Evaluation of Powder Activated Carbon for the Removal of Amine-Containing Organic Micropollutants

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ABSTRACT

The accidental release of hydrophilic organic micropollutants (h-OMPs) into surface waters can pose a challenge to conventional drinking water treatment (CDWT) because of their generally poor removal by CDWT processes. Among h-OMPs, amine-containing compounds are of particular concern because their incomplete removal may contribute to the formation of disinfection by-products (DBPs). This study investigated the adsorption behavior of 23 amine-containing compounds using powdered activated carbon (PAC). The mean removal efficiencies varied substantially among the target compounds, ranging from 0 to 76.8%, indicating compound-specific adsorption behavior. The observed trends show that aromaticity, hydrophobic substituents, and molecular structure may play an important role in enhancing interactions with PAC, while hydrated and predominantly protonated amines exhibited limited adsorption under circumneutral conditions. The generated PAC adsorption data for a broad range of amine-containing h-OMPs may support the assessment of PAC treatment effectiveness during accidental release events involving such compounds.

Keywords: Hydrophilic organic micropollutants/ Amine-containing compounds/ Powdered activated carbon/ Accidental release/ Drinking water treatment

1. INTRODUCTION

Organic micropollutants (OMPs) are emerging contaminants that originate primarily from anthropogenic activities and are typically present in trace concentrations in drinking water sources [19]. Thailand and Japan have established the Thailand List of Hazardous Substances (TLHS) and the Pollutant Release and Transfer Register (PRTR) system, respectively, to regulate OMPs and other hazardous chemicals [7,17]. These frameworks are systematically used to compile inventories of their releases and transfers to the environment and generate quantitative data on emission loads and temporal trends of chemical discharge. However, such regulatory frameworks cannot eliminate the risk of sudden accidental releases. When a large quantity of OMPs is unexpectedly introduced into a surface water source, the resulting contaminant load may arrive over a short period and challenge the capacity of existing drinking water treatment systems [18].

Conventional drinking water treatment (CDWT) processes can effectively remove many hydrophobic OMPs, but the treatment of hydrophilic OMPs (h-OMPs) can be challenging, particularly under accidental release scenarios involving elevated contaminant concentrations [14]. For example, the accidental release of hexamethylenetetramine (HMT) in the Tone River Basin affected the water supply of approximately 360,000 households in the Tokyo Metropolitan Area [9]. The HMT incident illustrates that h-OMPs, particularly amine-containing compounds, are poorly removed during conventional treatment, and their high concentrations may temporarily exceed the treatment capacity, causing large-scale disruptions to drinking water supplies. Furthermore, the incomplete removal of amine-containing compounds has been linked to the enhanced formation of disinfection by-products (DBPs), particularly *N*-nitrosodimethylamine (NDMA) and formaldehyde at concentrations exceeding drinking water quality standards [5,9]. Therefore, the accidental release of amine-containing compounds into surface water remains a major concern for safe drinking water production.

The limited effectiveness of CDWT processes for amine-containing compounds partly reflects a gap in mechanistic understanding rather than a lack of available treatment approaches. Among available options, powdered activated carbon (PAC) has emerged as a more cost-effective and easily deployable option in accidental release scenarios than complex and rigid advanced treatment methods [10]. Despite the widespread use of PAC, knowledge of physicochemical interactions that control the behavior of amine-containing compounds during PAC adsorption remains limited [3,12]. This study therefore conducted a screening assessment of the removal of 23 amine-containing compounds under fixed PAC treatment conditions using a total organic carbon (TOC)-based analytical approach. The objective of this study was to compare the removal performance of these compounds and identify differences in their adsorption behavior under the tested conditions, providing a basis for evaluating PAC treatment during emergency response to accidental releases.

2. METHODOLOGY

2.1 Reagents and solutions

All target compounds were selected from the PRTR system of Japan and the TLHS of Thailand based on their water solubility ranging from 300 to 1,000,000 mg/L. The target reagents were purchased from Wako Pure Chemical Industries (Osaka, Japan) and the Tokyo Chemical Industry (Tokyo, Japan). All reagents were of reagent grade or higher, with purities of >95.0% where specified, except for dimethylamine and trimethylamine, which were supplied as aqueous solutions at concentrations of 51% (w/w) and 29.0–32% (w/w), respectively. The purity grades and manufacturers of the target reagents are listed in Table 1. All aqueous solutions were prepared using ultrapure water (18.2 MΩ·cm) produced from a Milli-Q Plus (Millipore, Billerica, MA, USA) (hereinafter referred to as MQW) and stored at 4 °C. Stock solutions were prepared one day before measurement and used within one week.

2.2 PAC adsorption

The PAC adsorption test was performed as single-solute adsorption tests using a jar tester to evaluate the removal efficiency of the target compounds. The experiments were conducted in a 1 L beaker at 20 °C. Stock solutions were prepared in MQW at concentrations of 1 or 0.1 g/L, and each compound was prepared at an initial concentration of 3 mg C/L. The pH of the samples was maintained at 7 using phosphate buffer (0.2 mM) and measured before and after treatment. A wood-based PAC (5LPD, Swing Corporation, Tokyo, Japan) was used for adsorption tests. Selected physicochemical properties of the PAC including textural properties are summarized in Table 2. The surface oxygen-containing functional groups of the PAC were characterized by Boehm titration in this study following the procedure reported by Pawlicka et al. [13].

Table 1. List of target amine-containing compounds

CAS number	Compounds	Grade/purity (%)	Manufacturers
62-53-3	aniline	GR (guaranteed reagent)	Wako Pure Chemical Industries
141-43-5	ethanolamine	GR	Wako Pure Chemical Industries
107-15-3	ethylenediamine	Wako Special Grade	Wako Pure Chemical Industries
95-51-2	2-chloroaniline	>98.0% (GC)	Tokyo Chemical Industry
108-42-9	3-chloroaniline	>99.0% (GC)	Tokyo Chemical Industry
106-47-8	4-chloroaniline	>99.0% (GC)	Tokyo Chemical Industry
108-91-8	cyclohexylamine	Wako Special Grade	Wako Pure Chemical Industries
124-40-3	dimethylamine	51% (w/w)	Wako Pure Chemical Industries
100-97-0	hexamethylenetetramine	GR	Wako Pure Chemical Industries
121-44-8	triethylamine	Wako Special Grade	Wako Pure Chemical Industries

Table 1. List of target amine-containing compounds (cont)

CAS number	Compounds	Grade/purity (%)	Manufacturers
106-49-0	*p*-toluidine	>99.0% (GC, T)	Tokyo Chemical Industry
95-53-4	*o*-toluidine	>99.0% (GC, T)	Tokyo Chemical Industry
108-44-1	*m*-toluidine	Wako Special Grade	Wako Pure Chemical Industries
88-74-4	2-nitroaniline	>99.0% (GC)	Tokyo Chemical Industry
110-85-0	piperazine	>98.0% (GC, T)	Tokyo Chemical Industry
95-54-5	*o*-phenylenediamine	>98.0% (GC, T)	Tokyo Chemical Industry
106-50-3	*p*-phenylenediamine	>98.0% (GC, T)	Tokyo Chemical Industry
108-45-2	*m*-phenylenediamine	>98.0% (GC, T)	Tokyo Chemical Industry
124-09-4	hexamethylenediamine	Wako First Grade	Wako Pure Chemical Industries
101-77-9	4,4′-methylenedianiline	>98.0% (T)	Tokyo Chemical Industry
111-42-2	diethanolamine	GR	Wako Pure Chemical Industries
122-20-3	triisopropanolamine	Wako First Grade	Wako Pure Chemical Industries
75-50-3	trimethylamine	29.0–32% (w/w)	Wako Pure Chemical Industries

Before the adsorption test, the PAC was dried at 110 °C for 3 h to remove moisture. Typical PAC doses are insufficient to treat accidental releases of h-OMPs [10]. Therefore, a PAC dose of 30 mg/L was selected as a realistic yet sufficiently high level for emergency application in CDWT plants [2]. The experiments were conducted under typical operating conditions of Japanese CDWT plants using slow mixing at 50 rpm and a contact time of 1 h [6,15]. Initial samples (C_0) were collected before PAC addition without filtration. After 1 h of contact, the supernatant was collected and filtered through a 0.2 µm hydrophilic PTFE membrane filter (ADVANTEC, Tokyo, Japan) to obtain the final concentration (C_e). A 0.2 µm filter blank was conducted to confirm negligible carbon release from the filter. C_0 and C_e were then measured using a TOC-V_{CPH} analyzer (Shimadzu Corporation, Kyoto, Japan) operated in non-purgeable organic carbon (NPOC) mode using the combustion catalytic oxidation method at 680 °C. The TOC analyzer was calibrated using potassium hydrogen phthalate (KHP) standards at 0.1, 0.3, 1, 3, and 5 mg C/L. The calibration curves showed $R^2 \geq 0.99$. MQW blanks were measured between batches to monitor background carbon and potential carryover.

Table 2. 5LPD PAC properties

PAC property	value	source
Product name	5LPD	Swing Corporation (Tokyo, Japan)
Material	wood-based	
Textural properties		
BET specific surface area (m^2/g)	1163	Tada et al. [16]
Particle size (µm)	15	
Micropore volume (cm^3/g)	0.47	
Mesopore volume (cm^3/g)	0.08	
Macropore volume (cm^3/g)	0.02	
Surface functional groups		This study
Carboxylic (–COOH) (mmol/g)	0	
Lactonic (–COO–) (mmol/g)	0.13	
Phenolic (–OH) (mmol/g)	0.1	
Total acidic functional groups (mmol/g)	0.23	

Each adsorption experiment was conducted in duplicate using independent experimental runs (n = 2), and the removal efficiencies reported represent the mean of the two replicate measurements. Duplicate experiments were selected for this screening study to enable consistent evaluation across the full compound set while providing an initial assessment of reproducibility. The removal efficiency was calculated using Eq. (2.1), where C_0 and C_e are the initial and final concentrations (mg C/L) measured before PAC addition and after 1 h of contact, respectively.

$$\text{Removal efficiency } (\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2.1)$$

3. RESULTS AND DISCUSSION

3.1 Adsorption trends for aromatic amines

As shown in Figure 1, 12 amine-containing compounds were classified as aromatic amines. Among this group, 4,4′-methylenedianiline (4,4′-MDA) showed the highest removal efficiency (76.8 ± 11.2%) (Figure 2). The high removal efficiency observed for 4,4′-MDA is likely attributable primarily to its molecular structure, as it contains two aromatic rings. The presence of multiple aromatic rings provides a larger π-electron-rich surface that can interact with the aromatic and graphitic regions of PAC through π–π dispersive interactions, thereby enhancing its adsorption onto the PAC surface [8]. Previous studies have also reported that π–π dispersive interactions increase as the number of aromatic rings increases because of improved planarity and π–π stacking interactions between aromatic compounds and PAC basal planes [8]. Hydrophobic interactions are also important, as 4,4′-MDA possesses nonpolar substituents, such as a methylene (–CH_2–) bridge, which promote hydrophobic interaction and solvent-motivated adsorption [8]. These observations suggest that hydrophobic substituents contribute to the adsorption of amine-containing aromatic compounds. However, the adsorption behavior for substituted anilines followed the order CH_3 > NO_2 > Cl > NH_2, with NO_2-substituted aniline showing higher removal than chloro-substituted analogs, which are considered more hydrophobic [11].

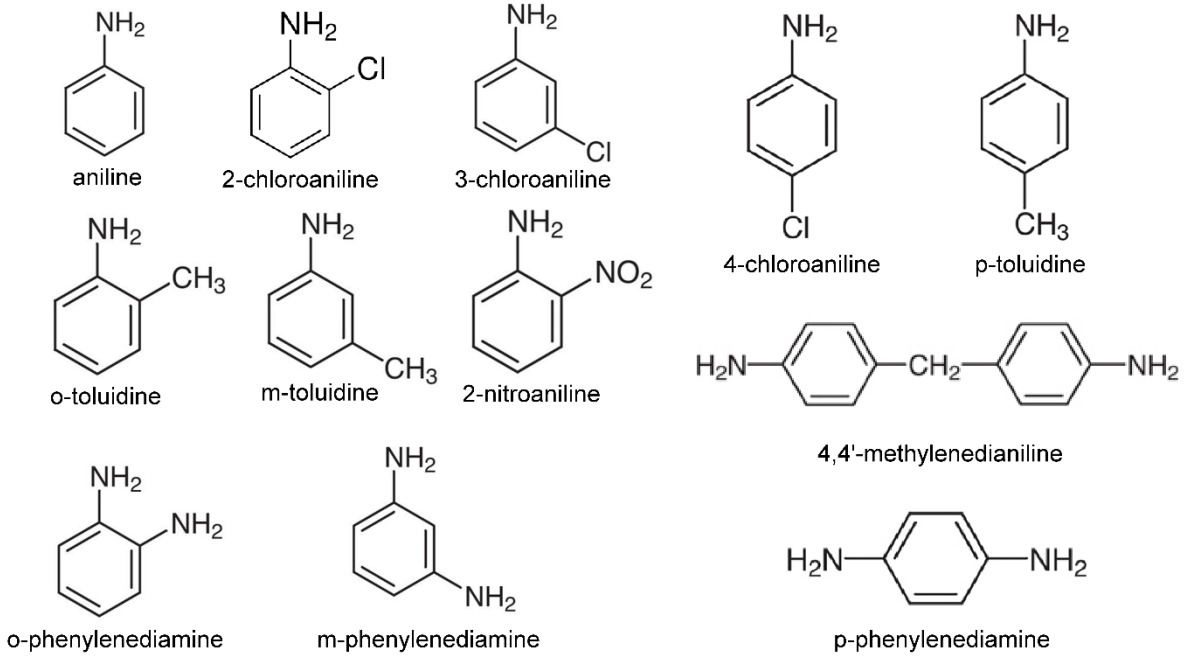

Figure 1. Chemical structure of the selected aromatic amines.

This trend is consistent with the stronger electron withdrawing nature of the $–NO_2$ group compared with the –Cl group. Using the Hammett constant (σ_p) as a general indicator of electron-withdrawing strength, 2-nitroaniline (σ_p = 0.78) exhibited slightly higher removal (21.2 ± 2.5%) than 2-chloroaniline (19.2 ± 2.7%), which has a lower Hammett constant (σ_p = 0.23) [4]. In addition, $–NO_2$ substitution substantially reduces the basicity of aniline, giving 2-nitroaniline a much lower conjugate acid (pKa < 1) than 2-chloroaniline (pKa ≈ 2.7). At pH 7, however, both compounds exist almost entirely in the neutral form [11], so protonation is unlikely to explain the difference in removal. Instead, the stronger electron-withdrawing nature of $–NO_2$ may enhance electron donor–acceptor (EDA) interactions with the PAC surface. In general, all monosubstituted anilines exhibited lower removal efficiencies than aniline, and the $–CH_3$ and –Cl substituents did not enhance removal compared with aniline. This suggests that the $–NH_2$ group largely governs the adsorption of aromatic amines at neutral pH. Moreover, it has been reported that oxygen-containing surface groups reduce the electron density of the PAC basal planes and weaken dispersive interactions with aromatic amines [1].

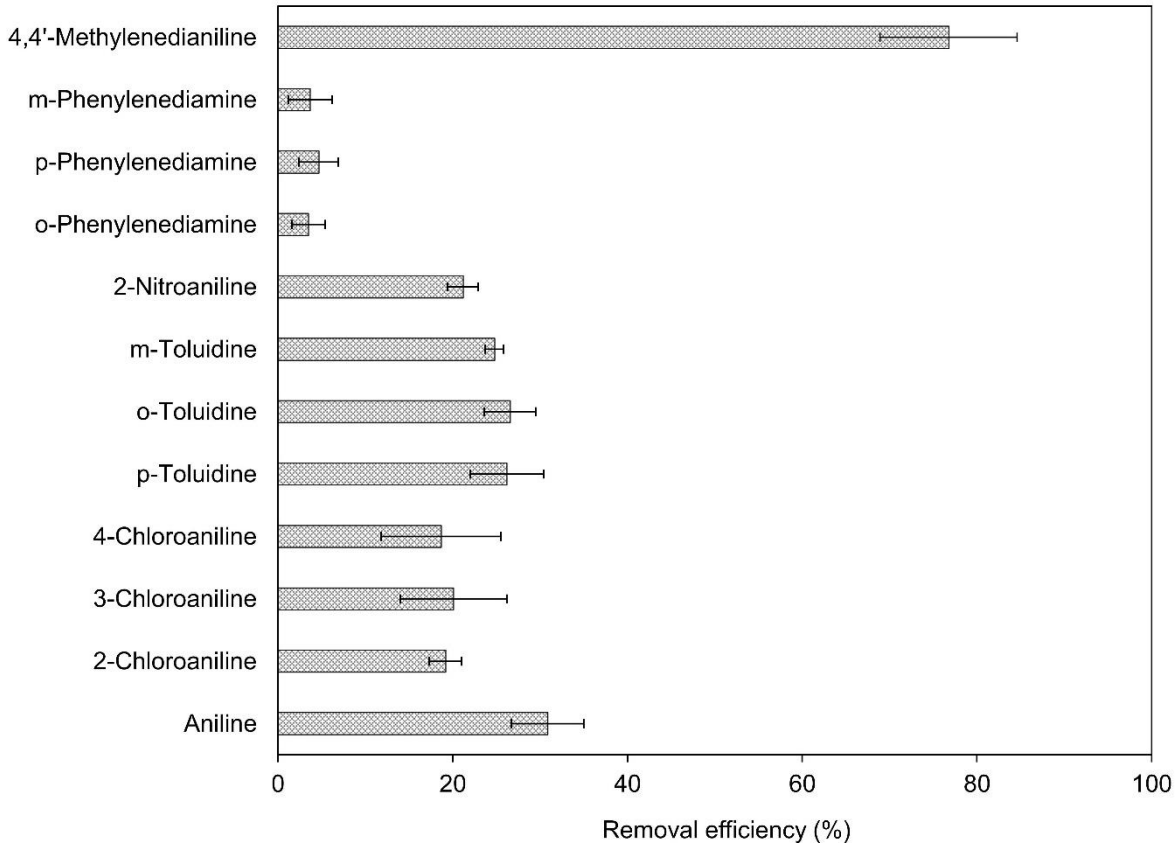

Figure 2. Removal efficiency for aromatic amines

3.2 Adsorption trends for aliphatic amines

Generally, amine-containing compounds classified as aliphatic amines (Figure 3) showed extremely low removal, with a mean of 2.8% (Table 3). The highest removal was observed for piperazine (11.4 ± 5.5%) followed by triisopropanolamine (8.4 ± 7.3%). Despite lacking aromaticity, piperazine showed higher removal than phenylenediamine isomers. Piperazine is predominantly protonated at pH 7, and the near-neutral surface charge of 5LPD PAC likely minimizes electrostatic repulsion, allowing its non-planar aliphatic ring with two secondary amine groups to engage in hydrogen-bonding and acid-base interactions between its nitrogen atoms and the oxygenated functional groups on 5LPD PAC (Table 2).

In contrast, the phenylenediamine isomers contain two primary amine groups that form extensive hydrogen bonds with water, resulting in greater hydration and stronger solvation, which likely gives piperazine a modest adsorption advantage. Nevertheless, this trend was not consistent, as the substantially lower removal of cyclohexylamine (1.8 ± 1.6%) compared to aniline (30 ± 5.9%) highlights the generally poor removal of aliphatic amines and the importance of aromaticity in PAC adsorption.

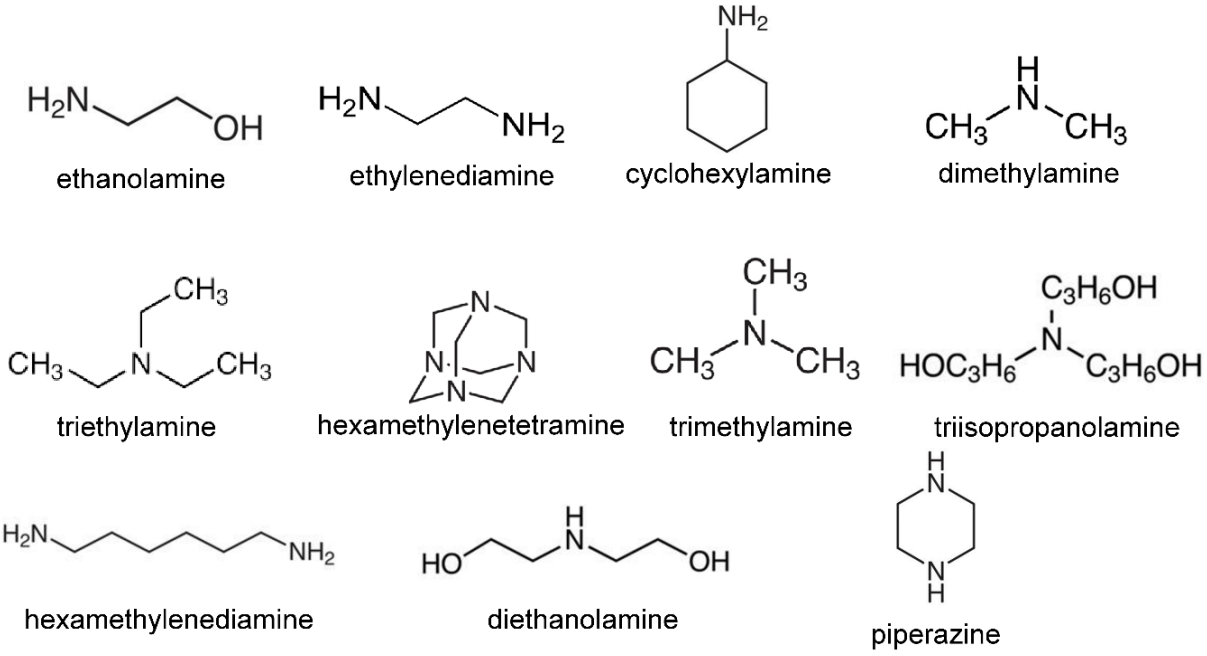

Figure 3. Chemical structure of the selected aliphatic amines.

Although both compounds contain a primary amine group, aniline possesses an aromatic π-electron system that enables π–π dispersive interaction and EDA complex formation with the basal plane of PAC, whereas the fully saturated ring of cyclohexylamine lacks π-electron density and therefore has less potential for such interactions. Furthermore, the absence of a strong adsorption driving mechanism under the experimental conditions limit the adsorption of aliphatic amines. Most aliphatic amines are ionized at pH 7 and therefore rely primarily on electrostatic attraction for adsorption. For example, Beita-Sandí et al. [2] reported that negatively charged (acidic) PACs were more effective in removing positively charged NDMA precursors. However, the near-neutral surface charge of 5LPD PAC limits electrostatic attraction, resulting in poor removal. In the absence of a dominant adsorption mechanism, these compounds experience strong competition with water molecules for adsorption sites [8]. The slightly higher removal of some compounds appears to rely mainly on increased hydrophobic character rather than nitrogen functionality. For example, triisopropanolamine showed 8.4 ± 7.3% removal, attributed to its bulky alkyl structure, which enhances dispersive interactions and partially mitigates hydration effects. Overall, under circumneutral conditions, nitrogen functionality alone is insufficient to promote adsorption on PAC, and solvation effects, lack of electrostatic attraction, and weak surface interactions primarily constrain adsorption of aliphatic amines.

Table 3. Removal efficiency for aliphatic amines

CAS number	Compound	Removal efficiency (%)
141-43-5	ethanolamine	3.0 ± 1.7
107-15-3	ethylenediamine	6.4 ± 7.6
108-91-8	cyclohexylamine	1.8 ± 1.6
124-40-3	dimethylamine	0
100-97-0	hexamethylenetetramine	0
121-44-8	triethylamine	0
110-85-0	piperazine	11.4 ± 5.5
124-09-4	hexamethylenediamine	0
111-42-2	diethanolamine	0
122-20-3	triisopropanolamine	8.4 ± 7.3
75-50-3	trimethylamine	0

4. CONCLUSIONS

Based on laboratory experiments and data analysis in this study, the following conclusions were drawn:

1. This study evaluated the removal efficiencies of 23 amine-containing compounds by PAC adsorption with observed mean removals ranging from 0 to 76.8%.

2. The removal efficiencies varied substantially among the 23 compounds under the tested PAC treatment conditions, indicating distinct compound-specific removal behavior. These results suggest that the removal performance of amine-containing compounds cannot be assumed to be uniform during accidental release situations. Therefore, screening the removal characteristics of individual compounds under relevant PAC treatment conditions may provide useful information for emergency response in CDWT systems.

3. In general, compounds with greater aromaticity and hydrophobic substituents were associated with higher removal efficiencies, which may be related to enhanced π–π dispersive interaction and hydrophobic interactions with the PAC surface. Conversely, aliphatic compounds predominantly containing NH_2-based functional groups generally exhibited poor removal.

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References

[1] Ahnert, F., Arafat, H. A., & Pinto, N. G. (2003). A study of the influence of hydrophobicity of activated carbon on the adsorption equilibrium of aromatics in non-aqueous media. *Adsorption*, 9(4), 311–319.

[2] Beita-Sandí, W., Ersan, M. S., Uzun, H., & Karanfil, T. (2016). Removal of *N*-nitrosodimethylamine precursors with powdered activated carbon adsorption. *Water Research*, 88, 711–718.

[3] Ebrahimzadeh, S., Wols, B., Azzellino, A., Kramer, F., & van der Hoek, J. P. (2022). Removal of organic micropollutants in a drinking water treatment plant by powdered activated carbon followed by rapid sand filtration. *Journal of Water Process Engineering*, 47, 102792.

[4] Hansch, C., Leo, A., & Taft, R. W. (1991). A survey of Hammett substituent constants and resonance and field parameters. *Chemical Reviews*, 91(2), 165–195.

[5] Hinneh, K. D., El Hanafi, A., He, K., Kosaka, K., Echigo, S., Asada, Y., & Itoh, S. (2019). Formation of *N*-nitrosodimethylamine by chloramination of anthropogenic nitrogenous compounds with dimethylamine monitored by Japanese water authorities. *Journal of hazardous materials*, *367*, 620-628.

[6] Japan Water Works Association (2020). *Standard Method for the Examination of Water* [in Japanese]; Japan Water Works Association (2012). *Water Supply Facility Design Guideline* [in Japanese]. Japan Water Works Association, Tokyo.

[7] Kan-atireklap, S., Subramanian, A., & Tanabe, S. (2007). Persistent toxic substances in Thailand. *Developments in Environmental Science*, 7, 487–514.

[8] Knappe, D. R. U. (2006). Surface chemistry effects in activated carbon adsorption of industrial pollutants. In *Interface Science and Technology* (Vol. 10, pp. 155–177). Elsevier.

[9] Kosaka, K., Asami, M., Nakai, T., Ohkubo, K., Echigo, S., & Akiba, M. (2014). Formaldehyde formation from tertiary amine derivatives during chlorination. *Science of the Total Environment*, 488, 325–332.

[10] Lompe, K. M., Solliec, M., Rivas, M., Peldszus, S., & Barbeau, B. (2022). Selecting a single powdered activated carbon against multiple threats: taste & odour and benzene. *Environmental Science: Water Research & Technology*, 8(12), 3091–3100.

[11] Mattson, J. A., Mark, H. B., Jr., Malbin, M. D., Weber, W. J., Jr., & Crittenden, J. C. (1969). Surface chemistry of active carbon: specific adsorption of phenols. *Journal of Colloid and Interface Science*, 31(1), 116–130.

[12] Najm, I. N., Snoeyink, V. L., Lykins, B. W., Jr., & Adams, J. Q. (1991). Using powdered activated carbon: a critical review. *Journal AWWA*, 83(1), 65–76.

[13] Pawlicka, A., & Doczekalska, B. (2013). Determination of surface oxygen functional groups of active carbons according to the Boehm's titration method. *Annals of Warsaw University of Life Sciences – SGGW, Forestry and Wood Technology*, 84.

[14] Stackelberg, P. E., Gibs, J., Furlong, E. T., Meyer, M. T., Zaugg, S. D., & Lippincott, R. L. (2007). Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds. *Science of the Total Environment*, 377(2–3), 255–272.

[15] Suzuki, Y., Takahashi, K., Kondo, R., Tamai, S., Annaka, Y., Chuganji, N., & Tanaka, H. (2025). Ballasted flocculation with powdered activated carbon adsorption for the simultaneous removal of odorous substances and suspended solids. *Journal of Water Process Engineering*, 77, 108380.

[16] Tada, Y., Tsujisaka, Y., Hinneh, K. D., Asada, Y., Kosaka, K., Echigo, S., & Itoh, S. (2025). Treatability of high-molecular-weight and ultra-hydrophilic haloacetic acid precursors from freshwater raphidophytes in water treatment. *Total Environment Engineering*, 2, 100012.

[17] Wexler, P., & Harjula, H. (2005). Pollutant release and transfer registers (PRTRs).

[18] Whelton, A., McMillan, L., Novy, C.-R., White, K., & Huang, X. (2017). Case study: the crude MCHM chemical spill investigation and recovery in West Virginia USA. *Environmental Science: Water Research & Technology*, 3(2), 312–332.

[19] Wołowicz, A., & Munir, H. M. S. (2025). Emerging organic micropollutants as serious environmental problem: A comprehensive review. *Science of the Total Environment*, 958, 177948.