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Evaluating Powdered Activated Carbon for Adsorption of Nitrogenous Organics in Water Using HDPairFinder

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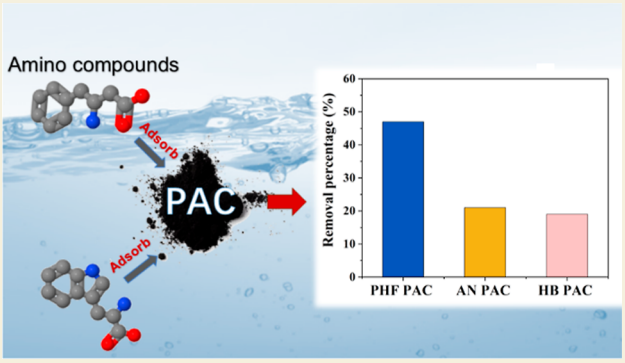
ABSTRACT: Amino-containing compounds are key precursors to highly toxic nitrogenous disinfection byproducts (DBPs) and odorous DBPs, posing a critical challenge for drinking water utilities. This study systematically evaluated the adsorption performance of six commercial powdered activated carbons (PACs) for removing soluble amino-containing compounds using amino acids as model compounds. Among them, PHF and AN PAC demonstrated superior removal efficiencies for six tested amino acids, ranging from 77 to 98% for PHF PAC and 83 to 96% for AN PAC. Subsequent analysis focused on PHF, AN, and HB PACs to investigate adsorption kinetics and effects of water parameters, including initial amino acid concentration, pH, and natural organic matter (NOM) on removal efficiencies. Optimal removal efficiencies were observed for PHF and AN PACs at pH levels between 6 and 8, while increased NOM levels significantly reduced amino acid adsorption. Finally, a hydrogen/deuterium isotopic labeling-based nontargeted analysis was applied to evaluate the removal of amino-containing compounds from source water (represented by Suwannee River standard reference materials). PHF exhibited the highest removal efficiency, achieving a 47% reduction in the total ion chromatogram (TIC) intensity of labeled amino-containing features, followed by AN at 21% and HB at 19%. The decrease in the TIC intensity and number of labeled amino-containing features aligned with the trends observed in adsorption, establishes a consistent ranking of PHF > AN > HB PAC. PAC can be seamlessly integrated into existing drinking water treatment processes and applied on an as-needed basis. Our results could provide valuable guidance for its effective application in water treatment plants.



KEYWORDS: *drinking water, adsorption, powdered activated carbon, amino-containing compounds, HDPairFinder*

1. INTRODUCTION

Disinfection of drinking water reduces microbiological risk by inactivating pathogens but unintentionally increases chemical risks because of the formation of disinfection byproducts (DBPs), resulting from the reaction between disinfectants and organic matter in water.[1,2] Epidemiological and toxicological studies have reported associations between long-term DBP exposure and increased incidence of bladder cancer, preterm delivery, and spontaneous abortion.[3−6] According to the elemental composition, DBPs can be divided into carbon-containing DBPs (C-DBPs) and nitrogen-containing DBPs (N-DBPs). Compared with C-DBPs, N-DBPs [e.g., haloacetonitriles (HANs), nitrosamines (NAs), and haloacetamides (HAMs)] are of particular concern because of their high toxicity potential. HANs and HAMs have been reported to be 1−3 orders of magnitude more toxic than regulated C-DBPs such as halomethanes (THMs) and haloacetic acids based on Chinese hamster ovary cell bioassay data.[7,8] NAs are another significant class of N-DBPs that have been identified as potent carcinogens. For instance, *N*-nitrosodimethylamine (NDMA) poses a 10^{-6} cancer risk at just 0.7 ng/L, approximately 600 times greater than that of any regulated THMs.[9] Richardson et al. conducted a comprehensive study of drinking water toxicity, measuring the chronic cytotoxicity of extracted whole water on mammalian cells and analyzing over 70 regulated and unregulated DBPs. The results showed that N-DBPs, specifically dihaloacetonitriles, are important drivers of toxicity.[10] Concerns over toxic N-DBPs have resulted in extensive attention to their control.

An effective strategy for controlling DBP formation is to remove their precursors before disinfection.[11,12] It is commonly acknowledged that the dissolved amino-containing compounds in water, particularly amino acids, serve as primary precursors of N-DBPs.[13] The formation of N-DBPs (e.g., HANs, HAMs, and NAs) from amino acids during chlorination

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and chloramination has been extensively studied.[14−16] Chlorine can rapidly chlorinate the α-amine group, leading to the formation of HANs and HAMs through decarboxylation, chloride elimination, and imine hydrolysis.[17] A particular concern is the potency of small amino-containing compounds, such as amino acids, to serve as precursors of odorous N-DBPs during water disinfection, especially in regions where meltwater from ice and snow is used as a water source for extended periods.[18−20] Odorous N-DBPs pose a significant challenge for drinking water utilities in managing consumer complaints and require rapid responses. Conventional drinking water treatment processes (coagulation, sedimentation, and filtration) are poorly equipped to remove small amino-containing compounds, such as amino acids, because of their small size, polarity, and high solubility. Additionally, the biologically activated carbon filtration process may contribute to the release of amino acids.[16,21] Drinking water utilities are looking for a treatment process that can remove small amino-containing compounds efficiently and quickly.

Powdered activated carbon (PAC) has proven to be a versatile and widely used adsorbent in water treatment, demonstrating high effectiveness in removing a broad spectrum of organic contaminants (e.g., phenol) and heavy metals.[22,23] The high surface area, well-developed porosity, and strong adsorption capacity of PAC make it a promising candidate for the removal of amino-containing compounds from water. The use of PAC also minimizes the introduction of byproducts, thereby preventing secondary pollution.[24] Capital costs associated with PAC are relatively low, as it can be integrated into existing treatment processes and applied on an as-needed basis. Understanding the factors and mechanisms governing PAC removal of highly soluble, small amino-containing compounds is crucial for improving water treatment processes. However, available information on this topic remains limited. Additionally, previous studies on the adsorption of PAC have primarily focused on single model compounds, e.g., sulfamethazine.[25] The source water contains a high concentration of amino-containing compounds with diverse structures. In addition to investigating the adsorption kinetics and influencing factors of PAC using model compounds (i.e., amino acids), it is crucial to develop a comprehensive understanding of the overall adsorption efficiency of PAC for all amino-containing compounds present in water.

This study aims to (1) investigate the removal efficiency, adsorption kinetics, and mechanisms of different commercial PACs for removing highly soluble small amino-containing compounds, using amino acids as representative model compounds; (2) examine the effects of water parameters such as initial amino acid concentration, solution pH, and the presence of natural organic matter (NOM) on the removal of amino acids by PACs; and (3) evaluate the overall efficiency of PACs in removing amino-containing compounds from source water (represented by Suwannee River standard reference materials, SRSRMs) using HDPairFinder, a data processing platform based on hydrogen/deuterium (H/D) isotopic labeling for nontargeted analysis.

2. MATERIALS AND METHODS

2.1. Chemicals and Samples

Formic acid (FA, 98%), ammonium formate, and polyvinylidene difluoride (PVDF) syringe filters (0.22 μm) were purchased from MilliporeSigma (Oakville, Ontario, Canada). Optima grade water, Optima grade acetonitrile (ACN), Optima grade methanol (MeOH), aqueous ammonium hydroxide (30 wt %), HCl ACS grade, NaOH ACS grade, and six amino acid standards (phenylalanine, leucine, tryptophan, isoleucine, tyrosine, and threonine) were purchased from Fisher Scientific (Nepean, Ontario, Canada). The MAX cartridges (6 mL, 150 mg) were purchased from Waters (Mississauga, Ontario, Canada). Commercial PACs, including WPC, WPH, WPX, and Pulsorb HF 2To-A (PHF), were obtained from Calgon Carbon (Pittsburgh, PA). Aqua Nuchar-wood-based (AN) was purchased from Ingevity (North Charleston, SC), and hydrodarco B (HB) was obtained from Norit (Amersfoort, The Netherlands).

2.2. Batch Adsorption Experiment

The batch adsorption experiments included five scenarios, removal efficiency tests for six PACs, adsorption kinetics, and the effects of the initial amino acid concentration, pH, and presence of NOM on amino acid removal. For each scenario, 1 L of water containing the amino acid was prepared, and then PAC was added and mixed using a six-seat agitator operated at 180 rpm. After a specified contact time, a 100-mL sample was withdrawn and concentrated using solid phase extraction (SPE). The concentrated samples were analyzed by hydrophilic interaction chromatography and tandem mass spectrometry (HILIC−MS/MS) to determine the remaining amino acids. To balance cost-efficiency with the effective removal of amino-containing compounds, a PAC concentration of 30 mg/L was selected for all experiments in this study. To simulate the adsorption efficiency under conditions of amino acid coexistence, a standard mixture of six amino acids, each at a concentration of 0.5 g/L, was prepared in water. The stock solution was stored at 4 °C and used within one week. The amino acid working solution was freshly prepared by diluting the stock solution to the specified concentration with 1 L of water before each batch experiment. Except for experiments investigating the effects of the initial amino acid concentration on the adsorption performance, the initial concentration was set at 200 μg/L for each amino acid. SPE was used to obtain PAC-free samples, thereby preventing potential chromatography column clogging and ensuring better peak shape for accurate quantification of amino acids. MAX SPE cartridges were used for amino acid quantification; a detailed procedure can be found in the previous study.[20]

The removal efficiency of six amino acids by six commercial PACs was studied first. The pH of the working solution was adjusted to 7.0 ± 0.2 by NaOH and HCl. The initial concentrations of each amino acid were 200 μg/L. One control group (without the addition of PAC) was also included. The contact time was 30 min.

For adsorption kinetics experiments, the initial amino acid concentration was set at 200 μg/L, and the remaining concentrations were measured after different contact times, specifically 3, 6, 12, 18, 30, and 60 min. Pseudo-first-order (PFO) and pseudo-second-order (PSO) models were used to analyze the data. PFO is the modified model of the first-order model under a nonideal state, and its equation is as follows

$$Q_t = Q_e(1 - e^{-k_1 t}) \quad (1)$$

where Q_e (μg/mg) is the adsorption capacity of amino acids adsorbed on PACs at equilibrium time (min), Q_t (μg/mg) is the mass of amino acids adsorbed on PACs at t min, and k_1 is the adsorption rate constant (min^{-1}). Q_t can be calculated based on eq 2

$$Q_t = \frac{(C_0 - C_t) \times V}{m} \quad (2)$$

where C_0 (μg/L) refers to the initial concentration of amino acids and C_t (μg/L) refers to the concentration of amino acid at a specific time t (min). V (L) is the solution volume and m (mg) is the PAC mass.

PSO is a modified model of the second-order model under a nonideal state, and its eq 3 is as follows

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (3)$$

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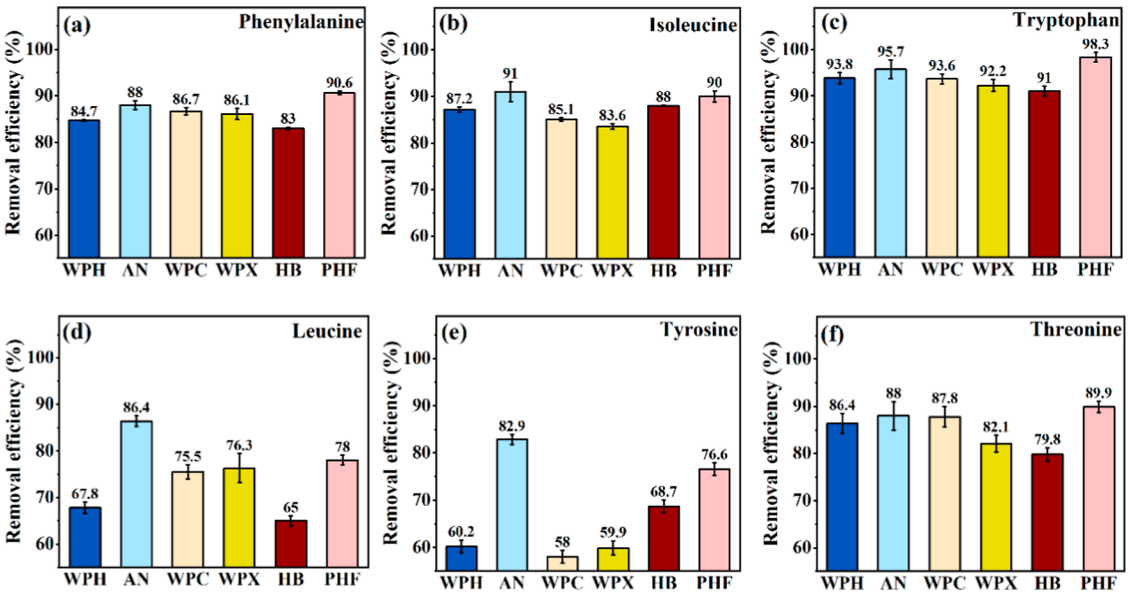

Figure 1. Removal efficiency of six different commercial PACs (WPH, AN, WPC, WPX, HB, and PHF) for phenylalanine (a), isoleucine (b), tryptophan (c), leucine (d), tyrosine (e), and threonine (f). Experimental conditions: initial amino acid concentration = 200 μg/L, pH = 7.0 ± 0.2, PAC = 30 mg/L, contact time = 30 min.

where Q_e (μg/mg), Q_t (μg/mg), and t (min) represent the same as PFO and k_2 is the PSO rate constant (mg·μg^{-1}·min^{-1}). By performing a linear fit of t/Q_t as the dependent variable and t as the independent variable, we can calculate Q_e and k_2.

Subsequently, the effects of the initial amino acid concentration on removal efficiency were investigated. Solutions with amino acid concentrations of 100, 200, 300, 400, 500, and 600 μg/L were prepared; the contact time of PAC and the amino acids was 30 min.

The impacts of pH on the removal efficiency of amino acids were also evaluated. The initial amino acid concentration was 200 μg/L, and the pH of the solutions was adjusted using NaOH and HCl to values ranging from 2 to 12 (2, 4, 6, 8, 10, and 12). The contact time of PAC and the amino acids was 30 min.

The removal efficiency of PAC for amino acids in the presence of NOM was evaluated. NOM solutions were prepared by dissolving SRSRMs at concentrations ranging from 1 to 10 mg/L (1, 2, 5, and 10 mg/L as C). The initial amino acid concentration was 200 μg/L, and the contact time of the PAC and amino acids was 30 min.

2.3. Removal of Amino-Containing Compounds by PAC Using Hydrogen/Deuterium Isotopic Labeling-Based Nontargeted Analysis

For the assessment of the removal of amino-containing compounds from source water by PAC, water samples prepared by dissolving SRSRMs were investigated using nontargeted analysis, incorporating a stable H/D isotopic labeling reaction, high-performance liquid chromatography–high-resolution MS (HPLC–HRMS) detection, and HDPairFinder analysis.[26] Two labeling reagents, formaldehyde (CH_2O) and deuterated formaldehyde (CD_2O), were used to react with the amino groups in amino-containing compounds, resulting in the formation of two isotopically methylated products.[26] After concentration using SPE, the samples were detected by HPLC–HRMS, and the generated HRMS data sets were processed using HDPairFinder.[27] HDPairFinder is a powerful bioinformatics tool designed to automatically extract H/D-labeled amino-containing compounds from raw HPLC–HRMS data, primarily based on the mass difference between H- and D-labeled features. It operates through four key modules: (a) extraction of H/D-labeled chemical features, (b) alignment, (c) evidence-based missing value imputation, and (d) putative compound annotation. The software is freely accessible on GitHub (https://github.com/HuanLab/HDPairFinder).[27] Details of the H/D isotropic labeling reaction and sample preparation are provided in Text S2.

The labeling experiments consisted of three groups: (1) a solution containing only SRSRMs was prepared to determine the amino-containing compounds before PAC treatment; (2) solutions containing only different PACs were prepared individually, used to determine the amino-containing compounds introduced by PAC; and (3) solutions containing both PAC and SRSRMs were prepared and mixed for 30 min to determine the amino-containing compounds after PAC treatment. SRSRM solutions were prepared by dissolving SRSRMs (2 mg/L as C) in 1 L of Optima water. The mixing of SRSRMs and PAC was conducted following the same protocol of amino acid adsorption experiments (180 rpm for mixing and contact time of 30 min). Solutions were filtered using 0.22 μm PVDF syringe filters. Then, filtered solutions were labeled, extracted, and analyzed using HPLC–HRMS.[27] Three replicates were included for the nontargeted analysis.

2.4. Analytical Methods

Amino acids were determined using the HILIC–MS/MS method previously reported.[20] Briefly, an Agilent 1290 series HPLC system (Agilent, Santa Clara, CA) coupled with a triple quadrupole mass spectrometer (Sciex 5500; Sciex, Framingham, MA) was used for the HILIC separation and MS/MS targeted analysis of amino acids. The column used was an InfinityLab Poroshell 120 HILIC-Z column (2.7 μm × 100 mm × 2.1 mm ID) (Agilent). The specific parameters for the HILIC separation, including mobile phase, gradient program, autosampler conditions, and column temperature, are described in Table S1. The optimized MS ionization parameters are also provided in Table S1, along with the optimized MRM transitions and corresponding parameters. Table S2 presents the limit of detection, limit of quantification, and relative standard deviation (RSD) of signals and retention times of the SPE–HILIC–MS/MS method used to analyze six amino acids (n = 3). The surface functional groups were characterized by using Fourier transform infrared spectroscopy (FTIR, Thermo Nicolet 8700; Thermo Fisher Scientific, Carlsbad, CA). Specific surface area and pore volume were measured at a nitrogen temperature of 77 K by surface area analyzer (Autosorb 6100 FKM XR XR). The specific surface area was analyzed by the BET method, and the pore volume was analyzed by the DFT method.

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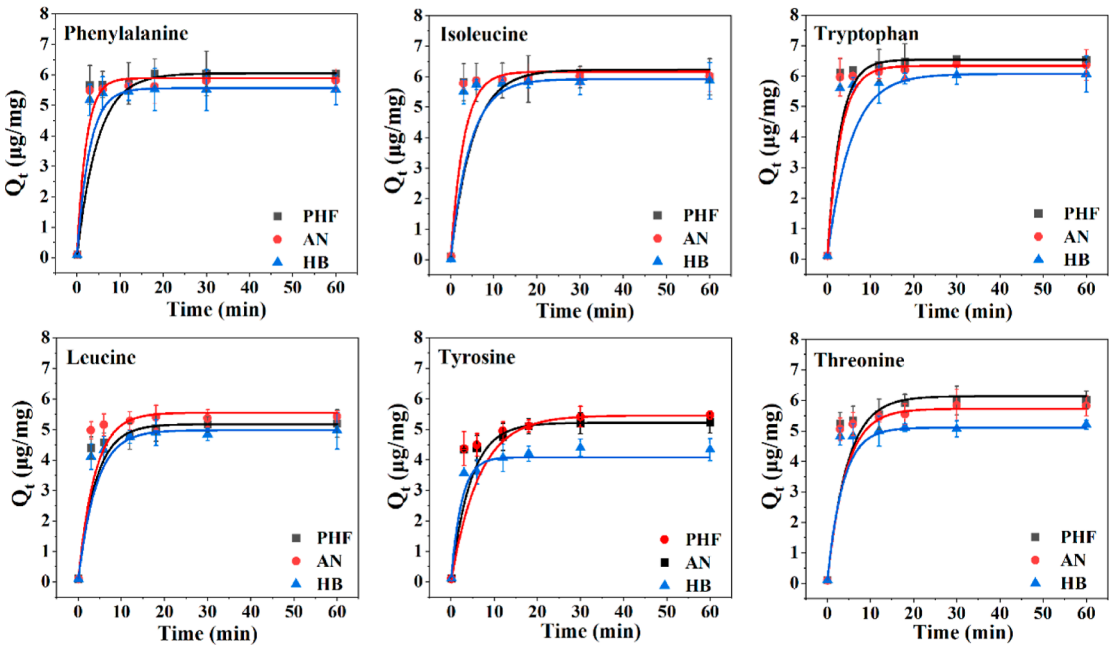

Figure 2. Pseudo-first-order (PFO) model fitting of six amino acids on PHF, AN, and HB PACs. Experimental conditions: initial amino acid concentration = 200 μg/L, pH = 7.0 ± 0.2, PAC = 30 mg/L, contact time = 3, 6, 12, 18, 30, and 60 min.

3. RESULTS AND DISCUSSION

3.1. Removal Efficiency of Amino Acids by Different Kinds of PACs

Amino acids are typical small, soluble amino-containing compounds found in source water. Among the 20 free amino acids present in source water, phenylalanine, isoleucine, tryptophan, leucine, tyrosine, and threonine were the most frequently detected at high concentrations.[20,28] For example, phenylalanine and threonine were detected in the source water of the drinking water treatment plants in this study at concentrations up to 5555.9 and 5059 ng/L, respectively. Accordingly, these six amino acids were selected as representative amino-containing compounds to evaluate the removal efficiency by six commercial PACs.[20] Given that amino acids represent a small fraction of amino-containing compounds, a high concentration of 200 μg/L was used. After 30 min of mixing each PAC with solutions containing the amino acids, the remaining amino acid concentrations were determined, and the removal efficiencies were calculated, as presented in Figure 1. The six PACs demonstrated varying removal efficiencies for the six amino acids, with removal efficiencies ranging from 58 to 98.3%.

Among the six amino acids tested, leucine and tyrosine demonstrated resistance to PAC treatment, with AN achieving the highest removal efficiencies of 86.4 and 82.5%, respectively. The other five PACs exhibited lower removal efficiencies for leucine and tyrosine, ranging from 58 to 78%. For the other four amino acids (phenylalanine, isoleucine, tryptophan, and threonine), the removal efficiencies across all six PACs were significantly higher, ranging from 80 to 98.3%. The properties of amino acids may significantly influence the adsorption efficiency of PAC. The hydropathy index quantifies the degree of hydrophilicity or hydrophobicity of the side chain of an amino acid, with lower values indicating greater hydrophilicity.[29,30] Tyrosine had the lowest hydropathy index value (−1.3, Table S2), indicating its high hydrophilicity. Consequently, tyrosine has the lowest propensity for adsorption because of its weak hydrophobic interactions with PACs. Isoleucine is slightly more hydrophobic than leucine (hydropathy index value 4.5 and 3.8 for isoleucine and leucine, respectively), resulting in better removal efficiency of isoleucine than leucine.

Among the six PACs, PHF demonstrated high removal efficiency for phenylalanine, tryptophan, and threonine, with removal efficiency ranging from 90.6 to 98.3%. AN showed high removal efficiency for leucine, isoleucine, and tyrosine, with removal efficiency ranging from 82.9 to 91%. The other four PACs (i.e., WPH, WPC, WPX, and HB) showed inconsistent removal efficiencies for the six amino acids. For instance, WPH achieved a removal efficiency of over 90% for tryptophan (93.8%) but demonstrated significantly lower removal efficiency for tyrosine, with only 60.2% removal. WPH, WPC, and WPX demonstrated weak removal efficiency for leucine and tyrosine, ranging from 58 to 76.3%. Low removal efficiency of nitrogenous organics by WPH has also been reported, with 95% removal of NDMA precursors achieved at doses up to 500 mg/L and contact times of up to 7 days.[31] HB, currently used in drinking water treatment plants, exhibited the lowest removal efficiency for four of the six amino acids (phenylalanine, tryptophan, leucine, and threonine), ranging from 65 to 91%.

Generally, the surface area of the PAC is positively correlated to its amino acid adsorption performance. The specific surface area and pore volume of the six PACs are summarized in Table S3. AN showed superior and consistent amino acid removal efficiency, probably due to its highest specific surface area (1398 m^2/g). HB has the lowest specific surface area of 560 m^2/g and exhibits poor amino acid removal performance. In addition, the raw material of PACs may affect their functional groups and, consequently, their adsorption performance. Among them, PHF and AN, produced from coal and wood, exhibit superior adsorption performance for amino acids. The FTIR results of the six PACs and the assignment of the FTIR vibrations are shown in Figure S2. Compared with

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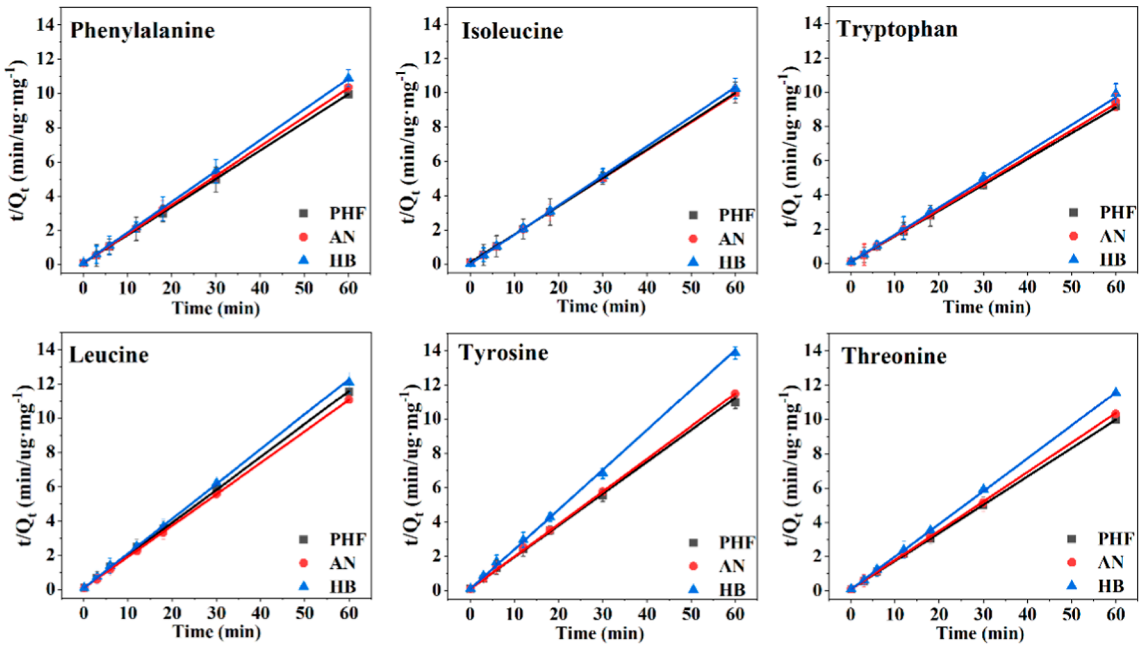

Figure 3. Pseudo-second-order (PSO) model fitting of six amino acids on PHF, AN, and HB PACs. Experimental conditions: initial amino acid concentration = 200 μg/L, pH = 7.0 ± 0.2, PAC = 30 mg/L, contact time = 3, 6, 12, 18, 30, and 60 min.

Table 1. Parameters of the Pseudo-First-Order (PFO) and Pseudo-Second-Order (PSO) Kinetic Models

		experimental Q_e (μg/mg)	PFO model			PSO model		
			k_1	Q_e (μg/mg)	R^2	k_2	Q_e (μg/mg)	R^2
phenylalanine	PHF	6.03	0.21	6.05	0.99	0.31	6.25	0.99
	AN	5.80	0.46	5.89	0.88	0.34	5.88	0.99
	HB	5.51	0.35	5.55	0.86	0.39	5.55	0.98
isoleucine	PHF	5.99	0.20	6.23	0.94	0.32	6.06	0.98
	AN	6.01	0.22	6.02	0.96	0.31	6.17	0.98
	HB	5.86	0.22	5.92	0.90	0.30	5.81	0.92
tryptophan	PHF	6.53	0.34	6.54	0.99	0.27	6.66	0.98
	AN	6.36	0.32	6.34	0.98	0.28	6.53	0.98
	HB	6.06	0.18	6.07	0.80	0.31	6.25	0.97
leucine	PHF	5.20	0.24	5.17	0.96	0.45	5.20	0.95
	AN	5.43	0.25	5.55	0.96	0.41	5.46	0.96
	HB	4.96	0.24	4.97	0.98	0.51	4.92	0.96
tyrosine	PHF	5.23	0.15	5.21	0.63	0.40	5.26	0.96
	AN	5.46	0.22	5.45	0.99	0.44	5.37	0.98
	HB	4.33	0.41	4.08	0.95	0.66	4.31	0.98
threonine	PHF	6.02	0.21	6.14	0.95	0.32	6.06	0.99
	AN	5.82	0.23	5.72	0.96	0.35	5.83	0.98
	HB	5.20	0.27	5.11	0.97	0.45	5.23	0.99

the other five PACs, AN contains fewer hydroxyl groups. The hydroxyl groups of PACs tend to interact with water molecules through hydrogen bonding, which can hinder amino acids from accessing micropores, resulting in low amino acid adsorption.[32−34] This can explain the superior adsorption performance of AN PAC for all six amino acids.

PHF and AN showed superior and consistent amino acid removal efficiencies; HB is the PAC currently used in drinking water treatment plants. Therefore, these three PACs were selected for in-depth analysis of adsorption kinetics and other factors that affect the removal efficiency of amino acids.

3.2. Adsorption Kinetics of Amino Acids on PACs

The adsorption of amino acids over time by PHF, AN, and HB PACs is illustrated in Figure S1. Figure S1 shows a rapid removal of amino acids within the first 3 min, after which the removal rate slows and gradually declines until equilibrium is reached. Initially, the adsorption process is rapid, with amino acids quickly occupying accessible sites on the PAC surface. Over time, the significantly reduced amino acid concentration weakens the interaction with PAC, resulting in slower diffusion to the PAC surface and extending the time required to reach equilibrium.[35] Overall, the adsorption of all six amino acids by PACs reached equilibrium within 30 min.

The PFO and PSO models were applied to identify the model that best describes the experimental data for amino acid adsorption on PACs. The PFO model is often used to evaluate systems in which physical adsorption dominates. It assumes monolayer adsorption on a homogeneous surface. The PSO

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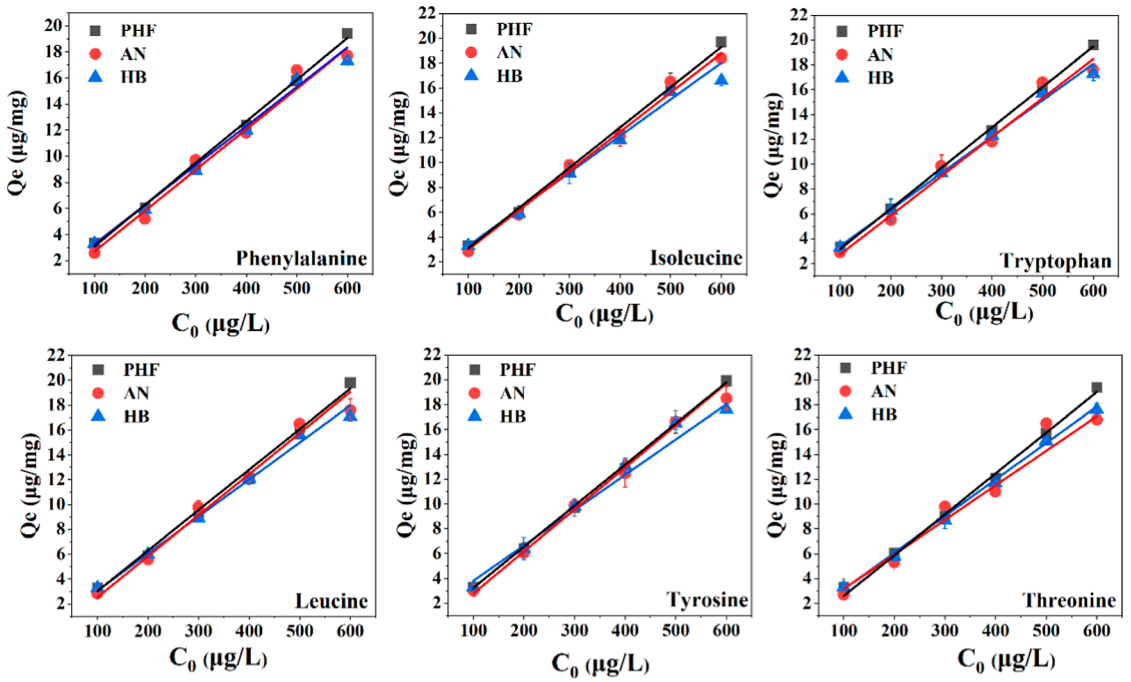

Figure 4. Q_e of phenylalanine, isoleucine, tryptophan, leucine, tyrosine, and threonine on PHF, AN, and HB PACs at varying initial amino acid concentration. Experimental conditions: initial amino acid concentration = 100, 200, 300, 400, 500, and 600 μg/L, pH = 7.0 ± 0.2, PAC = 30 mg/L, contact time = 30 min.

model is frequently associated with chemisorption mechanisms, in which electron sharing or covalent bonding between the adsorbate and adsorbent plays a significant role. It assumes that adsorption occurs on a heterogeneous surface, or involves multilayer adsorption, making it suitable for systems with a more complex adsorption process.[36] Figures 2 and 3 illustrate kinetic modeling of amino acid adsorption using the PFO and PSO models, respectively. The kinetic parameters k_1, k_2, and Q_e and correlation coefficients (R^2) for the PFO and PSO models of PHF, AN, and HB PACs are determined by fitting eqs 1 and 3 to the experimental data. The results of the kinetic modeling are summarized in Table 1. The R^2 values for the PSO model are consistently close to 1 for all three PACs compared to the R^2 values of the PFO model. Except for phenylalanine adsorbed on AN and HB, tryptophan adsorbed on HB, and tyrosine adsorbed on PHF, the R^2 values for both the PFO and PSO models were comparable, ranging from 0.90 to 0.99. Furthermore, the predicted Q_e values from the PFO and PSO models were compared with the experimental Q_e values to determine the most suitable adsorption model for amino acids (Table 1). For PHF, the predicted Q_e of phenylalanine, tryptophan, and tyrosine from PFO are close to the experimental Q_e, and the predicted Q_e of leucine, isoleucine, and threonine from PSO are close to the experimental Q_e. Considering the R^2 and predicted Q_e values, the PFO model provides an accurate description of phenylalanine, isoleucine, tryptophan, and tyrosine adsorption on AN, while the PSO model is more suitable for predicting the adsorption of leucine and threonine on AN. The PFO model is better suited for describing the adsorption of tryptophan and leucine on HB, while the PSO model is more appropriate for the adsorption of the other four amino acids. It has been reported that when the PFO model is applicable, physical adsorption is the rate-limiting step. In contrast, when the PSO model is more suitable, chemisorption serves as the rate-limiting step.[24,37,38] The FTIR spectra of three PAC before and after adsorption of amino acids is shown in Figure S3. No new peaks were observed after the adsorption of amino acids onto PHF, AN, and HB, indicating that the adsorption process did not involve the formation of new covalent bonds. Van der Waals forces are likely the main mechanism driving the adsorption of amino acids onto the PAC.

The results of the kinetic fitting parameters showed that the Q_e of the three PACs followed the order PHF > AN > HB for phenylalanine, tryptophan, and threonine. For isoleucine, leucine, and tyrosine, the Q_e of the three PACs followed the order of AN > PHF > HB. For PHF, the adsorption capacity of six amino acids followed the order of tryptophan > phenylalanine > threonine > isoleucine > tyrosine > leucine. For AN, the adsorption capacity of six amino acids followed the order of tryptophan > isoleucine > threonine > phenylalanine > tyrosine > leucine.

3.3. Effect of Initial Amino Acid Concentration on Amino Acid Removal

Amino acids vary in different kinds of source water, and the initial concentration of amino acids may affect the removal efficiency of PACs. Therefore, the adsorption of amino acids at different initial concentrations (100, 200, 300, 400, 500, and 600 μg/L) was investigated. The relationship between Q_e and initial amino acid concentration was analyzed using linear fitting, as shown in Figure 4. The slope and R^2 values of the fitted line are provided in Table S4. The Q_e values of all six amino acids demonstrated a linear correlation with increasing initial amino acid concentrations, with R^2 values ranging from 0.95 to 0.99 (Table S4). The increase in Q_e with rising initial amino acid concentration suggests that adsorption has not yet reached saturation within the tested concentration range (100, 200, 300, 400, 500, and 600 μg/L). Before saturation is reached, the increase in Q_e can be attributed to the higher availability of amino acid molecules at increased concen-

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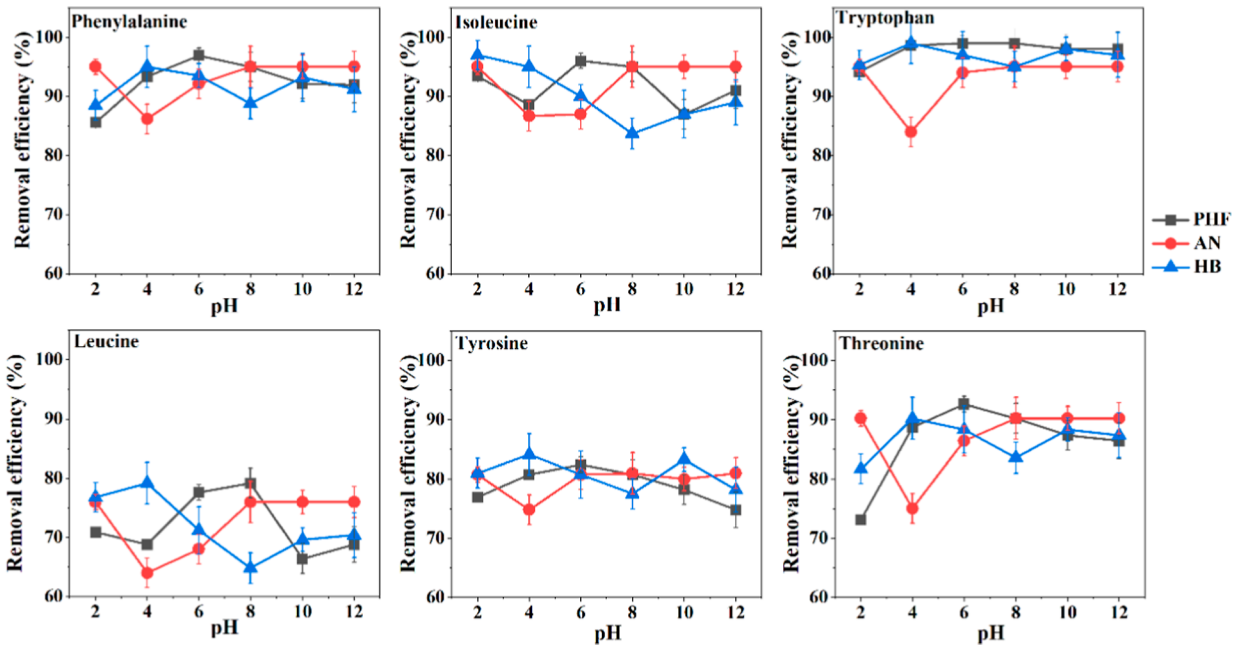

Figure 5. Effect of pH on phenylalanine, isoleucine, tryptophan, leucine, tyrosine, and threonine on PHF, AN, and HB PACs. Experimental conditions: initial amino acid concentration = 200 μg/L, pH = 2, 4, 6, 8, 10, and 12 ± 0.2, PAC = 30 mg/L, contact time = 30 min.

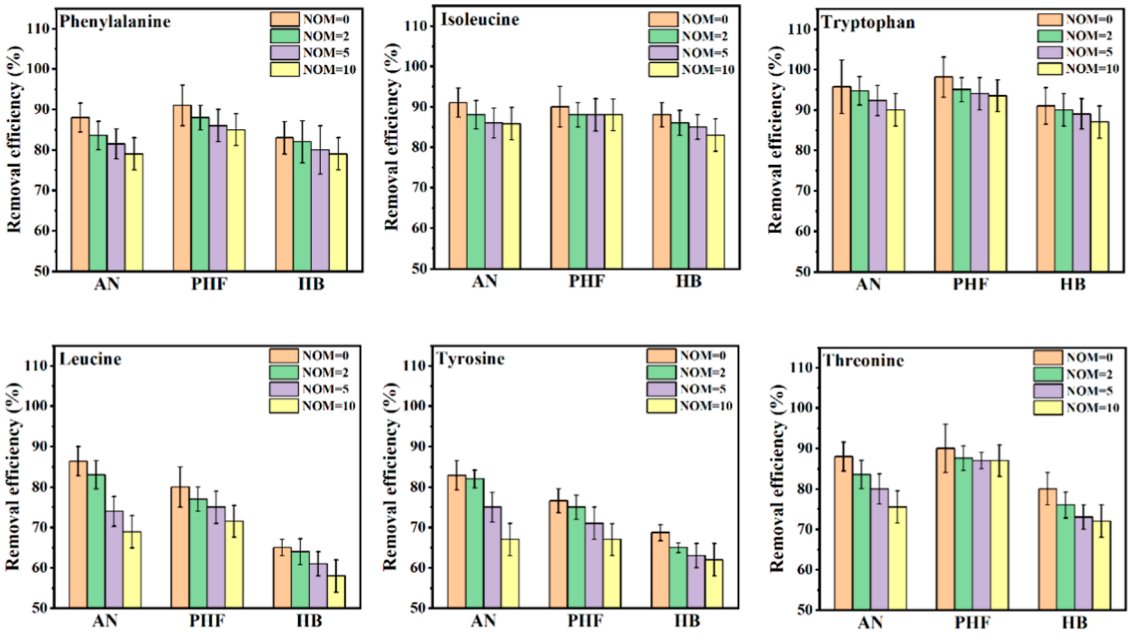

Figure 6. Effect of NOM on phenylalanine, isoleucine, tryptophan, leucine, tyrosine, and threonine on amino acid removal by PHF, AN, and HB PACs. Experimental conditions: initial amino acid concentration = 200 μg/L, pH = 7.0 ± 0.2, PAC = 30 mg/L, NOM concentration = 2, 5, and 10 mg/L as C.

trations, which enhances interactions with the PAC surface. The slopes for the three PACs across all six amino acids followed the order: PHF > AN > HB. The iodine number value of PHF is the highest, indicating the greatest number of adsorption sites. When the amino acid concentration is at the same level, PHF with more adsorption sites will facilitate the interaction with amino acids, resulting in more amino acid adsorption compared to other PACs.

3.4. Effect of pH on Amino Acid Removal

The effect of pH on the adsorption behavior of three PACs was tested across a pH range of 2 to 12, as shown in Figure 5. For PHF, a similar trend was observed for all amino acids: the removal efficiency increased with pH between 2 and 6 (for isoleucine between 2 and 8), and then decreased as pH exceeded 8. For AN, the removal efficiency significantly decreased as pH increased from 2 to 4, then increased within the pH range from 4 to 8, stabilizing after pH 8. For HB, the removal efficiency increased as pH increases from 2 to 4, then decreases in the pH range from 4 to 8, and slightly increases within the pH range from 8 to 12. Most water has a neutral pH, and HB exhibits poor adsorption under this condition. The pH of municipal water typically ranges from 6.5 to 8.5, as

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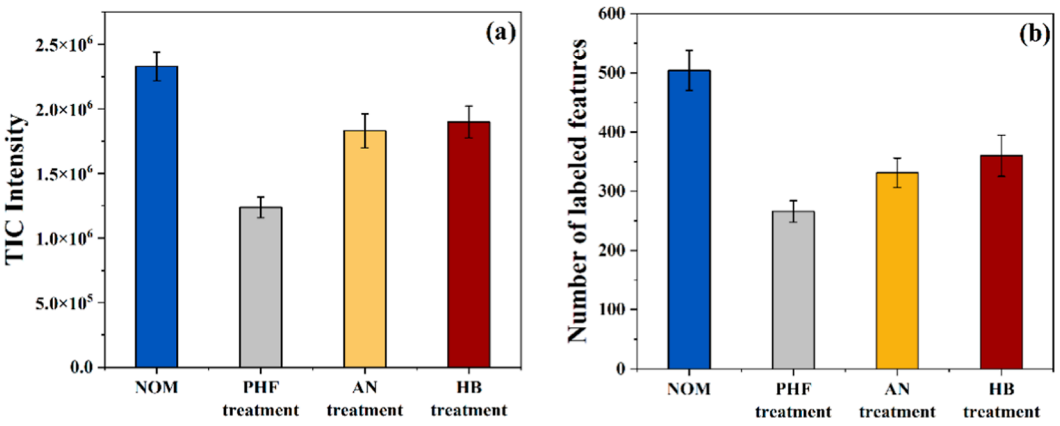

Figure 7. TIC intensity (a) and number of labeled amino-containing features (b) in NOM, before and after treatment with PHF, AN, and HB PACs. Experimental conditions: NOM = 2 mg/L as C, pH = 7.0 ± 0.2, PAC = 30 mg/L, contact time = 30 min.

recommended by the World Health Organization (WHO) and the U.S. Environmental Protection Agency (EPA). This range is considered optimal for both public health and protection of water distribution systems. In the pH range of 6.5−8.5, PHF and AN are more effective for amino acid removal. The effect of pH on the adsorption of organic compounds can be primarily attributed to the following factors: (1) the solution pH could affect the charge of the adsorbate. Under varying pH conditions (i.e., 2−12), adsorbates may be positively charged, negatively charged, or neutral, which impacts their electrostatic interactions with the PAC surface. For example, in the case of negatively charged adsorbates, an acidic (low pH) environment may promote adsorption because of the positive charge on the PAC surface. The optimal pH for PHF is around 6, which aligns with the isoelectric points of the tested amino acids. At pH 6, the amino acids are neutral, which may enhance the hydrophobic interactions between the amino acids and PHF. (2) The pH value affects the acidic and alkaline functional groups on the surface of the PAC, such as hydroxyl, carboxyl, and carbonyl groups, which can affect the adsorption process through hydrogen bonding, ion exchange, and coordination. pH changes may alter the activity of these functional groups, thus affecting the binding strength of the adsorbate on the surface of the PAC.[38−41]

3.5. Effect of NOM on Amino Acid Removal

In surface water treatment plants, elevated levels of NOM, such as those occurring during seasonal algal blooms or following heavy rainfall, can significantly challenge the effectiveness of PAC. Understanding the impact of NOM on PAC performance is essential for optimizing dosing strategies to maintain treatment efficiency. The adsorption of amino acids onto PACs in the presence of NOM, represented by SRSRMs, was investigated, as shown in Figure 6. The removal efficiencies of amino acids by all three PACs decreased as the NOM concentration increased. The removal efficiencies of AN and HB were more significantly affected than that of PHF. For example, the removal efficiency of tyrosine by AN decreased from 82.9 to 67% as NOM concentration increased from 2 to 10 mg/L. Similarly, the adsorption of NDMA precursor by PACs has been reported to decrease significantly in the presence of NOM; the higher the content of NOM, the more significant the effect.[42] The negative effect of NOM has been attributed to two mechanisms: (1) NOM is a mixture of compounds with varying molecule sizes. Larger components can preferentially cover the surface of PACs, block their pores, or fill micropores, thereby preventing amino acids from interacting with functional adsorption sites on PACs.[43] Additionally, NOM with small molecules may compete with amino acids for adsorption sites. (2) NOM, particularly humic acids, contains a large amount of oxygen-containing functional groups, which may negatively impact the hydrophobic interaction between amino acids and PACs.[38]

3.6. Removal of Amino-Containing Features from SRSRMs by PAC Using HDPairFinder

The above sections examine the removal properties of PAC for amino acids. However, amino acids constitute only a small fraction of the amino-containing organic compounds. There remains a gap in understanding the overall removal efficiency of PAC on all amino-containing organic compounds. The removal of amino-containing compounds from source water (represented by SRSRMs) by PAC was studied using a stable H/D isotopic labeling reaction coupled with HPLC−HRMS, as outlined in Section 2.3. The generated HRMS data sets were analyzed using the HDPairFinder data processing platform, which enabled the identification of amino-containing features.[27] SRSRMs are high-purity organic matter samples derived from the Suwannee River in Florida and are designed to serve as benchmarks for various studies, particularly those focused on the characterization of NOM, including its chemical composition and behavior in water treatment processes.[44−46] SRSRMs serve as a consistent and reliable reference for researchers to compare results. Therefore, SRSRM was selected as representative NOM components in surface water to investigate the removal of amino-containing organic compounds using PACs.

The total ion chromatogram (TIC) intensity and number of labeled amino-containing features from NOM before and after PHF, AN, and HB treatment are shown in Figure 7. After the adsorption of PHF, AN, and HB, the TIC intensity of NOM decreased from 2.33×10^6 to 1.24×10^6, 1.83×10^6 and 1.90×10^6, respectively. PHF demonstrated the highest removal efficiency, achieving a total reduction of 47% in TIC intensity for labeled amino-containing features, followed by AN at 21% and HB at 19%. Before PAC treatment (i.e., NOM in Figure 7b), 504 labeled features were detected, and 266, 331, and 360 compounds were detected after PHF, AN, and HB treatment, respectively. The reduction in the total number of labeled amino-containing features followed a similar trend: PHF > AN > HB. Up to 238 amino-containing organic features were removed by PHF. The removal efficiency of amino-containing

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features with the top 50 peak areas is shown in Table S5. The removal efficiencies of these 50 features by PHF ranged from 11.6 to 100% with a medium value of 59.6%. For AN, the removal efficiencies ranged from 1.6 to 100% with a median of 49.8%. For HB, the removal efficiencies ranged from 0 to 100% with a median of 25.4%.

4. CONCLUSIONS

The composition of organic amines varies in different water systems. There are many commercial PACs available. To achieve efficient and cost-effective removal of organics, utilities need information on PAC removal efficiency under different conditions. This study provides necessary information on PAC removal of amino-containing compounds in source water. Six amino acids, typical soluble small amino-containing compounds that are frequently detected in water, were selected for their removal by PACs to be studied. PHF and AN exhibited high removal efficiencies for the tested amino acids, with specific surface area being a key factor influencing their adsorption performance. In the pH range of 6.5−8.5, the recommended pH for drinking water, PHF and AN are more effective for amino acid removal. Increased NOM levels were found to reduce the adsorption capacity for amino acids. This has environmental implications, highlighting the high doses of PAC that may be needed to deal with source water quality changes, for example, resulting from spring runoff, and/or seasonal algal blooms. Using water samples containing complex SRSRMs, we demonstrated the overall efficiency of the PACs in removing amino-containing compounds from SRSRMs. The water samples before and after PACs were analyzed using nontargeted analysis with HDPairFinder. The decrease in the TIC intensity and number of labeled amino-containing features mirrored the amino acid adsorption results, showing a trend of PHF > AN > HB PAC. This study provides a theoretical basis for its application in drinking water treatment plants. However, the scalability of these results to full-scale water treatment plants requires further exploration, particularly regarding contact time requirements and interactions with coagulants and different source water systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenvironau.4c00133.

Recovery and RSD of SPE−HILIC−MS/MS method for the determination of amino acids, H/D isotopic reaction and sample preparation, HPLC parameters of HILIC−MS/MS method for determining amino acids, parameters of six commercial PACs, linear fitting of Q_e and initial amino acid concentration, removal efficiency of amino-containing features, and FTIR analysis of PAC before and after adsorption (PDF)

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Author Contributions

CRediT: **Di Zhang** data curation, formal analysis, investigation, methodology, validation, visualization, writing - original draft; **Qiming Shen** data curation, formal analysis, investigation, methodology, validation, visualization, writing - original draft, writing - review & editing; **Xing-Fang Li** conceptualization, funding acquisition, project administration, resources, supervision, validation, writing - review & editing.

Notes

The authors declare no competing financial interest.

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