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Laboratory Experiment on Copper and Lead Adsorption Ability of Microplastics

(Uji Kaji Makmal tentang Keupayaan Penjerapan Mikroplastik Kuprum dan Plumbum)

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ABSTRACT

The persistent presence of microplastics in the marine environment has become a major threat to many marine organisms and this issue continues with heavy metals pollution. Microplastics and heavy metals are commonly categorized in different type of pollutant group and the understanding of interlinkage between these two contaminants is less discovered. During 7 days laboratory controlled experimentation, we examined the heavy metals; copper (Cu) and lead (Pb) adsorption ability of microplastics fragment derived from plastic straws and plastic grocery bags. We found that both microplastic types adsorbed the two heavy metals through exposure to Cu and Pb spiked seawater with different concentrations, respectively. The adsorption kinetics was represented using partition coefficients that resulted in coefficients between the microplastic fragments and water ranged between 5 and 28 for Cu on plastic straws and bags fragment; 3 and 35 for Pb. The adsorption of Cu and Pb both was significantly higher in plastic bag micro fragments, probably due to higher surface area and polarity. Throughout the experiments time expansion, the concentrations of Cu and Pb significantly increased on both microplastic types. The results of consequential interaction between the selected microplastics and heavy metals strongly support the condition of microplastic ability to adsorb heavy metals and act as a vector for heavy metal ions distribution in the marine ecosystem.

Keywords: Adsorption; heavy metals; microplastics

ABSTRAK

Kehadiran mikroplastik yang berterusan dalam persekitaran marin telah menjadi salah satu ancaman utama pada kebanyakan organisma laut dan isu ini menjadi lebih serius bila digabungkan dengan pencemaran logam berat. Mikroplastik dan logam berat secara lazimnya dikategorikan dalam kumpulan bahan pencemar yang berbeza. Pemahaman serta pengetahuan tentang hubungan dan interaksi antara kedua-dua bahan pencemar ini masih sedikit. Kami mengkaji kemampuan mikroplastik yang dihasilkan daripada serpihan straw dan beg plastik untuk menyerap logam berat; tembaga (Cu) dan plumbum (Pb). Kami mendapati bahawa kedua-dua jenis serpihan mikroplastik ini berupaya untuk menyerap logam berat tersebut melalui pendedahan kepada air laut yang dicampur dengan Cu dan Pb dalam sukatan kepekatan yang berbeza. Daya kinetik penyerapan ditunjukkan melalui pekali pemetakan dengan nilai pekali antara serpihan mikroplastik dan air dalam lingkungan 5 dan 28 untuk Cu serta 3 dan 35 untuk Pb. Penyerapan Cu dan Pb adalah lebih tinggi dan ketara untuk serpihan beg plastik mungkin disebabkan kawasan permukaan yang lebih luas dan kekutuban yang lebih tinggi. Sepanjang tempoh pendedahan 7 hari, kepekatan Cu dan Pb dalam kedua-dua jenis mikroplastik meningkat dengan ketara. Hasil kajian ini membuktikan interaksi berlaku antara mikroplastik dan logam berat dalam masa yang sama menyokong keadaan kemampuan mikroplastik untuk menyerap logam berat serta bertindak sebagai vektor yang boleh menyebarkan logam berat dalam ekosistem marin.

Kata kunci: Logam berat; mikroplastik; penjerapan

Introduction

Define as plastic particles smaller than 5 mm in size; microplastics pose a risk to aquatic environments due to their permanent presence in marine ecosystems, long residence times, and propensity to be ingested by biota (Andrady 2011; Pradit et al. 2020). Due to constant modern era activities such as urbanization, waste dumping, global climate change and pollution, which contributes to marine plastic debris contamination; in time causing microplastics to be a substantial threat towards marine life (Jambeck et al. 2015; Pradit et al. 2021).

There have been various studies conducted in the South East Asia region regarding the availability of microplastics in the marine environment. Yet the discoveries made were more focused on the ingestion of microplastics in multiple marine biota samples such as *Anadara granosa* (blood cockles) from Jambi, Indonesia (Fitri & Patria 2019); *Spratelloides gracilis* (silver-stripe round herring) and *Decapterus macrosoma* (shortfin scad) from Eastern Indonesia (Rochman et al. 2015) and *Rastrelliger kanagurta* (Indian mackrerel) sold in a Malaysian local market (Karami et al. 2017). The studies of microplastics were also similar in Thailand with various studies were on the presence of microplastics in marine organisms such as *Rastrelliger brachysoma* (short mackerel), *Sardinella gibbosa* (slender sardine) from the lower Gulf of Thailand (Azad et al. 2018); *Parapenaeopsis hardwickii* (spear shrimp) and *Metapenaeous brevicornis* (yellow shrimp) from Songkhla Lake (Pradit et al. 2021) and occurrence of microplastics in beach sediment of Libong Island (Pradit et al. 2020). These studies discussed on the possibilities of microplastics being potential vector of pollutants and able to transfer toxic elements to marine organisms during ingestion and suggested further research on the matter.

Generally divided into two different pollutant classes, both microplastics and heavy metals are incompletely recognized and understood in terms of their relationship and interaction. Heavy metals pollution and microplastics contamination usually occurred in coastal areas with high anthropogenic pressures such as harbours and marinas (Browne et al. 2011; Gao et al. 2019). This circumstance may contribute to the interaction between these two pollutants whereby heavy metals attached or adsorb to microplastics' surfaces. Additionally, pollutants with sorbing capability towards plastic surface; for example polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCBs) will consequently be bioavailable to marine organisms through ingestion (Koelmans et al. 2014). Inorganic pollutant such as heavy metals exposure to marine organisms is increasing with the consideration that microplastics have the potential to be vectors for metals interaction with biota (Wagner & Lambert 2018).

Although in the past, polymers were appraised to being immobile towards metals (Ashton et al. 2010), growing awareness and focus has recently been considered and applied to progressively understand the interaction between heavy metals and microplastics (Gao et al. 2019; Holmes et al. 2014 Wang et al. 2017). Earlier studies found that plastic pellets collected from the coastline of Southwest England accumulated similar and higher concentration of Cu, Zn, and Fe compared to sediment samples, even though sediment often possess a greater surface area and contrived of charged minerals stimulating metal ions sorption (Ashton et al. 2010). Another study investigated metal sorption kinetics of heavy metals on both beached and virgin plastic pellets in which the capability of adsorption is higher for beached pellets (Holmes et al. 2012). Thus, suggesting that factors like weathering and fouling with organic matter gradually expanding surface area and anionic active plots generated for metals adsorption from seawater (Holmes et al. 2014). Contrarily, a research done in San Diego Bay, USA, using different plastic types, demonstrate no significant difference in term of metal adsorption capability amidst pellet compound (Rochman et al. 2014). A recent study in Indonesia, investigated the adsorption of Pb and Cu in microplastics in the Musi River (Purwiyanto et al. 2020). This study determined that both microplastics (PP, PE, PES, PVC, nylon) and water samples from the river accumulated high concentrations of both metal. Another study conducted in the natural tropical environment of the East Malaysian Coast found that seven type of metals (Cd, Pb, Ni, Cu, Zn, As, and Hg) adsorbed onto plastic particles with <10 mm size (Noik et al. 2015). An experimental study was carried out by a Malaysian researcher in order to investigate the relation between microplastics (PP and PE) and heavy metals (Cd, Cu and Pb) (Chua 2018). This study, which was conducted for a period of seven days, concluded the finding of both microplastics types absorbed the three heavy metals and not influenced by the type of microplastics used.

Nonetheless, the adsorption process of heavy metals can naturally take place in the environment occupied with many variables and quite complex as well (Vedolin et al. 2018). Factors and variables such as

modification of plastic surfaced exposed to atmospheric agents, accelerated decomposition of darker particles and aged particles rougher surface compared to virgin materials; are able to effect the interaction between metals and microplastics (Campanale et al. 2019). These mentioned components contribute to the acceleration of microplastics' degradation processes hence producing active and anionic sites that leads to the increment of interaction between microplastic particles and heavy metals (Wang et al. 2018). Variables that are related to salinity, pH, formation of biogenic biofilm, photo oxidative erosion, polymer polarity and porosity enhancement also considered as influencer that elevate microplastics and inorganic pollutants interactions (Holmes et al. 2012, 2014; Richard et al. 2019; Vedolin et al. 2018). Consequently, once unfurl into the marine environment, microplastics together with their consignment of intrinsic additives and extrinsic heavy metals; are capable of being transferred into the food web reaching marine organisms (Jinhui et al. 2019; Lusher et al. 2013) and then humans (Revel et al. 2018; Santana et al. 2017).

Adsorption mechanism of heavy metals to plastics relatively still less explored by the reason of being complex and varied. Hence, in the present study, we investigated the interaction between two types of frequently used commercial plastics product and heavy metals by exposing the product microplastics fragments to heavy metal pollution. Under controlled laboratory conditions, we exposed plastic straw and plastic grocery bag, which were cut into micro fragments to seawater treatment spiked with copper (Cu) and lead (Pb). Plastic straw and plastic grocery bag were chosen for this experiment as these materials are the highest single-used plastic products utilized in Thailand (Bangkok Post 2019). Furthermore, microplastics studies in marine environment of Thailand; in marine biota (Goh et al. 2021; Pradit et al. 2021) microplastics found mostly were PE (polyethylene), the main polymer material compound in making plastic bag and in marine sediment (Pradit et al. 2020) microplastics found were mostly PP (polypropylene) and nylon. PP is the main polymer compound used to make plastic straws. Previous studies showed that Cu and Pb were absorbed by PP, PE, PES, PVC, and nylon microplastic particles that were collected from estuarine waters (Purwiyanto et al. 2020) and these metals were also found to be absorbed by PP and PE pellets experiment in laboratory condition (Chua 2018). In the purpose of evaluating the ability of these microplastics fragment of commercial single-used plastic product to adsorb metals with the exemption of environmental condition such as weathering or fouling in order to solely, focus on the affinity level of the microplastics towards metal. The evaluation was conducted using the approach of no water exchange, calculation of partition coefficients (Kpw (plastic/water)) and comparison of adsorption differences of both microplastics type (Brennecke et al. 2016) after a 7-day period.

Materials and Methods

Experimental set-up

This study was conducted at the Marine and Coastal Resources Institute Laboratory, Prince of Songkla University. This experiment was based on acute toxicity test with modification since the samples were not live organisms. Two types of microplastics were exposed to filtered seawater spiked with heavy metals for a period of 168 h (7 days). The microplastics were made by manually cutting small pieces (1-5 mm) of plastic from two post-consumer products, which were plastic straws and plastic grocery bags. These plastic products were chosen based on the report by the Department of Marine and Coastal Resources, Thailand that was stated by Bangkok Post (2019), plastic bags (13%), and plastic straws (10%) were the leading plastic waste in Thailand.

Two types of heavy metals chosen for this experimental research which were copper (Cu) and lead (Pb). Hydrochloric acid and deionized water rinsed glass containers (550 mL volume) were used as experimental units. Each experimental unit consisted of one glass container with heavy metal spiked seawater and one type of microplastic. Approximately 8 g of plastic straws and grocery bags were added to each unit. Heavy metal spiked seawater consisted of 4 different treatments which were control, treatment A, B and C. Each treatment has 3 experimental units for replicate purpose and in total there were 48 experimental units. The experimental set-up treatment distributed as follows: a) Experimental set-up copper (Cu) treatment; i) Control, plastic straw/plastic bag, copper (Cu) non spiked water ii) Treatment A, plastic straw/plastic bag, copper (Cu) spiked water concentration 4 ppm iii) Treatment B, plastic straw/plastic bag, copper (Cu) spiked water concentration 8 ppm iv) Treatment C, plastic straw/plastic bag copper (Cu) spiked water concentration 16 ppm; b) Experimental set-up for lead (Pb) treatment; i) Control, plastic straw/plastic bag, lead (Pb) non spiked water ii) Treatment A, plastic straw/plastic bag, lead (Pb) spiked water

concentration 4.25 ppm iii) Treatment B, plastic straw/plastic bag, lead (Pb) spiked water concentration 8.5 ppm iv) Treatment C, plastic straw/plastic bag, lead (Pb) spiked water concentration 17 ppm.

METAL ANALYSIS

In analysis of heavy metal in seawater, each 24 h water samples were collected, then acidified with nitric acid (Merck) and stored until further analysis. In addition, after seawater collection, 1 g of plastic straw and bags pieces were also collected from the same treatment units using a filtering (nylon mesh) and a metal-free counting unit (paper box).

The water was filtered all to obtain the microplastic pieces of straw and bag. The same procedure was performed for each 24 h until the end of the 168 h. Due to its low affinity for metals (Jinhui et al. 2019; Richard et al. 2019), polyethylene tubes were used to conduct analysis and storing samples. All samples were then stored at 2 °C in a proper refrigerator. As a precaution procedure, all lab ware will be decontaminated in HCl (Loba Chemie PVT), 10% v/v baths prior to use.

Subsequently, using a modified Aqua Regia extraction, Cu and Pb were extracted from microplastic surfaces (Brennecke et al. 2016; Holmes et al. 2012). Aqua Regia were prepared by mixing 12 M HCl and 16 M HNO_3 in a ratio of 3:1. All plastic pieces samples from each unit were then grouped in a 15 mL polypropylene sterile centrifuge tube, followed by the addition of 10 mL of 20% (v:v) Aqua Regia. The tubes were then shaken at 150 rpm for a period of 24 h. The extraction happened at room temperature because of the plastic pieces' inert composition in which digestions heating is not necessary (Brennecke et al. 2016; Holmes et al. 2012).

Following the extraction process, the mixture then filtered through GF/C Whatman n° 42 filters (pore size 0.7 µm) in order to retain the plastic pieces. The filtered solution was immediately acidified with HNO_3 (9 mL of sample to 1 mL of HNO_3) for dissolved metal determination. All heavy metal concentrations were determined by using inductively coupled plasma - optical emission spectrometry (ICP-OES) and conducted through the laboratory service at Department of Chemistry, Faculty of Science, Prince of Songkla University. Blank tubes (without plastic pieces) were also subjected to the same procedure and its metals content used to correct the plastic pieces' metal concentration. In order to examined any possible interferences from saline matrix in water samples, the seawater was also analysed using the exact same procedure as the plastic pieces. In accordance to previous studies (Brennecke et al. 2016; Duarte et al. 2014), the saline matrix of water samples did interfere with the analysis and thus ICP-EOS could be valid to analyse dissolved heavy metals in water samples. In addition, as per acquirement from the laboratory service for ICP-OES, the scientist verified the accuracy of the results by processing CRM 145 R (due to unavailable reference materials for plastic) as well as internal standard solutions.

ADSORPTION KINETICS DATA ANALYSIS

To better describe and understand the rate of metal adsorption to the microplastic pieces, the partition coefficients (Kpw) were calculated for mean average concentration for each treatment (Holmes et al. 2014). The application of partitioning coefficient is based on the concentration ratio of adsorbed metals on the respective plastic to aqueous metals (metals accumulated in seawter) on a w/v basis. The Kpw is determined as follows:

$$Kpw = \frac{[MeP]}{[MeW]}$$

where [MeP] (µg/g) is the concentration of the respective metal on the surface of the plastic indicating the adsorption and [MeW] (µg/mL) is the concentration of the metal in the surrounding seawater of the respective experimental unit.

STATISTICAL ANALYSIS

The mean average concentration for every 24 h of each experimental unit were calculated and then presented in line graphs. For adsorption over the 7 days (168 h) period, one-way ANOVA were employed to analyse whether metal concentrations for each plastic type and each metal differ overtime. One-way ANOVA also used to compare concentrations of Cu and Pb in microplastics pieces according to treatment, as well as to compare the difference between plastic type in the same metal treatment (same concentration). To test the significant differences found, a two sample t-test were applied.

Results and Discussion

COPPER (CU) AND LEAD (PB) CONCENTRATION IN MICROPLASTICS PIECES OF PLASTIC STRAW AND PLASTIC BAG AFTER 7 DAYS EXPOSURE

The graphs showed different concentration of Cu and

Pb in the straw and plastic bags pieces for every 24 h. Cu concentration (Figure 1) seems to subtly increase for treatment A, as for treatment B the concentration increase in a steady pace and elevate at maximum on the 144 h with the measurement of 3.753±0.01 mg/L (ppm). Treatment C showed the most rapid increase that began on hour 72 and stopped at hour 144 with the concentration of 9.232±0.02 mg/L (ppm). On the final day for all treatment; 168 h, the Cu concentration increment slowed down and maintained a slightly similar value. In Figure 2, treatment A showed Cu concentration increase very slowly and reached low concentration of 0.921±0.01 mg/L (ppm). Cu concentration increase in a slower manner as well for treatment B and increase highest on 144 h with the concentration of 3.06 ±0.14 mg/L (ppm). The results differ for treatment C whereby Cu concentration increased up to 6.098±0.03 mg/L on the first 24 h window. The concentration continued to increase significantly until the last day and recorded a value of 8.511±0.05 mg/L.

From Figure 3, the ability of Pb to be adsorb in microplastic straw increased each day. Treatment A showed a subtle increase for 72 h and increase higher on 96 h with the concentration of 1.486±0.01 mg/L and continue to slightly rise up until end exposure period. As for treatment B, the concentration gradually increases for each day and ending with concentration of 3.392±0.02 mg/L. Treatment C showed a rather interesting Pb adsorption rate whereby the concentration increased on 72 h with value of 5.583±0.04 mg/L then the rate went slower for 2 days. The concentration increased highest on the 144 h with value of 8.164±0.06 mg/L. As for Figure 4, the concentration of Pb in microplastics bag increase in a gradual manner for treatment A and B. At the end of exposure period concentration of Pb from treatment A was 4.189±0.01 mg/L and treatment B was 5.536±0.03 mg/L. Microplastics bag in treatment C showed a significant increase throughout the 168 h exposure and ended with the highest concentration of 10.42±0.05 mg/L.

Both metals were capable to adsorb on the surface of microplastics straw and bag. Cu concentrations changed significantly over the 7 days of the experiment; Cu in plastic straws $p<0.05$; Cu in plastic bag $p<0.05$. Pb concentrations also changed significantly over the days of the experiment for all treatment; Pb in plastic straws $p<0.05$; Pb in plastic bag $p<0.05$. Both plastic straws and plastics bags pieces showed a continuous increase in both metal until the end of the trials. Cu and Pb concentrations drastically increased at 72-144 h for treatment C most probably due to the longer exposure time causing longer absorption time that contributes to greater absorption capacity (Chua 2018; Liu et al. 2021) with the addition of higher concentration (Liu et al. 2021) of Cu and Pb in the treatment unit. Cu concentrations in plastics straws and plastic bags were found to be significantly different when comparing (via one-way ANOVA) samples collected at the same time period ($p<0.05$). Pb concentrations in plastics straws and plastic bags also were found to be significantly different through the comparison of samples collected ($p<0.05$).

CU SPIKED SEAWATER TREATMENT

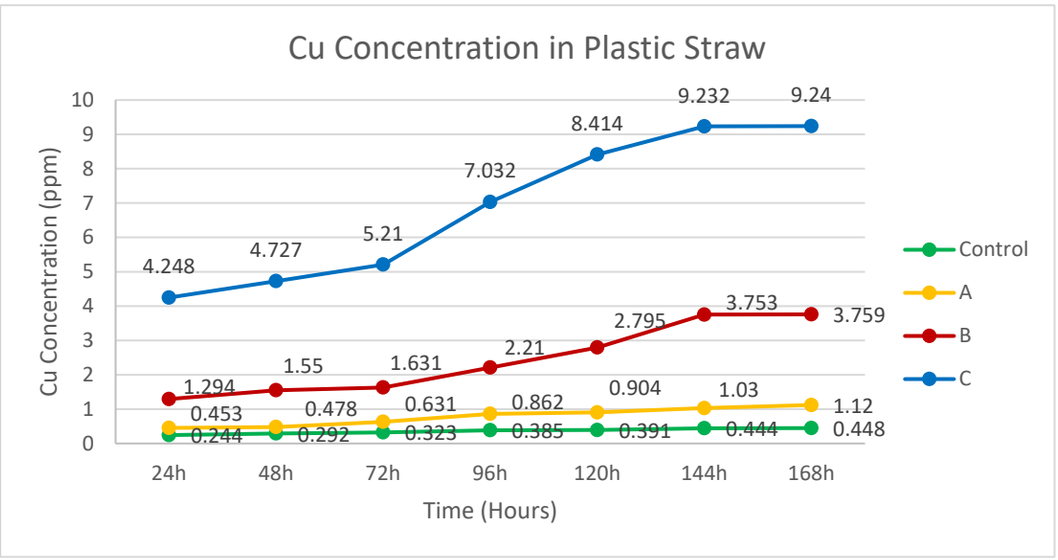

FIGURE 1. Cu concentration in microplastic pieces of straw versus time in 7 days exposure period. Different treatment represents four Cu spiked seawater concentrations; control, treatment A = 4 ppm, treatment B = 8 ppm, and treatment C = 16 ppm

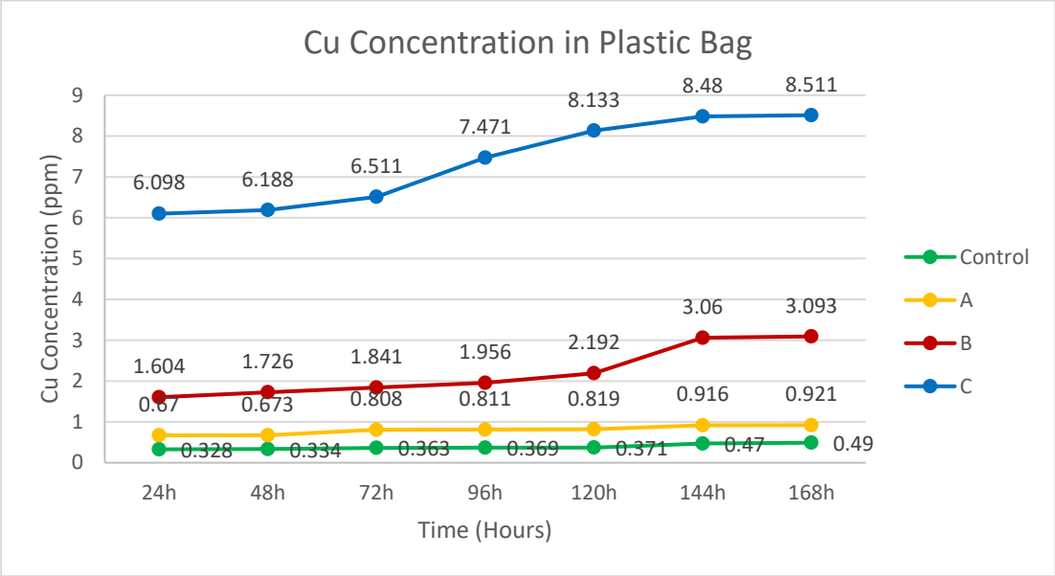

FIGURE 2. Cu concentration in microplastic pieces of bag versus time in 7 days exposure period. Different treatment represents four Cu spiked seawater concentrations; control, treatment A = 4 ppm, treatment B = 8 ppm, and treatment C = 16 ppm

PB SPIKED SEAWATER TREATMENT

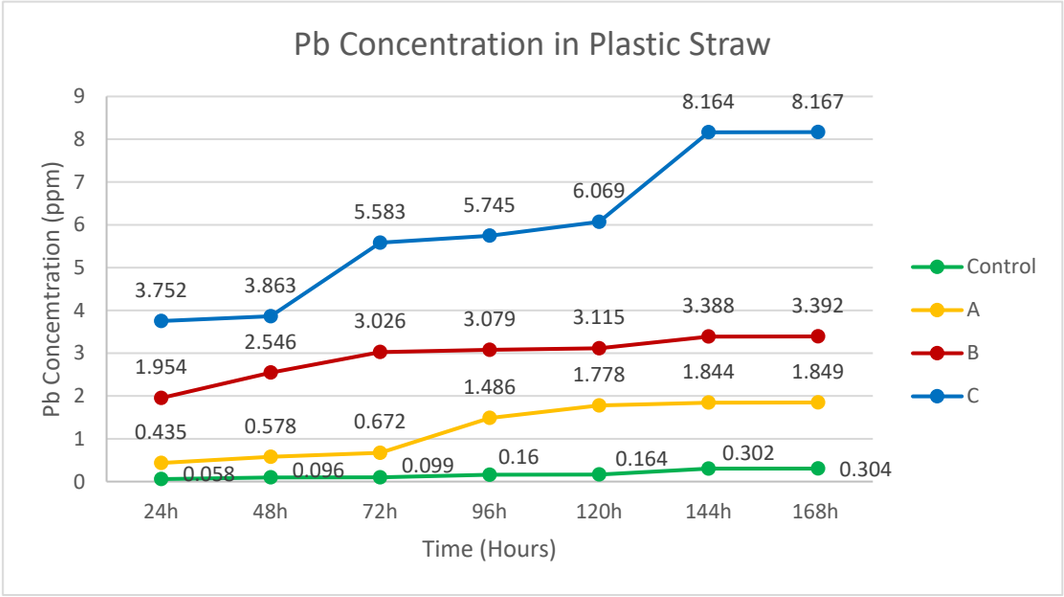

FIGURE 3. Pb concentration in microplastic pieces of straws versus time in 7 days exposure period. Different treatment represents four Pb spiked seawater concentrations; control, treatment A = 4.25 ppm, treatment B = 8.5 ppm, and treatment C = 17 ppm

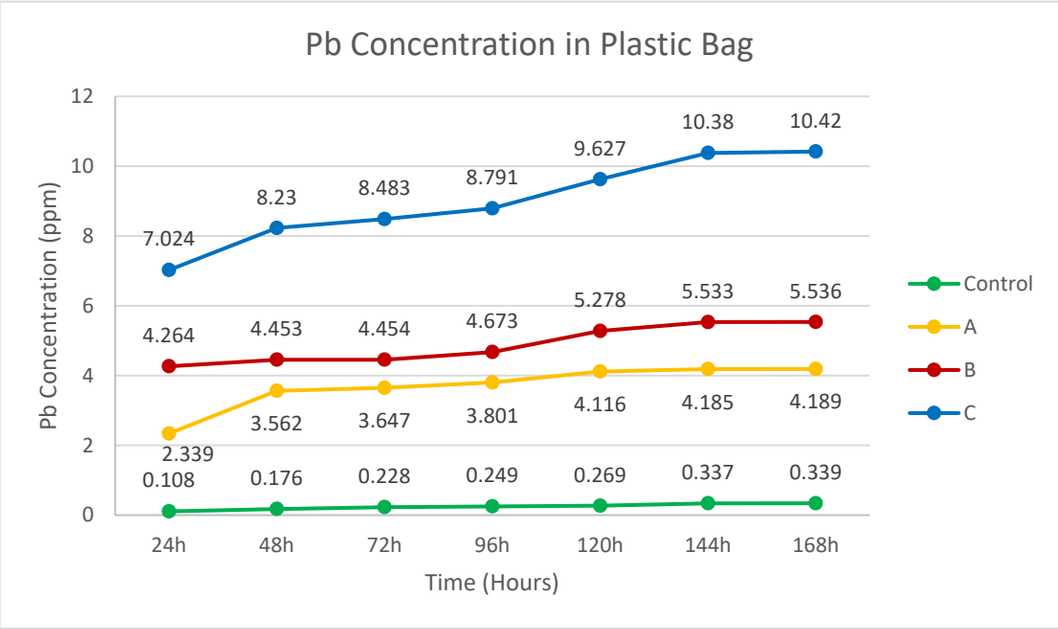

FIGURE 4. Pb concentration in microplastic pieces of bag versus time in 7 days exposure period. Different treatment represents four Pb spiked seawater concentrations; control, treatment A = 4.25 ppm, treatment B = 8.5 ppm, and treatment C = 17 ppm

PARTITION COEFFICIENTS (KPW)

Table 1 shows the values indicated that a higher Cu enrichment in plastic bag particles than plastic straws; for all treatment. In similarity, plastic bag found to have higher affinity to Pb than plastic straw.

MICROPLASTICS AS A VECTOR FOR HEAVY METAL CONTAMINATION

In the current study, the role of microplastics as a vector for heavy metals was investigated by examining the adsorption of copper (Cu) and lead (Pb), spiked into filtered seawater to micro sized plastic straw particles and plastic bag fragments. The study indicates that heavy metal spiked water can be a source of metals to be adsorbed by microplastics. It is safe to assume that existing metals in the marine ecosystem are able to adsorb in microplastics that polluted the same environment. Heavy metals availability in the aquatic environment can be a major source of metals in microplastics (Gao et al. 2019; Wang et al. 2017). A study in San Diego Bay found that concentration of each metal absorbed onto plastic pellets collected varied among sampling location. According to the study, Fe, Pb, Cr, and Al concentration were higher at Shelter Island as compared to Coronado Cays with greater concentration of Cd, Zn, Ni, Mn, and Co. The authors expected these differences based on their local sources to the bay such as shipyard activities, and storm water runoff or recreational boating (Rochman et al. 2014).

Both plastics used in this study, straw and grocery bag, are able to accumulate metals spiked into the seawater. Indication through partition coefficient (Table 1) and significant differences in metal concentration demonstrated while comparing plastics straw and bag fragments prior to the experiment became the evidence of metals concentrations on plastics were higher than in the surrounding seawater. In this context, microplastics may be considered as a vector for heavy metal contamination. Moreover, partition coefficient for Pb is mostly higher compare to Cu, which indicates greater enrichment of Pb (Table 1). Based on previous studies, Pb is found to be more reactive with higher partition coefficient and capacity for ion exchange (Chua 2018; Merrikhpour & Jalali 2015; Ouyang et al. 2019). This is due to the possibility of Pb is susceptible to being binded or absorbed with other materials (Mahdi et al. 2019) such as microplastics. The Kpw results of this study go along firmly with previous studies. For instance, another laboratory scale research determined that Pb has a higher binding ability than Cu (Kühn et al. 2018).

TABLE 1. Metal concentration [ppm] in seawater and on plastic particles, partitioning coefficient (Kpw) of copper (Cu) and lead (Pb) on plastic straw particles and plastic bag particles that were exposed for a 7-day period. Errors represent the standard deviation; mean concentrations on final day (168 h) in ppm (mean ± SD)

TREATMENT A					
		Cu (4ppm)	Kpw	Pb (4.25ppm)	Kpw
Plastic Straw	Particles	1.12 ± 0.01	5	0.185 ± 0.01	3
	Seawater	0.22 ± 0.01		0.07 ± 0.01	
Plastic Bag	Particles	0.92 ± 0.01	18	4.19 ± 0.01	35
	Seawater	0.05 ± 0.01		0.12 ± 0.01	
TREATMENT B					
		Cu (8ppm)	Kpw	Pb (8.5ppm)	Kpw
Plastic Straw	Particles	3.76 ± 0.01	10	3.39 ± 0.01	14
	Seawater	0.36 ± 0.03		0.24 ± 0.01	
Plastic Bag	Particles	3.09 ± 0.14	16	5.54 ± 0.03	21
	Seawater	0.19 ± 0.01		0.27 ± 0.01	
TREATMENT C					
		Cu (16ppm)	Kpw	Pb (17ppm)	Kpw
Plastic Straw	Particles	9.24 ± 0.02	19	8.17 ± 0.06	21
	Seawater	0.48 ± 0.01		0.39 ± 0.04	
Plastic Bag	Particles	8.51 ± 0.05	28	10.42 ± 0.05	30
	Seawater	0.31 ± 0.01		0.35 ± 0.01	

Previously, compared to heavy metals, plastic particles were known to be slightly inert compared (Ashton et al. 2010), with adverse effects associated to physical deterioration impacts caused by their ingestion were advocated rather than chemical contaminants sources related to microplastics. However, researches that are more recent implies that these particles have the ability to accumulate metals at similar rates to which is occasionally observed in estuarine sediments (Duarte et al. 2010) and suspended particles (Duarte et al. 2014). Microplastic's metal adsorption behavior is greatly influenced by its surface properties and porosity upon released into the water column. Increased in absorption capacity are generally associated with wider surface area and higher polarity that includes reactivity rate (Holmes et al. 2014; Rochman et al. 2014).

Results of this study demonstrated that plastic straw fragments with a square or triangular shape possessed a smaller surface/volume ratio, while plastic bag fragments with an irregular rectangular shape have a higher area for adsorption. In addition, the material itself could also represent a source of variability for metal adsorption as PP (plastic straw) and LDPE (plastic bag) exhibit different porosity characteristics (Holmes

et al. 2014; Rochman et al. 2014). This study results indicated that high affinity of metals in solution to plastic bag fragments directly from the water column. Direct cations adsorption and sites or plastic surface charged complexes plausibly able to regulate the mechanisms of metal sorption. In fact, organic polymers that have a high affinity towards heavy metals, is the composer of microplastics (Ashton et al. 2010).

However, the metals adsorption rates may differ as a result of differences in physical and chemical properties of each plastic type such as surface area (diffusivity), hydrophobicity and polarity (Teuten et al. 2007). In this study, plastic bag fragments adsorbed significantly higher concentrations of Pb compared to straw fragments, presumably because of the higher surface area. In contrast, plastic straw fragments adsorbed significantly higher concentrations of Cu. Following a preceding study, the authors concluded that spherical shape PS beads have smaller surface/volume ratio, in contrast with PVC fragments shaped in irregular rectangle with higher surface for adsorption (Brennecke et al. 2016). Furthermore, PS and PVC exhibit different porosity characteristics that could represent source of variability in metal absorption (Brennecke et al. 2016). Due to their different metal accumulation ability from the introduced

FIGURE 5. Plastic straw pieces cut into similar square and triangle shape. Plastic grocery bag fragments cut into irregular rectangle shape

metal sources; used post-consumer microplastics have the possibility to become a harmful threat to the marine ecology. The role of these particles as being a threat in term of vectors for marine organisms becomes more evident based on higher heavy metals in the plastic fragments compare to concentration of heavy metal in the water column.

The toxic component of plastic particles increases when the metal concentrations in plastic particles are higher than the ones found in the water column and the bioavailability of heavy metals adsorbed to microplastics are also at a high level (Holmes 2013). In marine organisms, digestive tract has the ability to extract toxic elements like heavy metal due to tract's acidic environment supported by the condition of high concentration adsorb heavy metals combined with high bioavailability (Holmes 2013). Nevertheless, the consumption rates of microplastics in marine organisms are highly variable (Van Franeker et al. 2011). Considering this aspect, the affirmation of adsorbed heavy metals in microplastics lead to acute toxicity should not be expected to occur immediately. Yet, through long-term exposure to the ingestion of these highly contaminated particles, marine organisms feasibly may experience adverse effects due to chronic toxicity that caused by biomagnification.

HYDROPHOBIC ADSORPTION OF CHEMICAL

The adsorption mechanisms of toxic chemicals to plastics are varied and complex and remain relatively less explored by researchers. However, the probable mechanism of sorption of toxic chemicals onto microplastics are discussed in this section, in order to relate the attachment of Cu and Pb onto the microplastics fragments sample in this study. Low polarity exhibition on their surface prompted microplastics to be more hydrophobic (water hating and immiscible in water) and

thus enabling hydrophobic chemical adsorption onto their surfaces from seawater (Brennecke et al. 2016). In the marine environment such as the sea and brackish waters, microplastics or other plastic debris simulate as hydrophobic adsorbents.

Microplastics tends to accumulate pollutants mostly in surface microlayer of seawater because of their lower density compare to water. Lipid-loving chemicals like persistent organic pollutants (POPs) which includes polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (such as DDT, DDE) are equip with the suitable factors and capacity enabling their adsorption and concentrate on the plastic hydrophobic surface forming a micelle shape-like structure (Vedolin et al. 2018). Adsorption partition coefficients can be used to determine the extent of adsorption rate by calculating the ratio of pollutant concentration adhered onto microplastics before and after adsorption (Brennecke et al. 2016; Gao et al. 2019).

As mentioned earlier, microplastics have low surface polarities. This particular characteristic could be the factor for adsorption of metals ions onto microplastic surfaces. The binding of positive charged aqueous metal ion (M^{+}) via electrostatic attraction to the negatively charged groups on the surface of plastic thus neutralizing their charge and the formation a micelle shape-like structure occur (Figure 5). This mechanism may goes the same for the Cu^{2+} ion (soluble from Copper (II) Sulphate 5-Hydrate, $CuSO_4.5H_2O$) and Pb^{2+} ion (soluble from Lead (II) Nitrate, Pb $(NO_3)_2$); which able to bind to negative charged groups on the surface of both plastic straw and bag micro fragments. Irrespective of adsorption medium (water, sediment, soil or air), despite various binding form with different plastic types and metal ion type (cationic or anionic), the adsorption mechanism is precept to comply with the same principle.

In the environment, amidst longer exposure period, toxic chemical adsorption on microplastics increased. A laboratory experiment demonstrated that trace metals (Cu, Cr, Cd, Co, and Ni) rapidly adsorb onto virgin polyethylene pellets exposed to seawater amended with trace metal. The absorption mechanism occurs in a Langmuir or Freundlich fashion with the partition coefficients equilibrium up to about 50 mL/g (Holmes et al. 2012). In this study, Pb and Cu rapidly adsorb onto microplastics straw and bags fragments within seven days exposure period, as it is a controlled laboratory experiment. In a contrary, in natural environment, metals absorption process requires more time compare to controlled laboratory experiment (Fischer et al. 2007). Consequently, this is due to plastics surface becomes more reactive because of generating oxygen groups while increasing charge and porosity during degradation (Holmes et al. 2012; Mato et al. 2001).

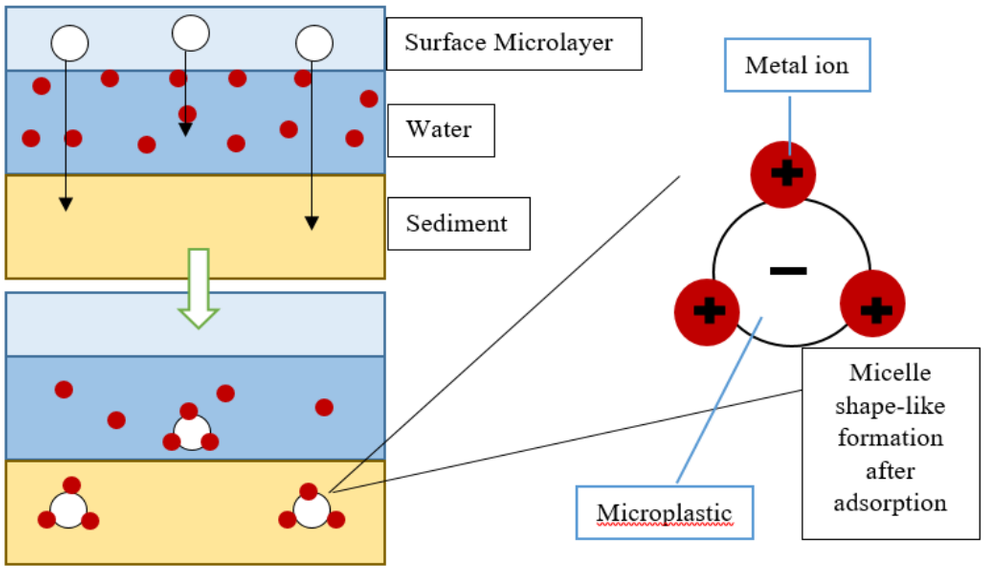

FIGURE 6. The mechanism transfer of metal ion (as contaminants) when microplastics are present and schematic of adsorption metal ion onto microplastic

Conclusion

Heavy metals and microplastics are two important emerging sources of pollution in the marine environment. To the best of our knowledge, this investigation represents the first study in Thailand to experiment the metal adsorption ability that purposely exposed to microplastics. According to the results obtained, it is shown patently that microplastics sample in this study have high affinity to heavy metals rapidly adsorbing these elements, Cu and Pb direct from the source (spiked seawater). The persistency and ubiquity of microplastics in the marine environment supported by the fact of very slow degradation process and the ability to accumulate other chemical pollutants including heavy metals become the major reason both microplastics and heavy metals have the relevance to be monitored as descriptors. The understanding of underlying mechanisms related the interaction between both pollutants should be one of the key principal in future marine framework.

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