the number of active sites. As negatively charged sites were more likely to be formed on the surface of PS, adsorption of Cr(VI) cations on PS should significantly improve after grinding. (The differences in adsorption sites between PET and PS MPs are detailed in section 3.4.)

The XPS spectra of PET and PS MPs after adsorption of Cr(VI) are shown in Fig. 8(c)–(j). Few differences were evident in the high-resolution spectra of C 1s and O 1s for both MPs before and after adsorption. However, peaks of Cr 2p and K 2p were detected at binding energies of 575 eV and 293 eV, respectively, supporting the adsorption of Cr(VI) on the surfaces of PET and PS MPs.

The adsorption capacity of Cr(VI) by PS was greater than that by PET at particle size ranging from 0.3–0.2 mm to 0.105–0.088 mm. The difference in adsorption capacity between PS and PET might reflect crystallinity differences, while the increase in crystallinity can reduce the absorption rate of pollutants through a polymer matrix (Karapanagioti and Klontza, 2008). The
adsorption capacity of Cr(VI) by PET (with higher crystallinity) was lower than that of PS, as the MP structure was similar to that of a polymer (Wang et al., 2019).

In our previous studies (Zhang et al., 2020a), the adsorption capacity of Cr(VI) by PE MPs was 0.22 mg·g⁻¹ at pH 5. However, the adsorption capacity of Cr(VI) by PET/PS MPs in this study was moderately lower, with a value of 0.08 mg·g⁻¹ at pH 8. The pH of Cr(VI) solution might play a crucial role in adsorption.

The PCs of PET and PS MPs were computed for the two types of pollutants, as summarized in Table 1. The PC values of SDBS were consistently larger than those of Cr(VI) for all types of MPs. The PC values for the two target species differed by approximately 9.5 and 19 times in PET and PS, respectively. The different adsorption performance of contaminants by MPs can be explained through the adsorption isotherm model.

### 3.4 Adsorption isotherm model

The adsorption capacity of Cr(VI) can be described by Eq. (7), which corresponds to a Langmuir adsorption isotherm for associative adsorption using two active sites for high liquid concentration values. This model is governed by two parameters, B’ and m, representing the proportionality between the number of active sites and particle surface area and the particle diameter dependency, respectively. The values of B’ and m in PS MPs were 0.017 ± 0.006 and 1.91 ± 0.68, respectively, while those for PET MPs were 0.253 ± 0.071 and 0.63 ± 0.18. The higher B’ value corresponded to the experimental trend of preferable uptake of Cr(VI) on PET compared with PS. The higher value of m for PS can be explained by the higher tortuosity of PS.
particles, as shown in Fig. 3(c) and (f). The fitting results for the adsorption behavior of Cr(VI)
were comparable between experimental and calculated data, as seen in the parity plots in Fig. 9.
The adsorption of SDBS can be described by the Freundlich isotherm (8), with parameters of
$B''$, $n$, $m$, and $\alpha$. Here, $B''$ and $m$ represent the active-site versus particle-area proportionality and
particle-diameter dependency, respectively, as described previously for the Langmuir model. In
addition, $n$ and $\alpha$ imply equilibrium liquid concentration dependency (degree of curvature, with
$1/n < 1$) and pH dependency of the adsorption coefficient, respectively. The parameter $\alpha$ is
related to zeta-potential measurements (see Fig. S3). Repulsion of negative ions can result in
fewer active sites at the MP surface. The values ($B''$, $n$, $m$, and $\alpha$) for the adsorption capacity on
PS were $1.21 \pm 0.14$, $3.50 \pm 0.39$, $0.63 \pm 0.07$, and $0.38 \pm 0.05$, respectively. For PET, the
corresponding estimates were $2.95 \pm 0.39$, $8.47 \pm 1.12$, $0.38 \pm 0.02$, and $0.29 \pm 0.04$, respectively.
The relative enhancement in $B''$ for PET (e.g., compared with PS) can be accounted for by the
improved crystallinity and possibly corresponding number of adsorption sites, as seen in Fig. 5(c)
and (d). The two-fold enhancement in $n$ value of PET (over PS) indicates the prominence of its
physical adsorption, which is likely due to van Der Waals interactions (carbon chain versus
polymer surface). In other words, adsorption saturation, corresponding to a lower $1/n$ value, was
reached more quickly on PET compared with PS. The $m$ value on PS is a factor of 1.6 higher
than that on PET. This difference between the two MPs can be associated with their so-called
“sphericity,” which is a measure of resemblance to a perfect sphere (Wadell and Hakon, 1935).
The SEM images (Fig. 1) indicate that the MPs used in this experiment were not perfect spheres.
The area-to-volume ratio included in Eq. (6) might require an additional exponent of $m$. The $m$
parameter is higher in PET than in PS. The pH dependencies for PS and PET, as represented by $\alpha$ values, were $0.38 \pm 0.05$ and $0.29 \pm 0.04$, respectively, which were not significantly different from each other. This might reflect the similarity in zeta potential behavior between the two MP polymer types, as shown in Fig. S3. Parity plots for Cr(VI) and SDBS are supplied in Fig. 9 and Fig. 10, respectively. Comparison of their patterns indicates that adsorption by MPs proceeded more predictably with SDBS than with Cr(VI). Compatibility between the PS and PET MPs can be assessed in terms of $R^2$ values for each target pollutant in each parity plot. The $R^2$ values for SDBS by these two MPs were 0.903 and 0.972, respectively, while those for Cr(VI) were 0.561 and 0.597. This does not necessarily conflict with general expectations, as the equilibrium concentration of SDBS was significantly different from the initial concentration value (up to 53%). The Freundlich isotherm was used efficiently to describe the influence of pH and MP particle size on the adsorptive equilibrium of SDBS. The Langmuir isotherm, which considers associative adsorption across two active sites, was used to explain the effect of such variables on the adsorptive equilibrium of Cr(VI).

4. Conclusions

To study the environmental significance of MP-related pollution in aquatic systems, the adsorption behavior of two waterborne pollutants, SDBS and Cr(VI), was investigated using two MPs (PET and PS). The results were evaluated to address the interactive uptake processes between adsorbates and adsorbents. The basic aspects of adsorption by the two types of MPs were explored using these pollutants with respect to a list of variables controlling such process (solution pH, particle size, and dose of the MPs in the solutions). The adsorption capacity of
SDBS/Cr(VI) increased with reduction in hydrodynamic diameter of MPs. The adsorption of ionic pollutants was sensitive to variables such as pH of solution and dose of MPs. The larger PC of Cr(VI) ions in PET (e.g., by up to 2 times in the case of PS) can be attributed primarily to large differences in crystallinity and hydrophobicity. The MPs tended to adsorb more SDBS than Cr(VI) as the former cannot only increase the active sites, but also reduce the hydrophobicity of the surface MPs. It is therefore desirable to identify the pollutant types that are easily carried and transported by MPs. This will help establish a new guideline for control of MP-based pollution in aquatic environments. This work is expected to lead to improved understanding of the potential impacts of MPs in aquatic ecosystems. Continuous experimental and modeling efforts are underway to accurately address the extent of MP pollution and associated environmental impacts.

Acknowledgments

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### List of symbols

**Roman symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tr>
<td>B', B''</td>
<td>coefficients in Eqs. (6) to (10)</td>
<td>dep.</td>
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<tr>
<td>C</td>
<td>concentration</td>
<td>(m)g L⁻¹</td>
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<tr>
<td>d</td>
<td>diameter</td>
<td>mm</td>
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<tr>
<td>K&lt;sub&gt;eq&lt;/sub&gt;</td>
<td>equilibrium coefficient</td>
<td>L (m)g⁻¹</td>
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<tr>
<td>m</td>
<td>mass</td>
<td>mg or g</td>
</tr>
<tr>
<td>m</td>
<td>exponent in Eqs. (7)</td>
<td>-</td>
</tr>
<tr>
<td>n</td>
<td>Freundlich exponent, see Eq. (8)</td>
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</tr>
<tr>
<td>q</td>
<td>adsorbate or total active site concentration</td>
<td>mg g⁻¹</td>
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<tr>
<td>T</td>
<td>temperature</td>
<td>°C</td>
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<td>V</td>
<td>volume</td>
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**Greek symbols**

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<tr>
<th>Symbol</th>
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<tr>
<td>α</td>
<td>pH dependency factor, see Eq. (9)</td>
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**Subscripts**

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<td>0</td>
<td>initial</td>
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**Abbreviations and acronyms**
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<td>404</td>
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<td>AR</td>
<td>adsorption ratio</td>
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<td>406</td>
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<td>polyamide</td>
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<tr>
<td>408</td>
<td>PC</td>
<td>partition coefficient</td>
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<tr>
<td>409</td>
<td>PE</td>
<td>polyethylene</td>
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<tr>
<td>410</td>
<td>PET</td>
<td>polyethylene terephthalate</td>
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<tr>
<td>411</td>
<td>POM</td>
<td>polyformaldehyde</td>
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<tr>
<td>413</td>
<td>PVC</td>
<td>polyvinylchloride</td>
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<tr>
<td>414</td>
<td>SDBS</td>
<td>sodium dodecyl benzene sulfonate</td>
</tr>
<tr>
<td>415</td>
<td>SI</td>
<td>supporting information</td>
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Fig. 1. Appearance and SEM images of MPs used in this experiment: (a) original PS; (b)–(c) PET MPs after crushing; (d) original PET; (e)–(f) PS MPs after crushing.
Fig. 2. Effect of particle size on adsorption performance of SDBS by MPs (SDBS concentration of 40 mg·L⁻¹, initial pH of 9.4, and temperature of 298 K for 12 h): (a)–(b) effect of MP particle size on adsorption capacity and rate of SDBS by PET and PS MPs; (c)–(d) hydrodynamic diameter distribution of PET and PS MPs in deionized water at pH 8.0, respectively; (e) a proposed schematic for adsorption of SDBS by PET/PS MPs.
Fig. 3. SEM images of PET (a–c) and PS MPs (d–f) after adsorption of SDBS.
Fig. 4. XPS spectra from PET and PS MPs after adsorption: (a) full-range scan XPS spectra of PET; (b) full-range scan XPS spectra of PS; (c) S 2p from PET; (d) S 2p from PET (duration time of 12 h, SDBS concentration of 40 mg·L⁻¹, initial pH of 9.4, and temperature of 298 K).
Fig. 5. Effect of pH on the adsorption performance of SDBS by MPs (SDBS concentration of 40 mg⋅L⁻¹ and temperature of 298 K for 12 h): (a) adsorption capacity; (b) adsorption rate; (c) XRD of PET after adsorption of SDBS; (d) XRD of PS after adsorption of SDBS; (e) diffusion double-layer structure and adsorption mechanism; (f) diffusion electric double-layer structure; (f) ion-pair adsorption; (g) ion exchange adsorption; (h) dispersive force adsorption; (i) hydrophobic interaction adsorption.
Fig. 6. Effect of MP dose on the adsorption performance of Cr(VI) at a concentration of 20 mg·L⁻¹, initial pH of 6.2, and temperature of 298 K for 12 h: (a)–(b) effect of MPs dose on adsorption capacity and rate of Cr(VI) by PET and PS MPs; (c) XRD after adsorption of Cr(VI) by PET MPs; (d) PS XRD after adsorption of Cr(VI) by PS MPs; SEM images of PET (e–g) and PS MPs (h–i) after adsorption of Cr(VI).
Fig. 7. Schematic for the adsorption process of (a) PET and (b) PS.
Fig. 8. Effect of particle size on the adsorption performance of Cr(VI) by MPs at a Cr(VI) concentration of 20 mg·L⁻¹, initial pH of 6.2, and temperature of 298 K for 12 h: (a)–(b) effect of MPs particle size on adsorption capacity and rate of Cr(VI) by PET and PS MPs; XPS spectra of PET and PS after adsorption procedure: (c) C 1s spectrum of PET; (d) C 1s spectrum of PS; (e) O 1s spectrum of PET; (f) O 1s spectrum of PS; (g) Cr 2p spectrum of PET; (h) K 2p spectrum of PET; (i) K 2p spectrum of PET; (j) K 2p spectrum of PET.
Fig. 9. Calculated versus experimental Cr(VI) adsorption capacity using Eq. (7) (a) on PS ($R^2 = 0.561$), (●) entry 32–38 ($d_{MP} = 0.2$ mm, CMP = 2.4–8.4 g L$^{-1}$) and (●) entry 44–48 ($d_{MP} = 0.105–0.450$ mm, CMP = 4 g L$^{-1}$) in Table S2; and (b) on PET ($R^2 = 0.597$), (●) entry 25–31 ($d_{MP} = 0.2$ mm, CMP = 1.2–8.4 g L$^{-1}$) and (●) entry 39–43 ($d_{MP} = 0.105–0.450$ mm, CMP = 4 g L$^{-1}$). Grey line is the first bisector; pH = 8 for all experiments.
Fig. 10. Calculated versus experimental SDBS adsorption capacity using Eq. (9) (a) on PS ($R^2 = 0.903$), (●) entry 18–24 (d$_{MP}$ = 0.2 mm, CMP = 4 g L$^{-1}$, pH = 2–11) and (●) entry 13–17 (d$_{MP}$ = 0.105–0.450 mm, CMP = 4 g L$^{-1}$, pH = 8) in Table S2; and (b) on PET ($R^2 = 0.972$), (●) entry 6–12 (d$_{MP}$ = 0.2 mm, CMP = 4 g L$^{-1}$, pH = 2-11) and (●) entry 1–5 (d$_{MP}$ = 0.105–0.450 mm, CMP = 4 g L$^{-1}$, pH = 8). Grey line is the first bisector.
Table 1. Comparison of partition coefficients between SDBS and Cr(VI) in MPs.

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<tr>
<th>Entry</th>
<th>MPs</th>
<th>Adsorption condition (T in °C, pH)</th>
<th>Contaminant</th>
<th>Initial conc. (mg L⁻¹)</th>
<th>Final conc. (mg L⁻¹)</th>
<th>AC (mg g⁻¹)</th>
<th>PC. (L g⁻¹)</th>
<th>Reference</th>
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<tr>
<td>1</td>
<td>PET</td>
<td>25, 6.44</td>
<td>SDBS</td>
<td>40</td>
<td>39.853</td>
<td>1.473</td>
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<td>This study</td>
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<td>2</td>
<td>PET</td>
<td>25, 6.2</td>
<td>Cr(VI)</td>
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<td>19.992</td>
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<td>1.434</td>
<td>0.0360</td>
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<td>PS</td>
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<td>Cr(VI)</td>
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<td>This study</td>
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<tr>
<td>5</td>
<td>PE</td>
<td>25, 5</td>
<td>Cr(VI)</td>
<td>100</td>
<td>99.968</td>
<td>0.320</td>
<td>0.0032</td>
<td>(Zhang et al., 2020b)</td>
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<tr>
<td>6</td>
<td>PE</td>
<td>25, 5</td>
<td>Pb(II)</td>
<td>15</td>
<td>9.560</td>
<td>13.600</td>
<td>1.422594</td>
<td>(Fu et al., 2020)</td>
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<tr>
<td>7</td>
<td>PE</td>
<td>25, 5.8</td>
<td>Cu(II)</td>
<td>0.25</td>
<td>0.159</td>
<td>0.911</td>
<td>5.735146</td>
<td>(Wang et al., 2020c)</td>
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</table>
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Credit Author Statement

1] Liying Zhang        Methodology and investigation
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3] Wenxia Wang         Investigation
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5] Qiting Zuo          Supervision
6] Amor Abdelkader     Writing- Reviewing and Editing
7] Kai Xi              Writing- Reviewing and Editing
8] Philippe M. Heynderickx Supervision
9] Ki-Hyun Kim         Supervision and Methodology
Declaration of interests

√ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

√ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Dear Editor,

Enclosed please find our manuscript entitled “The potential of microplastics as adsorbents of sodium dodecyl benzene sulfonate and chromium in an aqueous environment” for publication in Science of The Total Environment.

The author confirmed that the manuscript was prepared in compliance with the ethics in publishing policy as described in the guide for authors. This manuscript is an original work that has not been submitted or published previously, and it is not under consideration for publication elsewhere. The publication has been approved by all the coauthors who have provided their consent for the submission of this manuscript in Science of The Total Environment. We have no conflicts of interest to disclose.

Sincerely yours,

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