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Microplastic and heavy metal interactions (adsorption and desorption) at different salinities

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Abstract. Heavy metals and microplastics (MPs) are two pollutants that are currently gaining a lot of attention, and it has been observed that they can interact. The objective of this research was to observe the adsorption and desorption of heavy metals concerning various types of MP particles, different heavy metals and concentrations, and salinity. The findings demonstrate that among all particle types, PP particles absorb heavy metals at the highest rate. Contrarily, PP particles release lower heavy metals and more slowly than other particles. Pb consistently absorbed more metal by MPs than Cu, Zn, or Cd. Cd had the highest rate of heavy metal desorption, followed by Pb, Cu, and Zn. The adsorption capacity of MPs particles increases together with the concentration of heavy metals, whereas the adsorption rate decreases. Salinity has an enormous impact on how MPs and heavy metals interact. The adsorption and desorption of heavy metal in MPs particles decreases and takes longer to reach equilibrium at increased salinities. Between the three different salinities, even the adsorption and desorption results demonstrate a significant difference ($p<0.05$). Finally, our results indicate that MPs particles have the potency as a vector for heavy metal in freshwater, brackish water, and ocean.

1 Introduction

Plastic garbage has multiplied and spread due to rising plastic manufacturing and use, with an estimated 6300 million metric tons of it throughout the world at the end of 2015 [1]. Recent years have seen an increase in public and governmental concern over the fragmentation of plastic trash into microplastics [2,3,4]. Microplastics have size less than 5 mm and can take on regular or irregular shapes in the aquatic environment [5,6]. Due to their longevity and mobility, MPs are an important anthropogenic adsorbent in aquatic habitats, acting as a vector for different toxins over an extended period of time or over a considerable distance [7,8]. Moreover, a wide range of microbes, including fungi, bacteria, algae, protozoa, archaea, and protists, which are associated with a polymeric matrix of extracellular polymeric substances

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(EPSs), can easily colonize on the surfaces of MPs in the form of biofilms, giving rise to the "plastisphere" [9]. According to Rummel et al. [10], the creation and growth of biofilms may change the morphology and physicochemical characteristics of microplastics (BMPs) as well as their ability to adsorb pollutants. Biofilms are a dynamic microbial system that are common in freshwater habitats and are made up of complex, taxonomically diverse bacteria. They function as an intricate adsorbent system that can capture and gather a range of substances with different adsorption methods and binding locations [11,12,13]. The ability to anticipate the adsorption of MPs may therefore depend on biofilms, which may also have a big impact on environmental processes and the fate of various pollutants in aquatic environments.

Due to their distinct traits of high toxicity, bioaccumulation, and non-degradability, heavy metals can pose major risks to ecosystems and human health. Their adsorption to natural solid materials, including as surficial sediment (SS) and suspended particles (SPs), is assumed to be largely responsible for controlling their environmental behavior and fate in natural aquatic environments. [14,15]. Though it has already been shown that heavy metals can bind to MPs, this finding raises the possibility that they can potentially serve as carriers for trace metals [16,17]. The ability of virgin polyethylene (PE) pellets to adsorb heavy metals from seawater, including iron (Fe), lead (Pb), manganese (Mn), silver (Ag), and copper (Cu) was discovered by Ashton et al. [7] after suspending virgin PE pellets in a port for 8 weeks. Using virgin polypropylene (PP) and polyvinyl chloride (PVC) that had been deployed for six months at three locations along the Chinese coastline, MPs that were enriched in a number of heavy metals, including cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn) and lead (Pb) [18]. Similarly, PVC and PS matured for three months in seawater had potent Cu and Cd adsorption [19]. Previous research showed that when plastics age, they have the capacity to collect larger levels of mercury (Hg) in the marine environment [20]. Additionally, it has been documented that MPs can adsorb other heavy metals as cobalt (Co), nickel (Ni), molybdenum (Mo), uranium (U), antimony (Sb), and thallium (Ti) [21,22]. The chemical and physical characteristics of MPs, including as their kinds, colors, and functional groups, as well as the local environmental factors like salinity, pH, and DOM, influence how heavy metals bind to them [23,24]. Beach-sourced pellets have a substantially higher capability for adsorbing trace metals than virgin pellets do in aquatic environments [25]. In order to systematically and exactly assess the vector effects of MPs, it is required to compare the interaction between MPs and heavy metals because salinity has a significant impact on natural waters.

Few studies have been done on these criteria as of yet [16,17]. Even though there have been several research on heavy metals and MPs, there have been very few on their interactions, particularly under settings of varying salinity. The goal of this study was to observe the adsorption and desorption of heavy metals namely lead (Pb), zinc (Zn), cadmium (Cd), and copper (Cu) on MPs particles of different types and sizes, heavy metal types and concentration, and salinity.

2 Materials and methods

2.1 Materials

Tersulan Chemical Co., Ltd. provided the virgin (new) microplastics particle used in this investigation. In this study, the analysis of the adsorption and desorption of heavy metals was conducted using PP, PE, and PET with the same size of 150 µm and PS, PE, and PP with the same size of 20 µm. Aquatic habitats frequently contain all of the chosen forms of microplastics [26].

In the present research, a total of four kinds of heavy metals were utilized: lead (Pb), copper (Cu), cadmium (Cd), and zinc (Zn) (Merck, Germany). In one liter of distilled water, heavy metals were dissolved to produce a stock solution of 1000 mg L^{-1}. The heavy metal test solution was then created by diluting this stock solution to 1, 2, 5 and 10 mg L^{-1}. Various salt concentrations were used in the testing as well. To create heavy metal test solutions, heavy metals were dissolved in artificial seawater that has salinities of 0, 15, and 30‰.

2.2 Adsorption experiment

This experiment looked at the effects of various microplastic kinds, heavy metal types, and salinities on the ability of heavy metals to adsorb on MPs particles.

Ten ml of heavy metals were added to a beaker containing a PS sample weighing 0.05 g and swirled at a steady speed of 180 rpm using a magnetic stirrer. The MPs and heavy metal were exposed for various amounts of time (5, 15, 30, 60, 75, and 90 min), and the test was maintained until the equilibrium adsorption point was attained. There is no discernible change in the adsorption level after reaching the equilibrium adsorption level because every layer of the MPs particles has reached its optimum ability for absorption of heavy metals. MPs dust was collected used filter paper 0.45 µm,. Three times each test was run. For the test, various starting salinities (0, 15, and 30‰) and heavy metal with concentrations 1, 2, 5, and 10 mg L^{-1} were utilized. To determine the metal concentrations in the filtrate, a spectrophotometer (SpeactAA 240-FS, USA) was employed. According to equation (1) [27], the adsorption % was calculated:

$$\%Ads = (100 - \frac{[A]_{t_a}}{[A]_0}) \times 100\%$$

where the adsorption rate is expressed as %Ads, while [A]ta represents the heavy metal concentration that is still in solution at time t and [A]0 represents the heavy metal concentration at time 0 respectively.

2.3 Desorption experiment

This experiment examined the desorption efficiency (µg g^{-1}) of heavy metals from PS particles in relation to various salinities and particle sizes. As the standard starting values for heavy metal desorption, the observed heavy metal adsorption for the MPs particles were employed. In this experiment, the amount of heavy metal absorbed by MPs particles was set at 0.1 µg g^{-1}. To determine the heavy metal desorption efficiency (µg g^{-1}) from MPs particles, 10 ml of distilled water (salinity 0‰) was used to wash the particles after they had been exposed to 0.1 µg g^{-1} of heavy metals. Additionally, the test was conducted using synthetic saltwater under various salinity values (15 and 30‰). After varying exposure intervals (5, 15, 30, 60, 120, 150, 180, and 240 mins), the heavy metal concentration in the filtered water was examined. For each test, three replicates were run. Glass tubes holding 50 ml of the filtrate were used. With the help of a spectrophotometer (SpeactAA 240-FS, USA), the heavy metal contents in the filtered water were examined. Equation (2) was used to compute the desorption rate.

$$\%Des = (100 - \frac{[D]_{t_r}}{[D]_0}) \times 100\%$$

where %Des stands for desorption rate, $[D]_{tr}$ for the amount of heavy metal remained in the solution at time t, and $[D]_0$ for the amount of heavy metal at time 0 respectively.

2.4 Data analysis

The entire set of adsorption and desorption data was evaluated using a two-way analysis of variance (ANOVA). If the results revealed that there were differences between all treatments ($p<0.05$), the Duncan's Multiple Range Test was run to look at the level of differences. In present study, we investigated the effects of different MP types, salinities, and heavy metal types and concentrations on the adsorption capacities (μg g^{-1}) and adsorption rates (%) of heavy metals. Significant variations in the desorption efficiency (g g^{-1}) and desorption rate (%) of heavy metals with respect to various MP types and salinities were also evaluated. Using Statistica software and a general linear model, the linear associations between the adsorption and desorption rates of each heavy metal in this study were examined under all circumstances. All tests had a 0.05 level of statistical significance.

3 Result

3.1 Heavy metals adsorption

In general, larger MPs particles absorb more heavy metals. All experiments with various salinities produced same findings. The value of the adsorption and the length of time needed to establish equilibrium adsorption are what set it apart, though. When exposed to heavy metal solutions for 45 minutes at salinity 0‰, MPs particles with a diameter of 20 µm absorb the metals and reach the equilibrium point, whereas MPs particles with a diameter of 150 µm require a longer exposure period of 60 minutes.

When tested with MPs particles of a greater diameter (150 µm) at salinity 0‰, PP absorbs heavy metals at the highest rate, followed by PE, and PET at the lowest. For each heavy metal employed in this study, similar outcomes were discovered (Fig. 1). The adsorption capacities of Zn metal by PP, PE, and PET particles with a diameter of 150 µm were 0.133±0.002, 0.113±0.003 , 0.095±0.003 μg g^{-1}, respectively, at the equilibrium point.

PP remained the heavy metal that was the most absorbent for MPs particles with a small diameter (20 µm), followed by PE and PS as the least absorbent. All of the heavy metals employed in this investigation yielded the same findings as well (Fig. 1). At the equilibrium point, PP, PE, and PS particles with a diameter of 20 µm had a capacity to adsorb Zn metal of 0.077±0.002 , 0.065±0.003, and 0.055±0.003 µg g^{-1}, respectively.

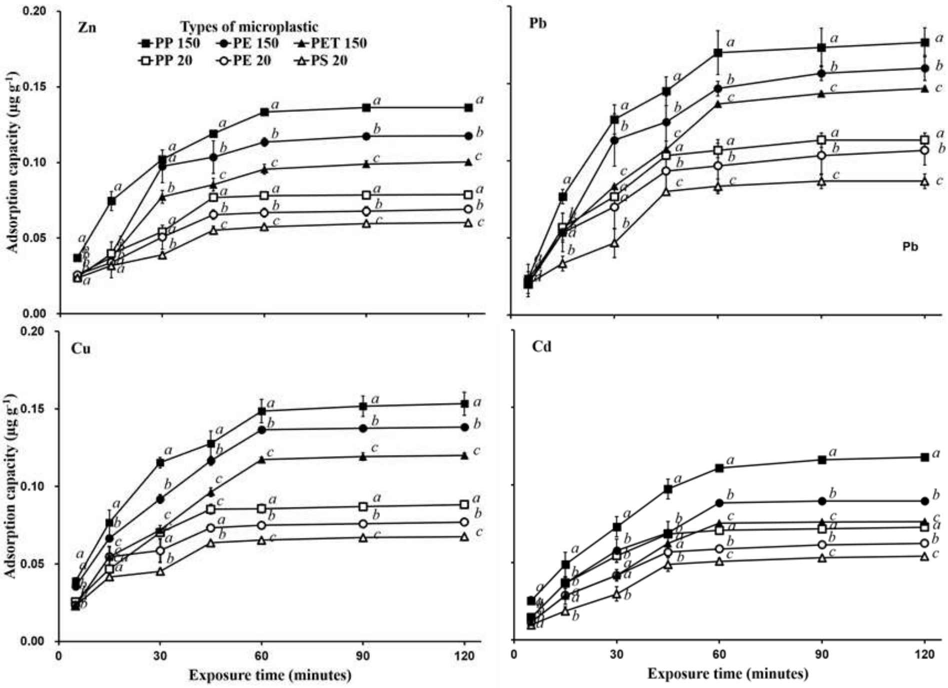

Fig. 1. Adsorption capacity (g g^{-1}) of various microplastic types (PP 150, PE 150, PET 150, PP 20, PE 20, and PS 20) at a concentration of 1 mg L^{-1} heavy metal and 0‰ salinity. Data for the adsorption capacities (g g^{-1}) of heavy metals denoted by the letters a, b, and c differ considerably (p<0.05) for each type of microplastic having the same size.

After 90 minutes of exposure to heavy metal solutions in the test with a salinity of 15‰, MPS particles of all diameter sizes had absorbed the heavy metals and reached equilibrium adsorption sites (Fig. 2). When exposed to heavy metal solutions for 90 minutes at salinity 30‰, MPs particles with a diameter of 20 µm reached the equilibrium adsorption point, but particles with a diameter of 150 µm required 120 minutes (Fig. 3). For particles with a diameter of 150 µm, PP continues to absorb the most heavy metals in both salinity settings, followed by PE and PET. The absorption of heavy metals by PP, followed by PE and PS, is still higher than that of particles with a diameter of 20 µm.

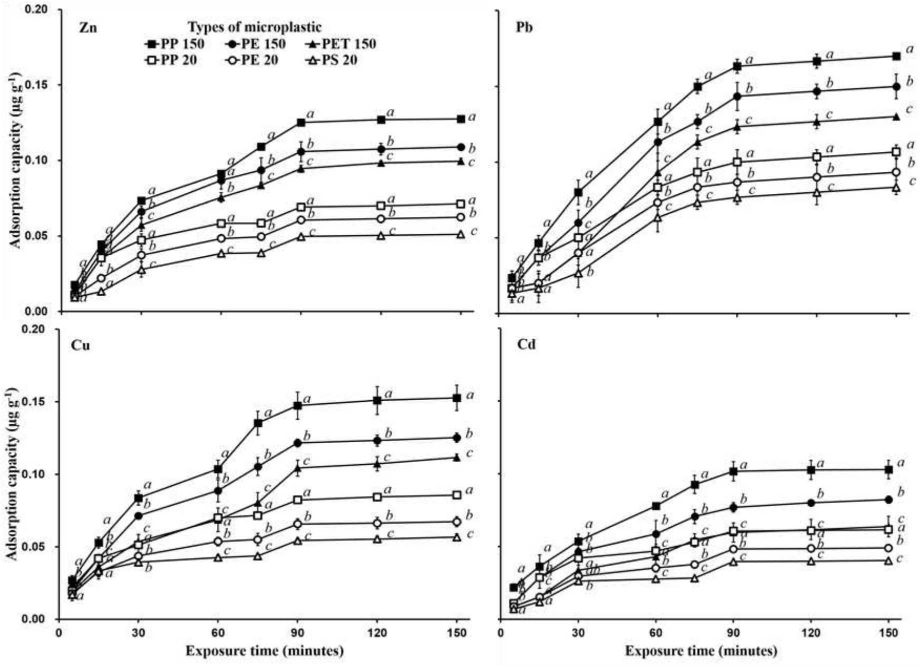

Fig. 2. Adsorption capacity (µg g^{-1}) of several of microplastic types at a salinity of 15‰ and a heavy metal concentration of 1 mg L^{-1}. For statistical details, see Fig. 1.

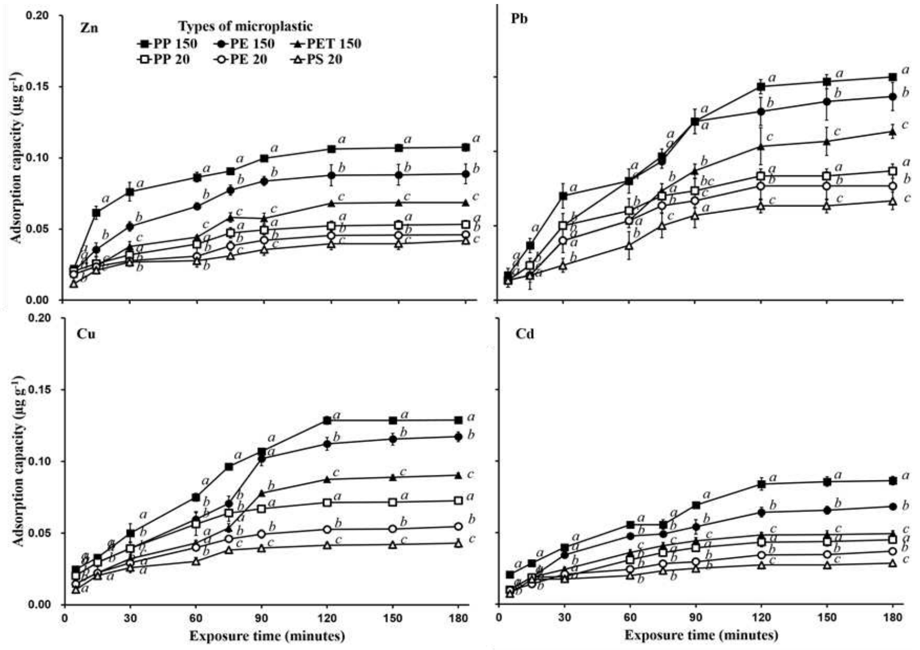

Fig. 3. Adsorption capacity (g g^{-1}) of several microplastic types at a salinity of 30‰ and a heavy metal concentration of 1 mg L^{-1}. For statistical details, see Fig. 1.

The statistical evaluation revealed that the adsorption equilibrium of all the heavy metals used in the present research was significantly influenced by the particle's type, the concentration of heavy metals, and the level of salinity. For each heavy metal studied in this work, the relationships between the heavy metal concentration, MPs particle type (P), salinity (S), and adsorption rate (Ads. Rate) are as follows:

MPs with diameter 20 µm :

$$\text{Ads. Rate Zn} = 1.474 - 8.287\,C + 1.244\,P - 1.175\,S \qquad (R^2 = 0.742)$$
$$\text{Ads. Rate Pb} = 2.021 - 17.724\,C + 1.656\,P - 1.099\,S \qquad (R^2 = 0.924)$$
$$\text{Ads. Rate Cd} = 2.024 - 3.324\,C + 1.811\,P - 1.747\,S \qquad (R^2 = 0.873)$$
$$\text{Ads. Rate Cu} = 2.751 - 5.537\,C + 2.421\,P - 1.030\,S \qquad (R^2 = 0.757)$$

MPs with diameter 150 µm :

$$\text{Ads. Rate Zn} = 1.876 - 7.715\,C + 1.557\,P - 1.198\,S \qquad (R^2 = 0.849)$$
$$\text{Ads. Rate Pb} = 4.344 - 15.251\,C + 3.729\,P - 1.241\,S \qquad (R^2 = 0.724)$$
$$\text{Ads. Rate Cd} = 2.375 - 4.124\,C + 2.077\,P - 1.323\,S \qquad (R^2 = 0.654)$$
$$\text{Ads. Rate Cu} = 4.908 - 11.759\,C + 4.260\,P - 1.147\,S \qquad (R^2 = 0.832)$$

The value of the particles' adsorption capacity varies as a result of the different salinities utilized during the test. Figure 4 demonstrates how variable each type and size of particle's adsorption capacity is. In general, salinity 0‰ had a considerably better adsorption capacity ($p<0.05$) than the other two salinities. Additionally, there was a significant difference in the adsorption capacity at salinity 15 and 30‰ ($p<0.05$). The adsorption capacity of PP particles with a diameter of 150 µm was 0.133±0.002, 0.125±0.002, and 0.106±0.002 µg g^{-1}, respectively, at salinities of 0, 15, and 30‰. Whereas, the adsorption capacity of PP particles with a diameter of 20 µm was 0.077±0.002, 0.069±0.002, and 0.049±0.003 µg g^{-1}, respectively.

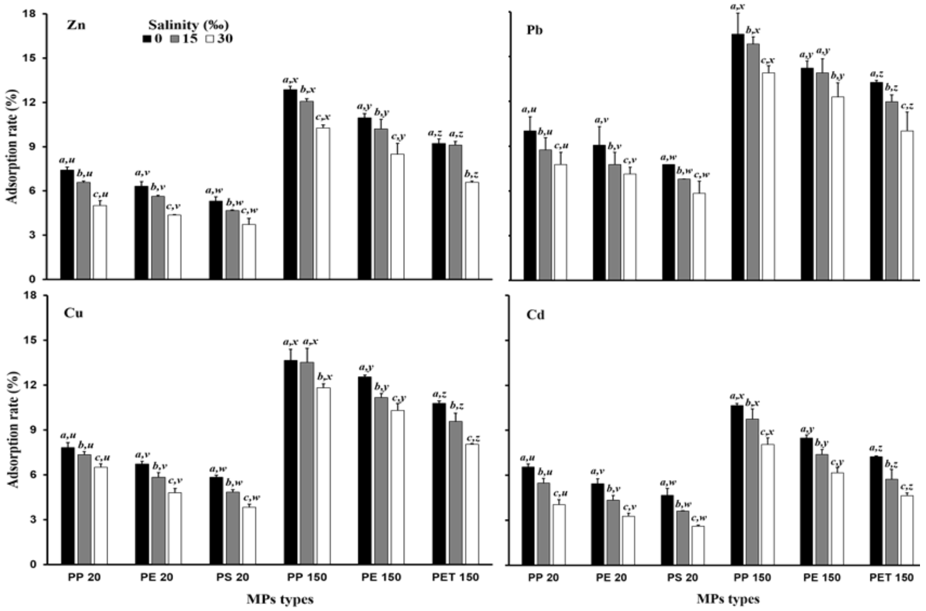

Fig. 4. Equilibrium adsorption rate (%) of different types of microplastic and different salinity (0, 15, and 30‰) with heavy metal 1 mg L^{-1}. Data for the same heavy metal's adsorption rate (%) with different letters (a, b, and c) are substantially different ($p<0.05$) for

each salinity, and data for different letters (u, v, w, x, y, and z) are significantly different ($p<0.05$) for each type of microplastic.

Interesting effects were also discovered in studies employing various heavy metal concentrations. The value of the adsorption capacity (µg g^{-1}) increases together with the concentration of heavy metals exposed to MPs particles, but the adsorption rate (%) decreases. In the test using concentration of 1 mg L^{-1} initially produced the best adsorption rate. In general, the experiment utilizing 150 µm-diameter MPs particles revealed that the adsorption rate at each initial concentration varied significantly ($p<0.05$) (Fig. 5). At concentrations of 1, 2, 5, and 10 mg L^{-1}, the heavy metal Zn adsorption rate on PP particles with a diameter of 150 µm was 12.87±0.35, 10.76±0.45, 9.46±0.69, and 5.86±0.24 %, respectively. All of the heavy metals employed in the investigation yielded these results. In the experiment using MPs with a 20 µm diameter, differences were discovered. At concentration of 2 mg L^{-1} in Cd metal, the adsorption rate of all types of MPs particles was not substantially different from that at a concentration of 5 mg L^{-1} ($p>0.05$) (Fig. 5). At concentrations of 1, 2, 5, and 10 mg L^{-1}, the rates of heavy metal Cd adsorption on PP particles with a diameter of 20 µm were 6.55±0.45, 5.01±0.25, 4.73±0.26, and 2.69±0.33 %, respectively. Other heavy metals were tested with the same outcomes. These findings suggest that the initial disparity in heavy metal concentrations has a substantial impact on the way that heavy metals are absorbed by MPs particles.

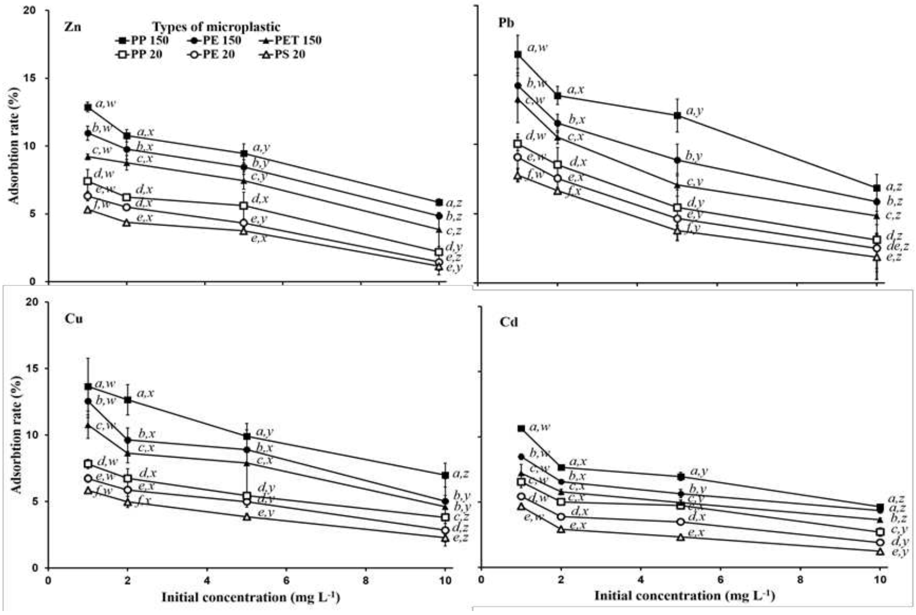

Fig. 5. Equilibrium adsorption rate (%) of different microplastic types with different heavy metal concentration (1, 2, 5, 10 mg L^{-1}) and salinity salinities 0‰. Data for the rate of adsorption (%) for each of the letters (a, b, c, d, e, and f) are significantly different ($p<0.05$) among all types of microplastic, and various letters (w, x, y, and z) are substantially different ($p<0.05$) among all heavy metals concentration.

All heavy metals in this investigation had significantly varied rates of adsorption in all trials with various salinities ($p<0.05$). Pb had the highest adsorption rate, which it shared with Cu, Zn, and Cd (Fig. 6). The adsorption rates of Pb, Cu, Zn, and Cd at a salinity of 0‰ by

PP particles with a diameter of 150 µm were 16.50±1.41%, 13.65±0.76%, 12.87±0.21%, and 10.65±0.14%, respectively. At a salinity of 15‰, the adsorption rates of Pb, Cu, Zn, and Cd by PP particles with a diameter of 150 µm were 15.85±0.47, 13.52±0.9, 12.07±0.18, and 9.75±0.66%, respectively; however, at a salinity of 30‰ were 13.92±0.47, 11.82±0.28, 10.27±0.21, and 8.06±0.43%, respectively. In a test with MPs particles of a 20 µm diameter, the same outcomes were also discovered. According to these findings, salinity and the kind of heavy metal both play significant parts in the heavy metals' ability to adhere to the surface of MPs particles.

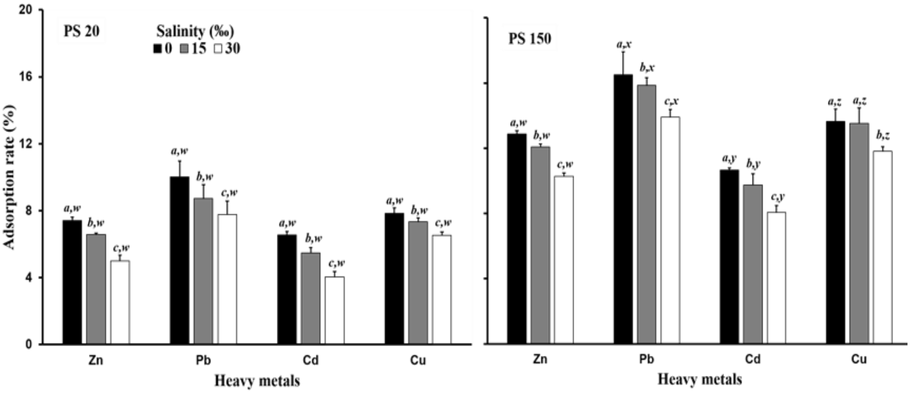

Fig. 6. The percentage of PP with diameters of 20 and 150 µm that adsorbed heavy metals at equilibrium at various salinities (0, 15, and 30‰). Data for the same heavy metal's adsorption rate (%) with different letters (a, b, and c) between each salinity are significantly different (*p*<0.05), and data for different letters (w, x, y, and z) between each heavy metal are significantly different (*p*<0.05).

3.2 Heavy metal desorption

Prior to determining the capacity for adsorption at a concentration of 5 mg L^{-1}, we first gathered adsorption values for all starting levels of heavy metals. Based on observations at each exposure times, MPs particles with a size of 20 µm required between 15 and 30 minutes to attain a capacity for adsorption of about 0.1 mg L^{-1}, although MPs particles with a size of 150 µm required longer to do so. We chose these exposure periods keeping in mind that the starting heavy metals adsorbed on the MPs particles' surfaces was nearly identical.

Depending on the particle type and water salinity, different heavy metals desorb differently. Different particle types would desorb heavy metal at varying rates. PET particles with a diameter of 150 µm showed the highest desorption values in all experiments with various salinities, followed by PE and PP with the lowest values. While PS had the highest desorption value for particles with a diameter of 20 µm, followed by PE and PP. The value of heavy metal desorption decreased as the salinity of the solution increased, and it took longer to reach equilibrium.

The desorption level at equilibrium of all the heavy metals in this investigation was significantly influenced by the particle size and salinity, according to statistical analysis. Following are the relationships between each heavy metal's rate of desorption (Des. Rate), MPs particle type (P), and salinity (S) in this investigation.

MPs with diameter 20 µm :

Des. Rate Zn = 3.141 + 13.313 P - 5.784 S ($R^2 = 0.749$)

Des. Rate Pb = 10.903 + 27.829 P - 55.099 S ($R^2 = 0.729$)

Des. Rate Cd = 26.761 + 51.961 P - 34.685 S (R^2 = 0.939)
Des. Rate Cu = 13.861 + 32.046 P - 50.867 S (R^2 = 0.856)

MPs with diameter 150 µm :

Des. Rate Zn = 12.747 + 32.073 P - 55.935 S (R^2 = 0.814)
Des. Rate Pb = 19.517 + 43.312 P - 46.829 S (R^2 = 0.660)
Des. Rate Cd = 11.940 + 47.673 P - 32.211 S (R^2 = 0.734)
Des. Rate Cu = 15.287 + 44.792 P - 36.493 S (R^2 = 0.765)

After 90 minutes of exposure to the fluid in the 0‰ salinity test, all particle types and sizes reached equilibrium desorption of heavy metals. The desorption value of particles of PET with a diameter of 150 µm at the point of equilibrium was significantly (*p*>0.05) in comparison to the value for PP, but it was not statistically (*p*>0.05) different than those of PE for any of the heavy metals tested. While not statistically different (p>0.05) than those of PE, the desorption value of PS particles for Cd and Cu metals was significantly different (*p*>0.05) than those of PP (Fig. 7). The desorption value for Zn and Pb metals at their equilibrium point did not differ significantly (*p*>0.05) for particles had a diameter of 20 µm regardless of the particle types.

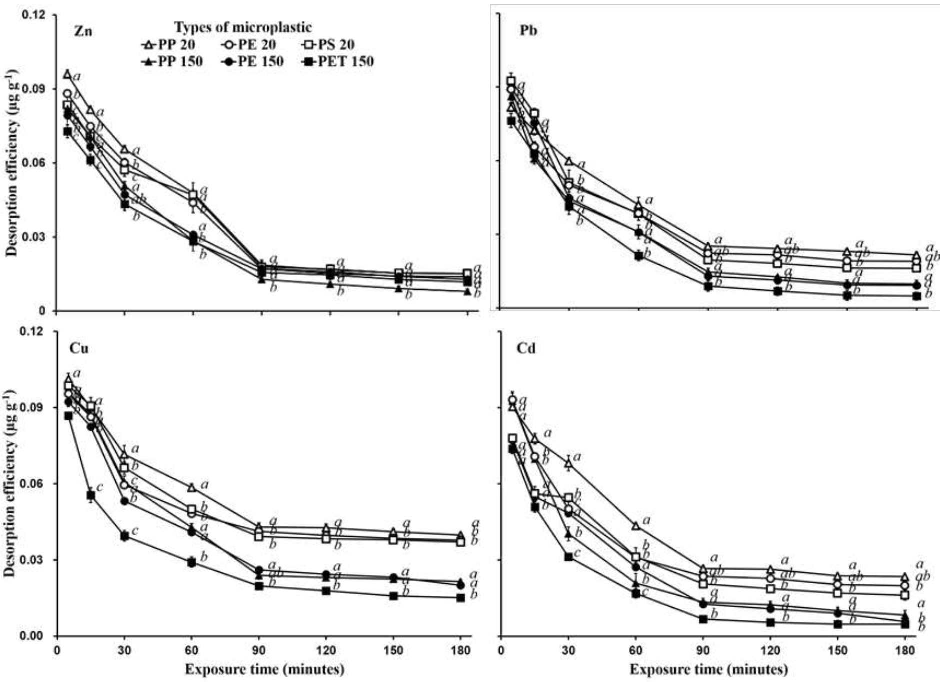

Fig. 7. Desorption efficiency (g g^{-1}) of several microplastic types at a salinity of 0‰ and a heavy metal content of 1 mg L^{-1}. For each type of microplastic with a similar size, the data regarding the desorption efficiency (g g^{-1}) of similar heavy metals with a single letter (a, b, and c) are significantly different (*p*<0.05).

It was discovered that at a salinity of 15‰, the desorption times of heavy metals for particles as small as 20 µm and as large as 150 µm varied. While particles of size 150 µm required the same amount of time as the test at salinity 0‰, particles of size 20 µm required a greater period of time, or 120 minutes, to reach the equilibrium desorption point. With the exception of Zn metal, both particle sizes' desorption times were constant at salinity 0‰. The desorption value of heavy metals by PET particles with a diameter of 150 µm at the equilibrium point was considerably different ($p<0.05$) than the value for of PP, but not statistically different ($p>0.05$) than the value for of PE. The same outcomes were seen at a size of 20 m, where the metal desorption value by PS was significantly different ($p<0.05$) than the value for PP but not statistically different ($p>0.05$) than the value of PE (Fig. 8). At the time of observation, it was discovered that the desorption value had undergone several variations after that.

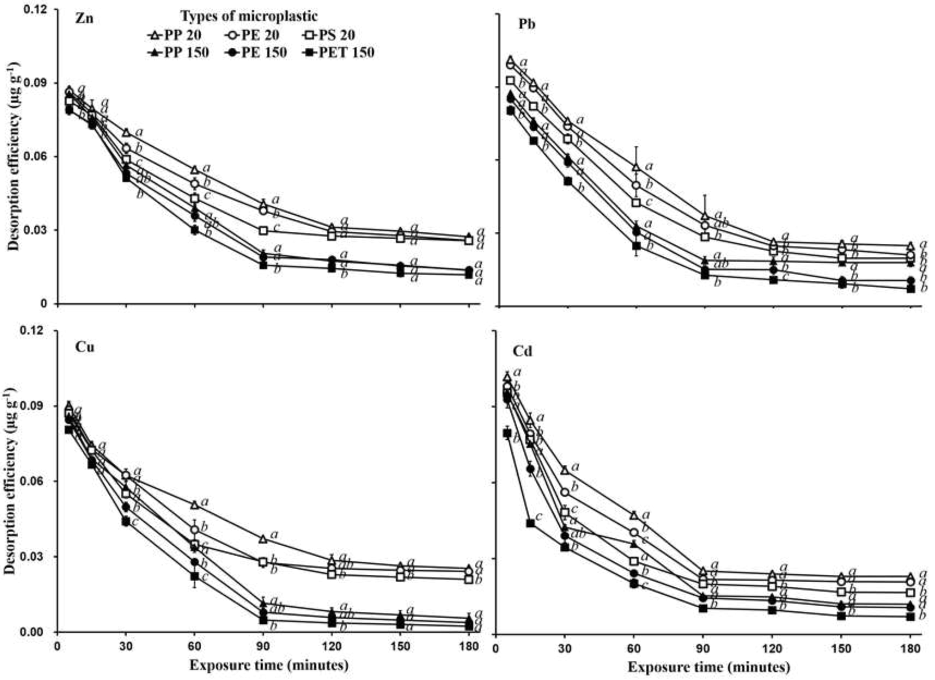

Fig. 8. Desorption efficiency (µg g^{-1}) of different types of microplastic with heavy metal with concentration 1 mg L^{-1} and salinity of 15‰. See Fig. 6 for statistical information.

When exposed to the solution for 120 minutes at a salinity of 30‰, MPs particles with a diameter of 150 µm reached the equilibrium desorption point of heavy metals, but it required 150 minutes for particles with a 20 µm diameter. The desorption time for Zn metal, however, is the same for all particle kinds and sizes as it was for the two prior salinities. The desorption value of PET with a 150 µm diameter at the equilibrium desorption point was statistically different ($p<0.05$) than the value of PP but not statistically different ($p>0.05$) from that of PE. Similar findings were made for small-sized particles, where the PS desorption value was not statistically different ($p>0.05$) than the value of PE, but statistically different ($p<0.05$) than the value of PP (Fig. 9). According to the aforementioned studies, the type of MPS has an impact on how much heavy metals can be removed from MPS particles.

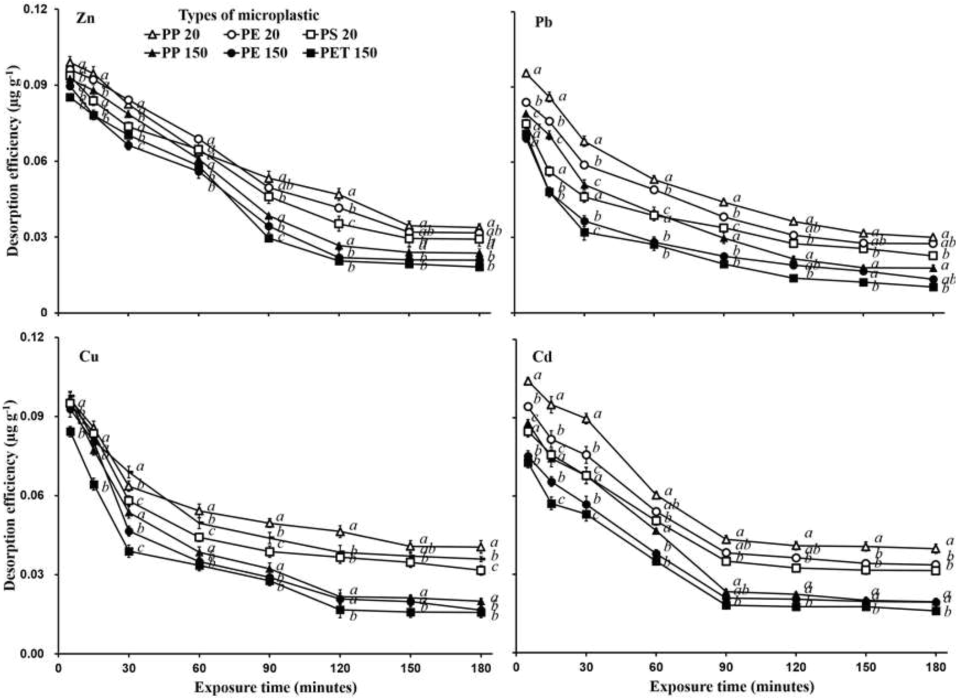

Fig. 9. Desorption efficiency (µg g^{-1}) of different types of microplastic with heavy metal with concentration 1 mg L^{-1} and salinity of 30‰. See Fig. 6 for statistical information.

The desorption value of the particles varies due to the different salinities utilized throughout the test. Figure 10 demonstrates that the desorption values are varied for all particle kinds and sizes. The desorption value was generally statistically different (p<0.05) at salinity 0‰ than the value at the other two salinities. Additionally, the desorption value at salinity 15‰ was statistically different (p<0.05) than the value at salinity 30‰. This suggests that a key factor in the desorption of these heavy metals from MPs particles is the amount of salt present in the heavy metal solution. For instance, at salinities of 0, 15, and 30‰, the heavy metal Zn desorption values of PP particles with a diameter of 150 µm were 0.103±0.001, 0.101±0.001, and 0.080±0.001 µg g^{-1}, respectively. At salinities of 0, 15, and 30‰, the desorption value of PP particles with a diameter of 20 µm was 0.094±0.002, 0.091±0.002, and 0.089±0.003 µg g^{-1}, respectively.

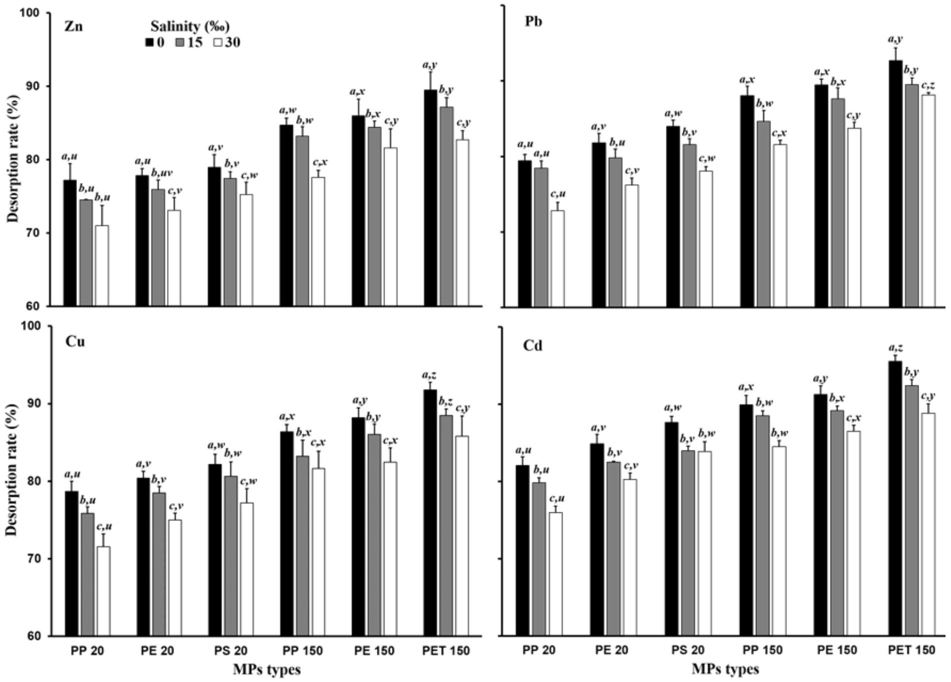

Fig. 10. Desorption rate (%) of various types of microplastic and various salinity (0, 15, and 30‰) with heavy metal with concentration 1 mg L^{-1}. Data regarding the desorption rate (%) of a single heavy metal with various letters (a, b, and c) among all salinity are noticeably different ($p<0.05$), and different letters (u, v, w, x, y, and z) among all kind of microplastic are noticeably different ($p<0.05$).

The results also show that each heavy metal's degree of desorption was different. Cd exhibited the greatest amount of heavy metal desorption in the test using all three salinity settings, followed by Pb, Cu, and Zn (Fig. 11). At zero salinity, Zn desorption on PP particles with a diameter of 150 µm did not differ substantially ($p>0.05$) from that of Pb and Cu, but it did differ significantly ($p<0.05$) from that of Cd. At equilibrium, Cd, Pb, Cu, and Zn desorptions rate were 89.90±1.25, 88.06±1.24, 86.38±0.91, and 84.72±0.94%, respectively. The desorption rate of Pb at a salinity of 15‰ was not considerably different ($p>0.05$) than the rate of Cu, but both were considerably different ($p<0.05$) than the rates of Zn and Cd. The desorption rate of Pb was not considerably different ($p>0.05$) than the rate of Cd at a salinity of 30‰, however both were considerably different ($p<0.05$) than the rates of Zn and Cu. The test utilizing MPs particles with small diameters (20 µm) revealed differences in desorption levels for all heavy metals (Fig. 11). Overall, the findings showed that heavy metal desorption rates are influenced by both the type and concentration of metals.

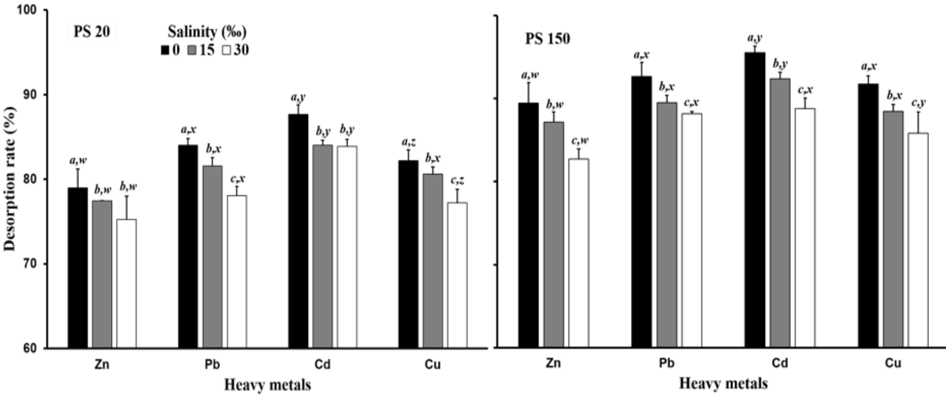

Fig. 11. Equilibrium desorption rate (%) of PP with diameters 20 and 150 μm with heavy metal with concentration 1 mg L^{-1} and various salinities (0, 15, 30‰). Data for the desorption rate (%) of the similar heavy metal with various letters (a, b, and c) are considerably different ($p<0.05$) among all salinity, and various letters (w, x, y, and z) are considerably different ($p<0.05$) among all heavy metal.

4 Discussion

Within the context of various MPs particle types, sizes, salinities, heavy metals, and concentrations, this study examines the short-term interactions between MPs particles and heavy metals. The efficiency of heavy metals adsorption and desorption on the surface of MPs particles was examined in this case to evaluate the interactions. Such an evaluation is crucial since it may reveal ways for MPs to spread contamination, especially in the case of heavy metals. There may be a link between particle MPs in the oyster body and the concentration of heavy metals. In oysters that had been exposed to microplastic contamination, heavy metal concentrations were found to be greater [28].

Our findings suggested that the size of the MPs particles plays a significant role in the heavy metal adsorption. MP particle size has an impact on the adsorption of contaminants [29]. While following 45 minutes, MPs particles of 20 m attained equilibrium in adsorption, those of 150 μm did not reach it until 60 minutes had passed. Aluminium (Al) and lead (Pb) require 60 minutes to each equilibrium for adsorption on the outer layer of MP particles [27]. This conclusion is consistent with their findings. Larger MPs particles require more time to cover the surface than smaller ones do because they have a larger surface area for the adsorption of heavy metals. The smaller microplastics achieved adsorption equilibrium with different pollutants more rapidly and easily than bigger particles lends support to this outcome. The outcomes also demonstrated that the MPs particle size had a significant impact on the degree of heavy metal desorption. Larger particles absorb heavy metals in pure water more quickly than smaller ones. The fact that smaller particles have a higher particle density than larger particles can be used to explain this outcome since this would make the heavy metals adsorbed on the particles more tightly bonded and more challenging to desorb [30].

Despite having the same size, MPs type is still crucial to the sorption process. The same-sized MPs (20 and 150 μm) were used in tests, which revealed that PP consistently absorbed larger levels of heavy metals, but release it slower and less than another types. These findings concurred with those reported by previous studies [25, 31, 18]. PP has a greater optimal adsorption at MPs sizes of 20 μm, followed by PE and PS. PP likewise has a greater optimal adsorption at MPs sizes of 150 μm, followed by PE and PET. The polarity and physicochemical characteristics of MPs have an impact on the ability of heavy metals to adsorb and release [7,32,33]. The physicochemical characteristics of their surfaces, such as hydrophobicity and diffusivity, can result in a variety of metal ion adsorption behaviors [16]. The direct adsorption of cations or complexes onto charged sites or neutral portions of the flexible surface is most likely the mechanism behind this metal sorption 7]. It indicates that the behavior of plastic's metal adsorption and desorption is strongly influenced by its surface characteristics and porosity.

Each kind of heavy metal has a big impact on how much of it adsorbs on the outermost layer of MPs. Pb had the highest quantity of heavy metal adsorption overall in this investigation, followed by Cu, Zn, and Cd. Our results showed that the amount absorbed of Pb was statistically higher ($p<0.05$) than the adsorption of Cu, Zn was statistically higher ($p<0.05$) than Cd, and Cu was statistically higher ($p<0.05$) than Zn. These outcomes mirrored those that previously reported [8,19]. Pb demonstrated a greater ability for adsorption in both freshwater and seawater than the three others [19]. As a result, Pb has a stronger affinity for particles of all shapes and sizes and may be more likely to combine with MPs to become a pollutant. Many key metal properties, including ionic radius, softness, and hydrolysis value may be linked to variations in heavy metal that is adsorbed [34,35]. The ionic radius has an inverse relationship with the adsorption affinity for a particular metal having the same charge [34,36]. Pb^{2+}, Cd^{2+}, and Cu^{2+} have hydrated ionic radii of 0.401, 0.426, and 0.419 nm, respectively. The order of adsorption affinity is comparable to the order of hydrated ionic radii, particularly for Pb^{2+}, which among the heavy metals under investigation has the lowest hydrated ionic radii and the strongest electrostatic interactions with MP. This suggests that metal adsorption on MP is somewhat influenced by electrostatic interactions. The likelihood of a heavy metal being adsorbed on the surface of MPs particles increases with the heavy metal's electrostatic strength. Pb had a stronger adsorption than Cu and Cd on PVC and chlorinated polyethylene (CPE), two PE plastic particles [24]. Pb's strong electrostatic properties were essential to this adsorption. The desorption from the surface of MPs was significantly influenced by the type of heavy metal as well. In this investigation, Cd had the greatest amount of desorption at equilibrium overall, followed by Pb, Cu, and Zn. Three distinct salinity tests revealed this circumstance. This outcome was also influenced by each heavy metal's ionic radius. In comparison to the other three heavy metals, Cd^{2+} has a higher ion radius. The bindings between a heavy metal ion and the surface of MPs particles become weaker as the ion's radius increases [34,36]. Upon getting into touch with a solution, a PVC plate (5 x 10 cm) containing two additional layers of copper and zinc absorbed a greater amount of copper than zinc [16]. The competition for free metals increases with a solution's salinity [25,33,37]. These elements led to a reduced adsorption and desorption and a longer time to reach the equilibrium.

Different heavy metals have different capacities for adsorption due to variations in their starting concentration. The adsorption capacity increases while the adsorption rate decreases as a result of the higher starting concentration of heavy metals. At extremely high beginning Zn concentrations (0.1-100 mg L^{-1}) [38], the adsorption capacity reached 236-7171 mg g^{-1}, which was significantly greater than that seen at low starting concentrations [8, 25]. Overall, there was a statistically different ($p<0.05$) in the rate of adsorption of heavy metals by all particles at an initial concentration of 1 mg L^{-1} in comparison to that at a concentration of 2 mg L^{-1}. Furthermore, contrasted to the initial amount of 10 mg L^{-1}, the initial amount of 5 mg L^{-1} showed a statistically higher ($p<0.05$) adsorption. Since low levels of heavy metal solutions might offer a significant number of adsorption sites for MP particles, the maximum heavy metal adsorption rates were found at lower levels (1 mg L^{-1}). On the other hand, when the concentration increases, the adsorption rate decreases, possibly because the surface has reached a certain degree of coverage, which subsequently affects the subsequent adsorption rate [18]. The statistics above show that the level of heavy metals in solution has a considerable impact on the level of the adsorption of heavy metals on the PS particles. Variations in the initial amount of heavy metals cause variations in MP particle capacity for adsorption [27].

According to earlier research [35,39], salinity has an impact on how MPs and pollutants adsorb to one another. Our findings demonstrated that salinity has an impact on the adsorption of heavy metals as well. Adsorption may decline as a result of cation competition [33,37]. Our results also show that salt can affect the removal of heavy metals from MPs particles, indicating that the competition for sites of adsorption on the outermost layer of the particle is intensifying and free ions have the most significant interactions with the surface of the particle, which is in similar with Holmes et al.'s [25] observation that the adsorption of Co, Ni, and Cd reduced when there was higher salinity. In general, when the salinity of the liquid rises due to direct contact with particles that have absorbed heavy metals, the process of desorption duration and efficiency increase (Figs. 7 and 8). This consequence can be directly related to free ion competition. It is more difficult to desorb ions of heavy metals that have adhered to the outer layer of MPs particles because to greater ion density and enhanced competition in solutions containing more salt [25,33,37].

By fully establishing the associations among MPs and heavy metals, our outcomes amply corroborated earlier findings that in aquatic conditions, plastic could be an important heavy metal transporter. The fact that the scope of this research was constrained to a lab environment with brief observations should be emphasized.

5 Conclusion

This present research found that the type of microplastic and the size of the microplastic particle had a significant impact on the adsorption and desorption of heavy metals on the microplastic particles. Both of the process was also influenced by environmental parameters in the vicinity of the microplastic, such as the salinity of the heavy metal solution, the kind of heavy metal, and the concentration of the heavy metal. The value of heavy metals for adsorption and desorption decreases with increasing salinity of the solution, and equilibrium takes longer to reach. Our research shows how heavy metals and MPs interact, and it is clear that MPs can transport heavy metals in aquatic systems.

References

1. R. Geyer, J.R. Jambeck, K.L. Law, Science Advances **3,** 7, e1700782 (2017)
2. R.C. Thompson, Y. Olsen, R.P. Mitchell, A. Davis, S.J. Rowland, W.G. John, Science **304**, 838 (2004)
3. J.A.I. do Sul, M.F. Costa, Environmental Pollution **185**, 352-364 (2014)
4. D. Eerkes-Medrano, R.C. Thompson, D.C. Aldridge, Water Research **75**, 63–82 (2015)
5. J.P.G.L. Frias, R. Nash, Marine Pollution Bulletin **138**, 145-147 (2019)
6. C. Zarfl, D. Fleet, E. Fries, F. Galgani, G. Gerdts, G. Hanke, Marine Pollution Bulletin **62**, 1, 589-1591 (2011)
7. K. Ashton, L. Holmes, A. Turner, Marine Pollution Bulletin **60**, 11, 2050-2055 (2010)
8. A. Turner, L.A. Holmes, Environmental Chemistry **12**, 600-610 (2015)
9. E.R. Zettler, T.J. Mincer, L.A. Amaral-Zettler, Environmental Science and Technology **47**, 7, 137-46 (2013)
10. C.D. Rummel, A. Jahnke, E. Gorokhova, D. Kühnel, M. Schmitt-Jansen, Environmental Science and Technology Letters **4**, 7, 258-267 (2017)

11. H.C. Flemming, J. Wingender, U. Szewzyk, P. Steinberg, S.A. Rice, S. Kjelleberg, Nature Reviews Microbiology **14**, 9, 563-575 (2016)
12. W.J.M. Seviour, F. Codron, E.W. Doddridge, D. Ferreira, A. Gnanadesikan, M. Kelley, Y. Kostov, J. Marshall, L.M. Polvani, J.L. Thomas, D.W. Waugh, Journal of Climate **32**, 5107-5121 (2019)
13. J. Wang, S.L. Han, D.L. Lu, L.Y. Li, S.M. Limbu, D.L. Li, Z.Y. Du, Frontiers in Physiology **10**, 1077 (2019)
14. W. Stumm, J.J. Morgan, John Wiley & Sons, New York, p. 1040 (2012).
15. A. Akcil, F. Vegliò, F. Ferella, M.D. Okudan, A. Tuncuk, Waste Management **45**, 420-433 (2015).
16. D. Brennecke, B. Duarte, F. Paiva, I. Caçador, J. Clode, Estuarine, Coastal and Shelf Science **178**, 189-195 (2016)
17. A.A. Koelmans In, M. Bergmann, L. Gutow, M. Klages (Eds.), Marine anthropogenic litter (pp. 313–328). Berlin: Springer (2015)
18. F. Gao, J. Li, C. Sun, L. Zhang, F. Jiang, W. Cao, Marine Pollution Bulletin **144**, 61-67 (2019)
19. W. Gao, X. Wei, K. Wu, Plastic Science Technology **49**, 111-116 (2021)
20. J. Santos-Echeandía, J.R. Rivera-Hern´ andez, J.P. Rodrigues, V. Molto, Marine Chemistry **222**, 103-788 (2020)
21. J. Prunier, L. Maurice, E. Perez, J. Gigault, A.C.P. Wickmann, M. Davranche, A. ter Halle, Environmental Pollution **245**, 371-379 (2019)
22. J. Wang, J. Peng, Z. Tan, Y. Gao, Z. Zhan, Q. Chen, L. Cai, Chemosphere **171**, 248-258 (2017)
23. D.A. Cooper, P.L. Corcoran, Marine Pollution Bulletin **60**, 650-654 (2010)
24. J. Zou, X. Liu, D. Zhang, X. Yuan, Chemosphere **248**, 126-064 (2020)
25. L.A. Holmes, A. Turner, R.C. Thompson, Marine Chemistry **167**, 25-32 (2014)
26. A.L. Andrady, Marine Pollution Bulletin **119**, 12-22 (2017)
27. N. Oz, G. Kadizade, M. Yurtsever, Applied Ecology and Environmental Research **17**(4), 7301-7310 (2019)
28. K.S. Vieira, J.A.B. Neto, M.A.C. Crapez, C. Gaylarde, B.S. Pierri, M. Saldana-Serrano, A.C.D. Bainy, D. Jos´e Nogueira, E.M. Fonseca, Marine Pollution Bulletin **166,** 112-225 (2021)
29. B.S. Barus, C.Y. Cheuch, S.Y. Cheng, Environmental Engineering and Management Journal **22**(2), 363-374 (2023)
30. B.S. Barus, K. Chen, M. Cai, R. Li, H. Chen, C. Li, J. Wang, S.Y. Cheng, Frontiers in Marine Science **8**, 671-802 (2021)
31. C.M. Rochman, E. Hoh, B.T. Hentschel, S. Kaye, Environmental Science and Technology **47**(3), 1646-1654 (2014)
32. F. Wang, K.M. Shih, X.Y. Li, Chemosphere **119**, 841-847 (2015)
33. J. Li, K. Zhang, H. Zhang, Environmental Pollution **237**, 460-467 (2018)
34. E.F. Covelo, M.L.A. Couce, F.A. Vega, Communications in Soil Science and Plant Analysis **35**, 2709-2729 (2011)
35. S. Hu, Y. Zhou, L. Zhou, Y. Huang, Q. Zeng, Environmental Science Pollution Research **11**, 356 (2018)

36. U.K. Saha, S. Taniguchi, K. Sakurai, Soil Science Society of America Journal **66**, 117-128 (2002)
37. B.S. Barus, Z. Zhu, C.Y. Cheuch, K. Chen, J. Wang, M. Cai, S.Y. Cheng, H. Wei, Frontiers in Marine **9**, 1014103 (2023)
38. M.E. Hodson, C.A. Duffus-Hodson, A. Clark, M.T. Prendergast-Miller, K.L. Thorpe, Environmental Science and Technology **51**, 4714-4721 (2017)
39. Z. Zhan, J. Wang, J. Peng, Q. Xie, Y. Huang, Y. Gao, Marine Pollution Bulletin **110**, 559-563 (2016)