Are carbon nanomaterials for the adsorption of contaminants perform better than nano/microplastics?

[OI]Gamze Ersan[1,*], [OI]Mahmut S. Ersan[2,‡]

[1]*Department of Environmental Engineering and Earth Sciences, Clemson University, Anderson, SC 29625, USA;* [2] *School of Sustainable Engineering and The Built Environment, Arizona State University, Tempe, AZ 85287-5306, USA*

Abstract: The presence of nanoplastics (NPs) and microplastics (MPs), and carbon-based nanomaterials in the aquatic systems may impact the fate and transport of existing organic contaminants (OCs). In this study, we investigated the adsorption of selected OCs (pyrene, bisphenol A, and phenanthrene) on MPs, NPs and carbon-based nanomaterials (graphene, graphene oxide [GO], single-walled carbon nanotube [SWCNT], multiwalled carbon nanotube [MWCNT]), and coal-based activated carbons (AC). This study includes a discussion of the adsorption mechanisms of OCs by commercial, consumer, and biodegradable MPs and/or NPs, and a comparison of their adsorption behaviors with those of graphene, GO, SWCNT, MWCNT, and AC. Single point adsorption descriptors (K_d values) at different equilibrium concentrations were calculated for each adsorbent, and the results showed that adsorption of pyrene and bisphenol A on MWCNT was higher than graphene and NPs. Besides, K_d values at different equilibrium concentrations ($K_{d0.0001}$ vs $K_{d0.001}$) also present that pyrene uptake on CNT and NPs were increasing more than graphene with increasing equilibrium concentrations. When the adsorption capacities (indicated by K_d) of graphene, GO, CNT and AC were compared with PS and PE based MPs, and biodegradable MPs, K_d values of carbon-based nonabsorbent, and AC were 1.5-2 times higher than MPs. This might be related to the higher surface area of carbonaceous adsorbents (i.e., 150-700 m^2/g). After adsorption capacity of phenanthrene was normalized by the BET surface area of adsorbents the adsorption capacity followed an order of PS-based MPs > PE-based MPs ~ Biodegradable MPs > MWCNT > GO ~SWCNT > graphene ~AC indicating that total surface area normalization decreased the differences in adsorption capacities of phenanthrene onto carbonaceous adsorbents.

Keywords: *Microplastics, Nanoplastics, Carbon Nanomaterials, Adsorption, Organic Contaminants*

Introduction

Carbon-based nanomaterials such as carbon nanotubes (CNTs), graphene, and graphene oxide (GO) can be formed by graphitic carbon sheets (Terrones, 2003; Iijima, 1991), and rolled into hollow cylinders of these graphitic carbon sheets are classified as multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) (Ajayan, 1999). The high surface area of nanomaterials brings new prospects for the management of organic pollutants, for example, CNTs are found to work effectively to remove organic contaminants (Zhang et al., 2010). Graphene, a fascinating two-dimensional carbon-based material possessing atomic thickness, has attracted considerable attention around the world (Novoselov et al. 2004). This excitement is greatly attributed to its excellent physicochemical and mechanical properties (Geim et al., 2007; Allen et al., 2010; Rao et al.,2009). Graphene has a large theoretical specific surface area (2620 m^2g^{-1}), (Zhu et al., 2010) which indicates its potential for the adsorption of organic pollutants in environmental pollution management. On the other hand, CNTs have attracted scientific interest worldwide due to their unique structure and superior physical and electronic properties. Although they hold promise as high-performance adsorbents, very little work has been done to evaluate their adsorption properties for organic compounds of interest to the water treatment industry.

Corresponding: E-Mail: gersan@g.clemson.edu; Tel: +1-864-707-6262; Fax: +1- 864-656-1041
‡ *These authors contributed equally to this work*

Graphene and CNTs offer several potential advantages over the existing state of the art adsorbents, activated carbons (ACs), and carbon fibers: 1) their surfaces are inherently more hydrophobic, which exploits entropic free energy of organic compound adsorption; 2) their electronic structure is favorable for supporting interactions with double-bonded carbon atoms, including aromatic structures; and, 3) when closed-ended, their shape and packing properties produce sorption surfaces that are not located in micropores. Taken together, these features may increase sorption uptake, speed adsorption kinetics, improve regeneration, and mitigate fouling by natural organic matters. Up to now, the adsorption of organic contaminants (100[+]) by carbon-based nanomaterials has been widely investigated in the literature (Su et al., 2010; Yu et al., 2012; 2014 Wang et al., 2012; Liu et al., 2014; Ersan et al., 2016a). Especially, when the nanomaterials have existed in our environment, originating from both natural and anthropogenic sources, they may favorably adsorb existed contaminants in the aquatic systems.

On the other side, with increasing nanoplastics (NPs) and microplastics (MPs) detected in aquatic environments, more studies focused on the adsorption behavior of NPs and MPs, and associated contaminants. During the last decade, more attention has been shifted to MPs and NP. As seen in Fig. 1, among all different sizes of plastic fragments, MPs can be one of the potential detrimental in the aquatic systems ranging between 0.1 to 1,000 μm in diameter. MPs are identified for small plastic particles of different origins, sizes, and chemical compositions. Up to now, the adsorption of various classes of organic contaminants (OCs) (i.e., polycyclic aromatic hydrocarbons [PAHs], halogenated aliphatic, pharmaceuticals and personal care products [PPCPs], dichloro-diphenyl- trichloroethane [DDT], and [poly]chlorinated biphenyls [PCBs], poly- brominated diphenyl ethers), and heavy metals by different types of MPs in distilled and deionized water (DDW), synthetic seawater, seawater or freshwater has been examined in the literature (i.e., Zuo et al., 2019; Li et al., 2018; Kedzierski et al., 2017; Wang et al., 2017; Brennecke et al., 2016; Velzeboer et al., 2014; Antunes et al., 2013; Bakir et al., 2012 Karapanagioti and Klontza, 2008; Pascall et al., 2005; Mato et al., 2001). Therefore, the presence of carbon-based nanomaterials and NPs/MPs in the aquatic systems may have altered the fate and impacts of existing OCs.
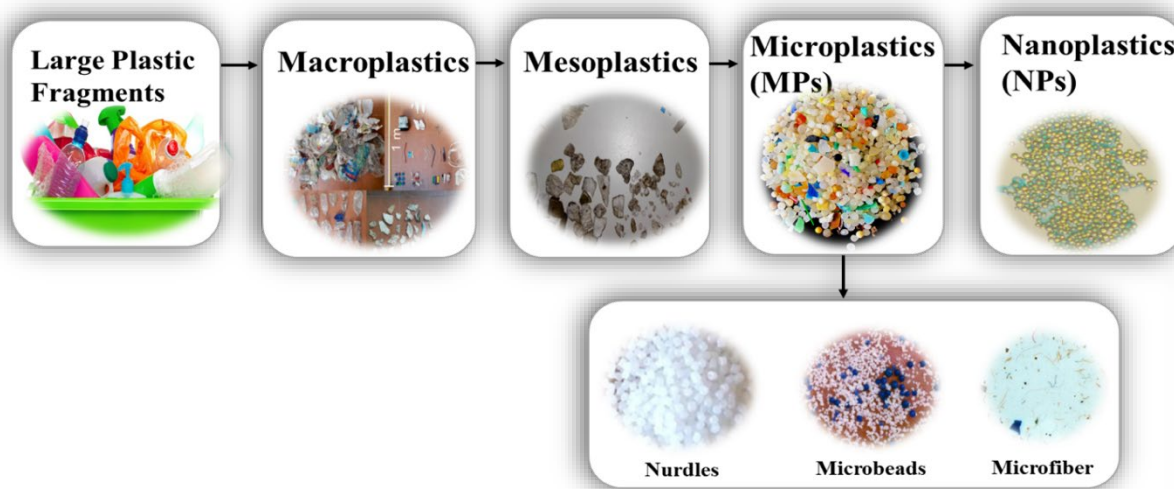

Figure 1. Break down of large plastic wastes into small fragments under natural exposure conditions
*Source: Arthur et al., 2009; Rochman et al., 2015; Bletter et al., 2017; Jahnke et al., 2017; Olubukola et al., 2018; Uhl, 2018).

In general, NPs/MPs are formed from abundant plastic types including polyethylene (PE), polystyrene (PS), polypropylene (PP), polyvinyl chloride (PVC) based, and biodegradable plastics, and therefore, these NP/MPs may carry different morphological and physicochemical characteristics. These differences may lead to different interactions between NP/MPs and OCs. On the other hand, the open-up layer structure of

graphene and super hydrophobic characteristics of CNTs may result in favorable adsorption of existed contaminants from natural systems (Ersan et al., 2019).

Therefore, this study specifically focused on a side-by-side comparison of carbon-based nanomaterials and NPs/MPs for adsorption of selected OCs. More specifically, the present study deeply discussed the mechanisms and factors controlling the adsorption of pyrene, bisphenol A, and phenanthrene by NPs and MPs. Also, a comparison of their adsorption behaviors with those of graphene, GO, SWCNT, MWCNT, and coal-based AC have been evaluated.

Materials and Methods
Data compilation from the literature

A comprehensive literature survey was performed to obtain the available adsorption isotherm data for pyrene, bisphenol A, and phenanthrene by PS based NPs, three different MPs (conventional, consumer, and biodegradable), graphene, GO, SWCNT, MWCNT, and AC (from the Web of Science database and Social Science Citation Index), including some of our previously published studies (Ersan et al., 2016b, 2017, 2019). The properties of tested OCs were presented in Table 1 and were acquired from the Absolv module of the ACD/Percepta, 2016.2v software.

Table 1. Properties of selected organic contaminants

Adsorbate	Chemical Formula	Planarity	Molecular weight (g/mol)	Density (g/cm^3)	Solubility in water (mg/L)	LogK$_{ow}$[*]
Phenanthrene	$C_{18}H_{10}$	Planar	178.25	1.063	1.15	4.54
Pyrene	$C_{14}H_{10}$	Planar	202.25	1.27	0.135	4.88
Bisphenol A	$C_{15}H_{16}O_2$	Nonplanar	228.29	1.2	120	3.32

[*]logK$_{ow}$: log octanol-water partition coefficient.

The adsorbents investigated in this study included pristine graphene and GO (Graphene Laboratories Inc.), SWCNT (Chengdu Organic Chemicals Co., Ltd.), MWCNT (Nanostructured & Amorphous Materials Inc.), and coal based ACs (F400, Calgon Inc.). In our previous study, Graphenes and CNTs were used as received from the manufacturers, while the AC was ground to 250-325 μm size before use in the experiments (Ersan et al., 2016a). Besides, one PS-based NPs, three different types of MPs (PE, PS, and biodegradable) datasets were collected from Liu et al., (2018), Wang et al., (2018), and Zuo et al (2019). The properties of all adsorbents were given in Table 2.

Table 2. Properties of selected adsorbents in the literature

Adsorbent	SA_{BET} (m²/g)	V_T (cm³/g)	V_{micro} (<20 nm)	V_{meso} (20-50 nm)	V_{macro} (>50 nm)	Oxygen content %	References
GNS	666	3.14	0.12	0.58	0.54	1.2	
GO	497	0.53	0.01	0.25	0.49	10.5	Ersan et al., 2016a
SWCNT	537	1.24	0.07	1.2	1.88	1.8	
MWCNT	179	0.75	0.08	0.38	0.07	0.01	
F400	849	0.5	0.37	0.01	0.13	4.6	
PS based NPs	N.R.						Liu et al., 2018
PE based MPs	2.47						
PS based MPs	0.97		N.R.				Wang et al., 2018 and Zuo et al 2019
Biodegradable MPs	2.21						

*Specific surface area (SA_{BET}) calculated with the Brunauer-Emmett-Teller (BET) model. Total pore volume (VT) calculated from single point adsorption at $P / P_0 = 0.99$. The pore volume fraction in each pore size range was obtained from the density functional theory (DFT) analysis. N.R.: Not reported.

Determination of single point adsorption descriptor (K_d)

In this study, we examined the sorption behavior of each adsorbent with single-point adsorption descriptor (K_d value) parameters. K_d values are, in general, used in various environmental models for estimating the OCs uptake on adsorbents. Therefore, single point adsorption descriptors ($K = q_e/C_e$, where q_e is solid-phase equilibrium concentration and C_e is liquid phase equilibrium concentration) at three different C_e values, 0.01%, 0.1%, and 1% of the aqueous solubility of each adsorbate were calculated and represented with $K_{d,0.0001}$, $K_{d,0.001}$, and $K_{d,0.01}$, respectively. The details of K_d determination and calculation were provided in Text S1 and Fig. S1 in Supporting Information (SI) Section.

Results and Discussion
Adsorbent characterization

According to Table 2, the significant differences among their structure properties were supported by their surface area and pore volume distributions. The BET surface areas of the adsorbents followed the order of: F400 > SWNT > GO > MWNT> PE based MPs > Biodegradable MPs> PS based MPs. Among all carbon-based nanomaterials, graphene had 3-4 times higher pore volumes than CNTs. The graphene had ~3-4 times higher pore volumes than CNTs, which may be attributed to their much less compact aggregate and bundle structures as compared to CNTs (Ersan et al., 2019). The graphene and GO had meso- and macropores. SWNT, F400 carbons were highly micropores, while MWCNT was mainly by meso- and macropores. Since the surface area of carbon-based materials is much higher than NPs and MPs, this might affect the organic contaminant uptake in the aquatic systems.

Adsorption of pyrene and bisphenol A by NPs: Compared with graphene and CNTs

The single point adsorption descriptors at $K_{d0.0001}$ for adsorption of pyrene and bisphenol A onto PS-based NPs, graphene, and CNTs (MWCNT) were calculated and presented in Fig. 2 and Table S2. Some major observations from the isotherms are: (i) there was a higher pyrene uptake by NPs, graphene, and CNTs on a mass basis isotherm. Bisphenol A (120 mg/L) is more soluble than pyrene (0.135 mg/L), and (ii) the order of bisphenol A adsorption capacities represented by $K_{d0.0001}$ was CNT> graphene> NPs for both OCs (Fig. 2). Although the surface area of MWCNT (179 m²/g) was lower than graphene (666 m²/g), K_d values of pyrene and bisphenol A on MWCNT were higher than graphene. This suggests that total surface area or pore volume was not the only controlling factor for the adsorption of pyrene and bisphenol-A. This finding is also consistent with previous studies (Chao et al., 2008; Ersan et al., 2016a). In this study, K_d values have been shown to depend on the accessibility of organic molecules to the inner surface of the

adsorbent (Fig. 2). The molecular size of organic molecules and oxygen contents of MWCNT (0.01%) were controlling both pyrene and bisphenol A uptake. This can be attributed to more hydrophobic surface of MWCNT. On the other hand, the availability of oxygen functional groups on the adsorbent surface has been shown a significant reduction of OCs adsorption due to the polar-polar interaction of the adsorbent surface with water molecules. Since graphene is containing oxygenated functional groups (1.2%), water molecules can interact with polar functionalities on the graphene surface via hydrogen bonding. Previous studies also emphasized that competition of water molecules with organic molecules on the oxidized sites of CNTs' surface may be responsible for the adsorption decrease of naphthalene, chlorophenol, and resorcinol, oxygen-containing groups on CNTs' surface are hydrophilic and can form strong H-bonds with water molecules to suppress adsorption of organic compounds, especially hydrophobic organic compounds (Yang et al., 2011; Shen et al., 20010; 2015; Choi et al., 2007). Therefore, the physicochemical characteristics of MWCNT showed that the surface is extremely hydrophobic because of lower oxygen content (0.01%). The observed linear correlation between adsorption capacities of pyrene and bisphenol A (q_e) with the oxygen content of MWCNT (Fig. 2) suggests that the hydrophobicity of MWNT is the dominant factor that controls the adsorption. When the compared carbon nanomaterials with PS-based NPs, the adsorption capacity of Bisphenol A is lower than graphene and CNTs. On the other hand, PS based NP and graphene was exhibited similar adsorption capacity for pyrene at $logK_{d0.0001}$. However, due to the lack of physicochemical properties of PS-based NPs (Liu et al., 2018), the adsorption mechanisms on PS-based NPs for pyrene and bisphenol A were still limited, which warrants further investigation with different types of NPs and OCs.
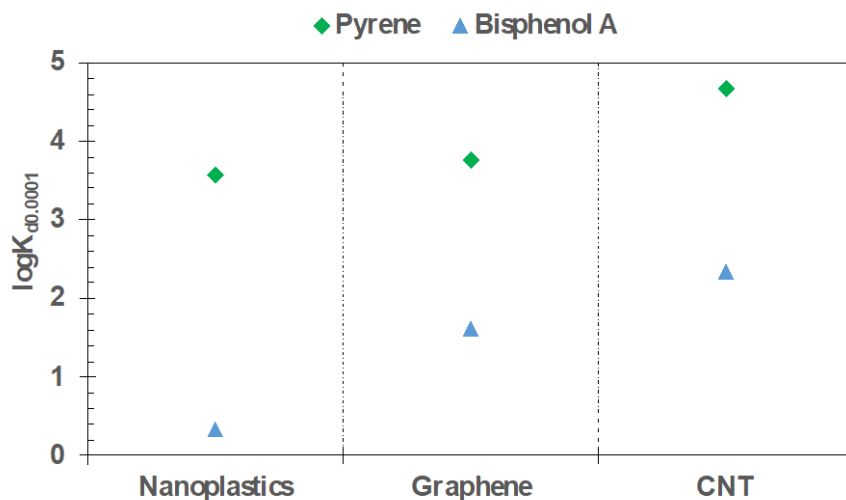

Figure 2. Comparisons on single point adsorption descriptors ($K_{d,0.0001}$) for pyrene and bisphenol A sorption to PS-based NPs, graphene, and CNT in DDW on a mass basis.

To evaluate the impact of equilibrium concentration on the pyrene uptake, the results for adsorption of pyrene on NPs, graphene, and CNTs were compared at different saturation levels. The single point adsorption descriptors, K_d values at different equilibrium concentrations for pyrene onto NPs, graphene, and CNTs (MWCNT) were calculated and presented in Fig. 3. Some major observations from the isotherms are: (i) MWCNT exhibited higher sorption capacity compared to other investigated adsorbents, (ii) increasing equilibrium concentration (from $K_{d,0001}$ to $K_{d0.001}$) did not impact adsorption capacity, which followed MWCNT > graphene > NPs, (iii) K_d values at different equilibrium concentrations also showed that pyrene uptake on CNT and NPs was higher with increasing equilibrium concentrations compared to

graphene (Fig. 3), this may be explained by strong π-π bonding between pyrene molecules and open-up layer graphene surface.
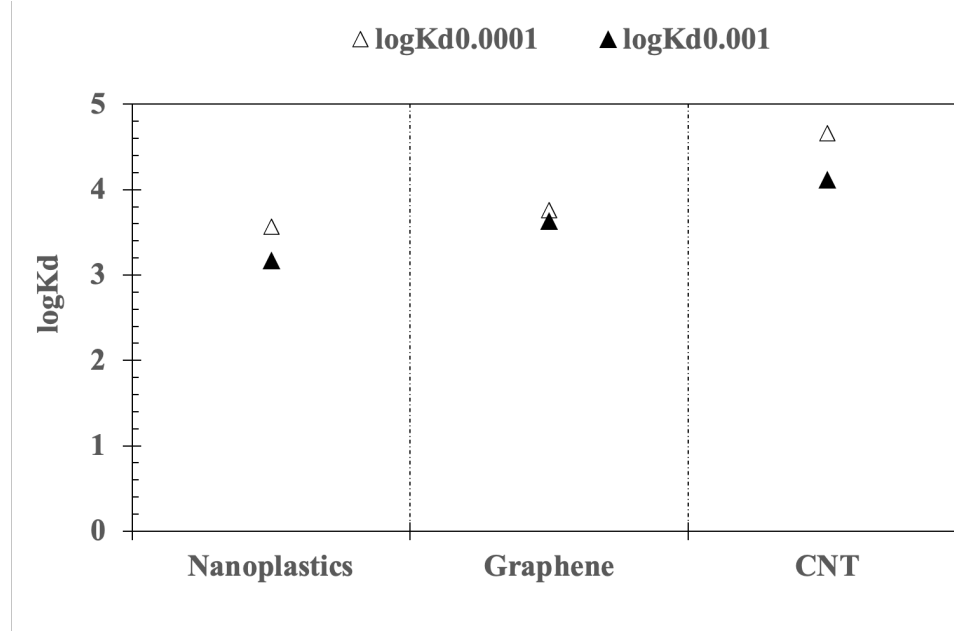

Figure 3. Effect of K_d concentrations on the pyrene sorption to PS-based NPs, graphene, and CNT in DDW on a mass basis.

Adsorption of phenanthrene by MPs: Compared with graphene, CNT, and AC

As we discussed in previous sections, among carbonaceous adsorbents, graphene (sheet form) and CNT (rolled form) are made from a two-dimensional sheet of sp^2-hybridized carbon (Allen et al., 2010). Due to their strong van der Waals forces, graphene and CNT prone to restack, thus may form interconnected pores within the aggregates. Although graphene and CNT are carried similar surface characteristics, their aggregation structure in water is different from the physical structure of rigid AC (Ersan et al., 2019). When compared to MPs and carbonaceous adsorbents, the specific surface area of MPs (i.e., 0.5-5 m^2/g) are much lower than carbon-based adsorbents (i.e., 150-700 m^2/g), and thus the adsorption behavior of MPs, graphene, CNT, and AC is changed depending on the physicochemical properties of the adsorbents (e.g., specific surface area, pore size distribution, functional groups, and surface chemistry). So far, only one study has been focused on the adsorption of OCs on PE-based MPs, PS-based NPs, carbonaceous adsorbents (MWCNT and fullerene (C_{60})), and natural sediment under seawater and freshwater conditions (Velzeboer, et al., 2014). The adsorption of PCBs onto MWCNT and C_{60} was 2-3 orders of magnitude higher than PS-based NPs, while sorption of PCBs to PS-based NPs was 1-2 orders of magnitude higher than PS-based MPs in seawater and freshwater. Thus, carbon nanomaterials have been shown to perform better for PCB adsorption in seawater and freshwater. However, in the presence of salinity and sediment organic matter, the adsorption behavior of PCBs may be impacted by the competition between natural organic matter molecules and ions on the accessible adsorption sites. Therefore, we obtained single-point adsorption descriptors of OCs for graphene, CNTs, AC, and MPs in a single solute system (DDW). The adsorption of phenanthrene onto graphene, GO, MWCNT, SWCNT, AC, and MPs at $logK_{d,0.001}$ values were presented in Fig. 4 to demonstrate the comparison of MPs with carbonaceous adsorbents (in Table S1). In the current literature, the K_d values of phenanthrene for MPs and carbonaceous adsorbents were only available at 0.01% of aqueous solubility. Therefore, we were only able to compare K_d values at single saturation conditions in this section. The phenanthrene single point adsorption descriptors (K= q_e/C_e, where q_e is solid-phase equilibrium concentration and C_e is the liquid phase equilibrium concentration) at $K_{d,0.01}$ were calculated. As seen in Fig. 4, the adsorption capacities (indicated by K_d) of graphene, GO, CNT and

AC were 1.5-2 times higher than PS and PE-based MPs, and biodegradable MPs. This might be related to the higher surface area of carbonaceous adsorbents (i.e., 150-700 m^2/g).
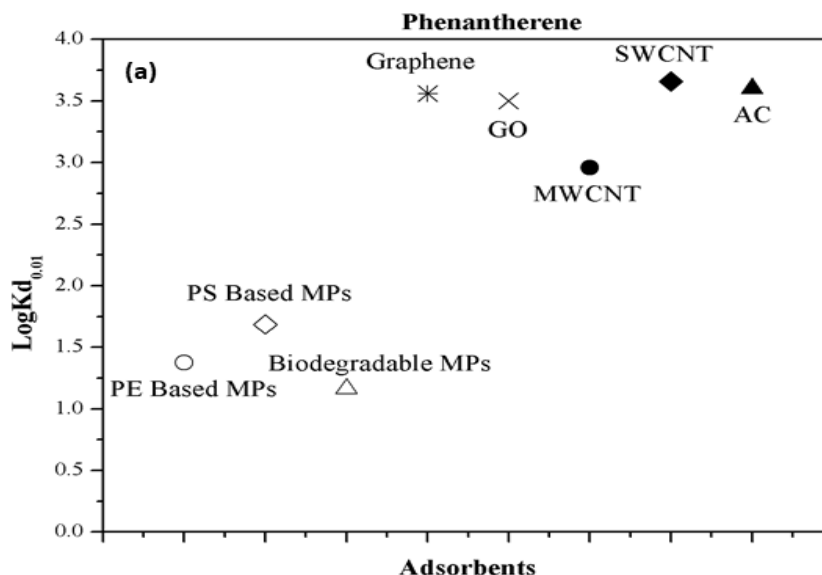

Figure 4. Comparisons on single point adsorption descriptors ($K_{d,0.01}$) for phenanthrene sorption to PE, PS based and biodegradable MPs, graphene, GO, MWCNT, SWCNT, and AC in DDW on a mass basis.

After the adsorption capacity of phenanthrene was normalized by the BET surface area of adsorbents (Fig. 5), the adsorption capacity followed the order of PS-based MPs > PE-based MPs ~ Biodegradable MPs > MWCNT > GO ~SWCNT > graphene ~AC indicating that total surface area normalization decreased the differences in adsorption capacities of phenanthrene onto carbonaceous adsorbents. After surface area normalization, the other factors (surface charge, functional groups etc.) played a more important role in understanding the adsorption difference of MPs. These findings suggest the need for additional research to identify the impact of OC properties and MPs characteristics on adsorption mechanisms under more complex background waters.
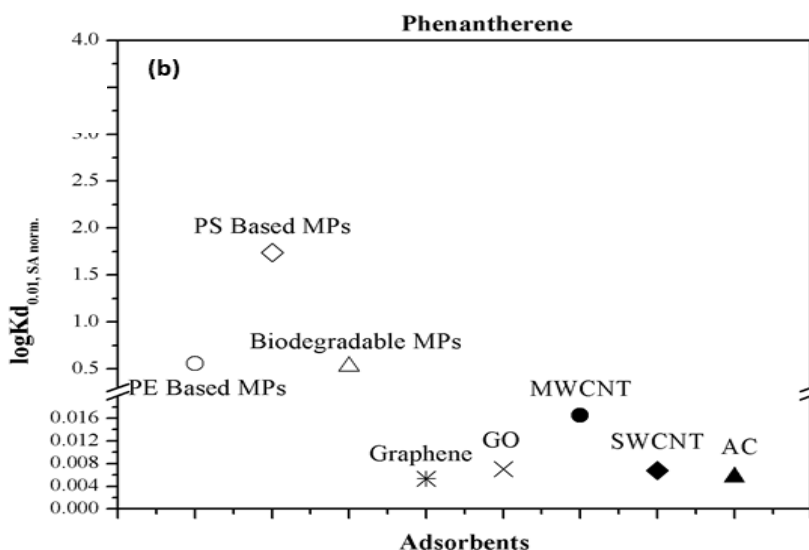
Figure 5. The single point adsorption descriptors ($K_{d,0.01}$ values) for phenanthrene sorption to PE, PS based, and biodegradable MPs, graphene, GO, MWCNT, SWCNT, and AC in DDW on a surface area normalized basis.

Conclusions

This study investigated the adsorption mechanisms of OCs on commercial, consumer, and biodegradable MPs and/or NPs, and a comparison of their adsorption behaviors with those of graphene nanosheets, CNTs, and AC. Overall, a cumulative summary of important findings is as follows:

- The single point adsorption descriptors (K_d values) at different equilibrium concentrations represent that adsorption of pyrene and bisphenol A on MWCNT was higher than graphene and NPs, which was due to hydrophobic interactions between MWCNT and OCs.
- The pyrene uptake on CNT and NPs was higher than graphene with increasing equilibrium concentrations, which can be associated with open-up layer structure of graphene.
- When the adsorption capacities (indicated by K_d) of graphene, GO, CNT and AC were compared with PS- and PE-based MPs, and biodegradable MPs, K_d values of carbon-based nanoabsorbents, and AC were 1.5-2 times higher than MPs. This might be related to the higher surface area of carbonaceous adsorbents (i.e., 150-700 m^2/g).
- After adsorption capacity of phenanthrene was normalized by the BET surface area of adsorbents, the adsorption capacity was in the order of PS-based MPs > PE-based MPs ~ Biodegradable MPs > MWCNT > GO ~SWCNT > graphene ~AC. This indicates that total surface area normalization decreased the differences in adsorption capacities of phenanthrene onto carbonaceous adsorbents.
- Overall, the much lower surface area and different surface functionalization of MPs can cause different adsorption behaviors compared with carbon-based adsorbents (graphene, CNTs, and AC). Further research should be investigated for the comparison of different classes of contaminants (i.e., aliphatic versus aromatics, hydrophobic versus hydrophilic, long versus short chain, etc.) sorption onto MPs (commercial, consumer, or biodegradable), graphene, CNTs, and ACs under varying background waters and changing adsorbent characteristics upon natural attenuation by weathering and aging.

Reference

Ajayan, PM., (1999) Nanotubes from carbon. Chemical Reviews, 99(7): 1787-1799. doi:10.1021/cr970102g

Allen, M.J. Tung, V.C. Kaner, R.B. (2010) Honeycomb Carbon: A Review of Graphene. Chemical Reviews, 110, 132 -145. doi:10.1021/cr900070d

Antunes, JC., Frias, JGL., Micaelo, AC., Sobral, P, (2013) Resin pellets from beaches of the Portuguese coast and adsorbed persistent organic pollutants. Estuarine, Coastal and Shelf Science, 130, 62–69. https://doi.org/10.1016/j.ecss.2013.06.016

Bakir, A.; Rowland, S. J.; Thompson, R. C. (2012) Competitive sorption of persistent organic pollutants onto microplastics in the marine environment. Marine Pollution Bulletin, 64 (12), 2782−2789. https://doi.org/10.1016/j.marpolbul.2012.09.010

Brennecke, D., Duarte, B., Paiva, F., Caçador, I., Canning-Clode, J. (2016) Microplastics as vector for heavy metal contamination from the marine environment. Estuarine Coastal & Shelf Science, 178:189-195. https://doi.org/10.1016/j.ecss.2015.12.003

Choi, J.W., Choi, N.J., Lee, S.J., Kim, D.J., (2007) Novel three-stage kinetic model for aqueous benzene adsorption on activated carbon. Journal of Colloid and Interface Science, 314, 367-372. https://doi.org/10.1016/j.jcis.2007.05.070

Ersan, G., Kaya, Y., Apul, O.G., Karanfil, T., (2016a) Adsorption of organic contaminants by graphene nanosheets, carbon nanotubes and granular activated carbons under different natural organic matter preloading conditions. Science of Total Environment, 565, 811-817. https://doi.org/10.1016/j.scitotenv.2016.03.224

Ersan, G., Apul, O.G., Karanfil, T., (2016b) Linear solvation energy development for adsorption of organic contaminants by carbon nanotubes. Water Research, 98, 28-38. https://doi.org/10.1016/j.watres.2016.03.067

Ersan, G., Apul, O.G., Perreault, F., Karanfil, T., (2017) Adsorption of organic com- pounds by graphene nanosheets: a review. Water Research, 125, 1-14. https://doi.org/10.1016/j.watres.2017.08.010

Ersan, G., Apul, O.G., Karanfil, T., (2019) Predictive models for adsorption of organic compounds by Graphene nanosheets: comparison with carbon nanotubes. Science of Total Environment, 654, 28-34. https://doi.org/10.1016/j.scitotenv.2018.11.029

Geim, A. K., (2009) Graphene: Status and Prospects. Science, 324, (5934), 1530-1534. https://doi: 10.1126/science.1158877

Geim, A.K. and Novoselov, K.S., (2007) The rise of graphene. Nature Materials, 6. 183. https://doi.org/10.1038/nmat1849

Iijima S., (1991) Helical Microtubules of Graphitic Carbone, Nature, 354, 56-58. https://doi.org/10.1038/354056a0

Karapanagioti, H.K., Klontza, I., (2008) Testing phenanthrene distribution properties of virgin plastic pellets and plastic eroded pellets found on Lesvos island bea- ches (Greece). Marine Environmental Research 65 (4), 283-290. doi: 10.1016/j.marenvres.2007.11.005

Kedzierski, M., Le Tilly, V., Cesar, G., Sire, O., Bruzaud, S., (2017) Efficient microplastics extraction from sand. A cost-effective methodology based on sodium iodide recycling. Marine Pollution Bulletin, 115, 120–129. https://doi.org/10.1016/j.marpolbul.2016.12.002

Liu, F. F., Zhao, J., Wang, S. G., Du, P., Xing, B. S., (2014) Effects of solution chemistry on adsorption of selected pharmaceuticals and personal care products (PPCPs) by graphenes and carbon nanotubes. Environmental Science & Technology, 48 (22), 13197-13206. https://doi.org/10.1021/es5034684

Li J, Zhang K, Zhang H. (2018) Adsorption of antibiotics on microplastics. Environmental Pollution. 237: 460-467. https://doi.org/10.1016/j.envpol.2018.02.050

Liu, J., Ma, Y., Zhu, D., Xia,T., Qi, Y., Yao, Y., Guo, X., Ji, R., and Chen, W. (2018) Polystyrene Nanoplastics-Enhanced Contaminant Transport: Role of Irreversible Adsorption in Glassy Polymeric Domain. Environmental Science & Technology, 52 (5), 2677-2685. https://doi.org/10.1021/acs.est.7b05211

Llorca, M., Farren, M., Karapanagioti, H.K., Barcelo D., (2014) Levels and fate of per-fluoroalkyl substances in beached plastic pellets and sediments collected from Greece. Marine Pollution Bulletins, 87, 2, 86-91. doi: 10.1016/j.marpolbul.2014.07.036

Mato, Y., Isobe, T., Takada, H., Kanehiro, H., Ohtake, C., Kaminuma, T., (2001) Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. Environmental Science & Technology, 35 (2), 318-324. https://doi.org/10.1021/es0010498

Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V., Firsov, A. A., (2004) Electric Field Effect in Atomically Thin Carbon Films. Science, 306, (5696), 666-669. doi: 10.1126/science.1102896

Pascall, M. A.; Zabik, M. E.; Zabik, M. J.; Hernandez, R. J. (2005) Uptake of polychlorinated biphenyls (PCBs) from an aqueous medium by polyethylene, polyvinyl chloride, and polystyrene films. Journal of Agricultural and Food Chemistry, 53 (1), 164−169. doi: 10.1021/jf048978t

Rao, C.N.R. Sood, A.K. Subrahmanyam, K.S. Govindaraj, A. (2009) Graphene: the new two-dimensional nanomaterial. Angewandte Chemie International Edition, 48, 77-52. https://doi.org/10.1002/anie.200901678

Shen, X., Guo, X., Zhang, M., Tao, S., Wang, X., (2015) Sorption mechanisms of organic compounds by carbonaceous materials: site energy distribution consideration. Environmental Science & Technology, 49, 4894-4902. https://doi.org/10.1021/es506034e

Sheng, G.D., Shao, D.D., Ren, X.M., Wang, X.Q., Li, J.X., Chen, Y.X., Wang, X.K., (2010) Kinetics and thermodynamics of adsorption of ionizable aromatic compounds from aqueous solutions by as prepared and oxidized multi-walled carbon nanotubes. Journal of Hazardous Materials, 178, 505-516. doi:10.1016/j.jhazmat.2010.01.110

Su, F. H., Lu, C. Y., Hu, S. K., (2010) Adsorption of benzene, toluene, ethylbenzene and p-xylene by NaOCl-oxidized carbon nanotubes. Colloids and Surfaces, 353 (1), 83-91. https://doi.org/10.1016/j.colsurfa.2009.10.025

Terrones, M., (2003) Science and technology of the twenty-first century: Synthesis, properties and applications of carbon nanotubes. Annual Review of Materials Research, 33: 419-501. https://doi.org/10.1146/annurev.matsci.33.012802.100255

Velzeboer, I.; Kwadijk, C. J. A. F.; Koelmans, A. A. (2014) Strong sorption of PCBs to nanoplastics, microplastics, carbon nanotubes, and fullerenes. Environmental Science & Technology, 48 (9), 4869−4876. https://doi.org/10.1021/es405721v

Wang, F., Zhu, D.Q., Chen, W., (2012) Effect of copper ion on adsorption of chlorinated phenols and 1-naphthylamine to surface-modified carbon nanotubes. Environmental Toxicology and Chemistry, 31 (1), 100-107. doi: 10.1002/etc.713

Wang, Z., Chen, M., Zhang, L., Wang, K., Yu, X., Zheng, Z., Zheng, R., (2018) Sorption behaviors of phenanthrene on the microplastics identified in a mariculture farm in Xiangshan Bay, southeastern China. Science of Total Environment, (628-629), 1617-1626. doi: 10.1016/j.scitotenv.2018.02.146

Wang, F., Wong, C.S., Chen, D., Lu, X.W., Wang, F., Zeng, E.Y., (2017) Interaction of toxic chemicals with microplastics: a critical review. Water Research. 139, 208-219. doi: 10.1016/j.watres.2018.04.003

Yang, C.Z., Yaniger, S.I., Jordan, V.C., Klein, D.J., Bittner, G.D., (2011) Most plastic pro- ducts release estrogenic chemicals: a potential health problem that can be solved. Environmental Health Perspectives, 119, 982–996. doi: 10.1289/ehp.1003220

Yang, K., Wang, X., Zhu, L., Xing, B.S., (2006) Competitive sorption of pyrene, phenanthrene, and naphthalene on multiwalled carbon nanotubes. Environmental Science & Technology, 40 (18), 5804-5810. https://doi.org/10.1021/es061081n

Yu, F., Ma, J., Wu, Y., (2012) Adsorption of toluene, ethylbenzene and xylene isomers on multi-walled carbon nanotubes oxidized by different concentration of NaOCl. Frontiers of Environmental Science & Engineering, 6 (3), 320-329. https://doi.org/10.1007/s11783-011-0340-4

Yu, F., Ma, J., Han, S., (2014) Adsorption of tetracycline from aqueous solutions onto multi-walled carbon nanotubes with different oxygen contents. Scientific Reports. 1-8. https://doi.org/10.1038/srep05326

Zhang, S., Shao, T., Kose, H.S., Karanfil, T., (2010) Adsorption of aromatic compounds by carbonaceous adsorbents: a comparative study on granular activated carbon, activated carbon fiber, and carbon nanotubes. Environmental Science & Technology, 44(16): 6377-6383. https://doi.org/10.1021/es100874y

Zhu, Y., Murali, S., Cai, W. Li, X., J. Suk, W., Potts, J. R. Ruoff, R. S. (2010) Graphene and graphene oxide: synthesis, properties, and applications. Advance Materials, 22, 3906. doi: 10.1002/adma.201001068

Zuo, L., Li, H., Lin, L., Sun, Y., Diao, Z., Liu, S., Zhang, Z., Xu, Z. (2019) Sorption and desorption of phenanthrene on biodegradable poly (butylene adipate co-terephtalate) microplastics. Chemosphere, 15, 225-32. doi: 10.1016/j.chemosphere.2018.09.173