Removal of cyanobacterial amino acids in water treatment by activated carbon adsorption

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ABSTRACT

The applicability of activated carbon for the adsorption of *phenylalanine*, *arginine* and *aspartic acid* from aqueous solution was evaluated in this study. These amino acids are plentiful in low-molecular weight algal organic matter produced by cyanobacteria, which is not satisfactorily removed by chemical coagulation. Because of this they may gravely disturb the water treatment process. Equilibrium adsorption of amino acids was studied on well-characterized activated carbons, Picabiol (PIC) and Filtrasorb (FTL), possessing different chemical and charge properties evaluated by Boehm titration. Adsorption experiments were conducted at various adsorbate initial concentrations, pH values and ionic strengths to elucidate the effect of solution properties on the amino acid removal. Distinct adsorption mechanisms were observed for individual amino acids depending on the pH and the type of carbon applied. Electrostatic interactions between functional groups of the adsorbents and *arginine* were deemed the predominant adsorption mechanism. The maximum *arginine* uptake was achieved through electrostatic attraction at pH 9 on PIC, which bears a higher number of acidic functionalities. Hydrogen bonds between protonated functionalities of adsorption participants were suggested as a possible explanation for the observed *arginine* adsorption on FTL in unfavourable conditions at pH 5 and 7, when electrostatic repulsion prevailed. *Phenylalanine* adsorption was dominated by hydrophobic interactions under all experimental conditions. Electrostatic interactions then caused the final differences in *phenylalanine* uptakes at particular pH values. Besides the direct hydrophobic interactions, *phenylalanine* removal was enhanced by intermolecular hydrophobic interactions leading to the formation of associates consisting of several *phenylalanine* molecules, which were then adsorbed as a unit. Insignificant adsorption of *aspartic acid* was observed on both carbons owing to its strong hydrophilicity. Generally, adsorption of amino acids decreased as the ionic strength of the solution increased. The added salt screened attractive electrostatic interactions, altered surface charge of the adsorbents or changed adsorbate solubility.

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1. Introduction

Free and combined amino acids (AAs) can be found in all types of natural waters including water sources used for drinking water production. AAs form together with peptides and proteins a dominant fraction of nitrogenous compounds of algal organic matter (AOM) [1]. Many deleterious effects on water treatment are related to AOM presence in raw water, e.g. coagulation failures accompanied by increased consumption of chemical reagents [2,3], membrane fouling [4,5] or production of harmful cyanobacterial

toxins [6]. Metabolic activity of cyanobacteria and green algae is the primary source of AOM nitrogenous compounds [1,7–9]. Cyanobacteria produce high amounts of polypeptides composed of *glycine* units, *aspartic* and *glutamic acid*, *alanine* and *serine* [10]. High concentrations of AAs have been detected during a period of rapid algal decomposition and subsequent degradation of their cells [11]. Concentrations of dissolved peptides/proteins and free AAs in raw water depend on biological activity of the microorganisms and increase with the age of the culture [1,9]. They can reach high mg L^{-1} concentrations during the period of algal blooms [1]. Concentration of free AAs usually ranges between 20 and 1000 µg L^{-1} [7,11] and it may account for 2–13% of the total dissolved organic carbon (DOC) in natural waters [7,8]. The incidence of peptides/proteins is up to 5 times higher than for free AAs in

natural waters [11]. The amount of AAs is stable throughout the water column, but decreases with water depth in the case of peptides/proteins [7,8].

Glycine, *glutamic acid*, *alanine*, *aspartic acid*, *leucine* and *serine* belong to the most frequent AAs in natural waters [7,8], and *arginine*, *lysine* and *glycine* dominate the cellular organic matter (COM) [9].

Amino acids are non-toxic compounds acting mainly as the building blocks of microorganisms' DNA, RNA, proteins, etc. [12] but their occurrence in the treated water is undesirable [8,11,13–15]. This brings about numerous problems across water treatment process. AAs may increase Cl_2 consumption during chlorination of water [11]. Under this treatment process, their presence also leads to the production of aldehydes, nitriles and other compounds negatively affecting the organoleptic properties of water, especially its taste and odour [12,13,15]. They also present a potential source of biodegradable organic carbon serving as a nutritive substrate for the growth of detrimental microorganisms in the water distribution network [8,14]. Finally, AAs belong to identified precursors of disinfection by-products (DBPs) and contribute to the formation of trihalomethanes (THMs) and haloacetic acids (HAAs) [10]. Hong et al. [8] discovered that especially aromatic AAs and two AAs with aliphatic side chain, *aspartic* and *glutamic acid*, are problematic in this context.

A coagulation-based treatment is often ineffective in removing organic compounds of high polarity and low molecular weight (MW) such as AAs [3]. Various concentrations of AAs are measured in all stages of the water treatment process [8,11,12], and increasing concentrations have been detected in some cases [11].

For the reasons mentioned above, it is necessary to pay attention to the removal of AAs from raw water sources and to search for effective ways how to do it. Adsorption onto activated carbon (AC) seems to be an appropriate method since it is effectively applied in drinking water production for the uptake of other organic nitrogenous compounds with a very low MW, e.g. cyanobacterial toxins [6] or AOM peptides [16]. Studies focusing exclusively on the adsorption of AAs onto AC in the water treatment process are rare, although numerous researches have been made to investigate the adsorption of AAs for applications in medicine, biochemistry, geochemistry and the food industry [17]. Various adsorbents have been assessed in these studies including zeolites [18], kaolinite [19], polymeric adsorbent [20], mesoporous silica [21,22] or activated carbon, which demonstrated adsorption capacity comparable to mesoporous carbon, a sorption material with well ordered pore system [23]. Carbon nanotubes have also been found to be promising adsorbent for AAs with sorption capacities much higher than those of many other macroporous and mesoporous sorption materials [24].

Recent adsorption studies have brought several conclusions. Adsorption efficiency for AAs is affected by their MW, size or geometry of molecules. Solubility, polarity and content of functional groups (e.g. —COOH, —NH$_2$, —OH, —S—) are also responsible for adsorption ability of AAs [22,25]. Besides the adsorbate properties, the adsorption is governed by the adsorbent nature (e.g. surface charge, pore structure, functional groups on the adsorbent surface) and solution properties (e.g. pH, ionic strength (IS), initial adsorbate concentration, temperature) [12,18–21,23–27]. Finally, a combination of these factors determines both the adsorption character and the mechanisms [18,22]. Hydrophobic interactions [23,27], electrostatic interactions [21] and hydrogen bonds [19] have been identified as the most common mechanisms in amino acid adsorption, unfortunately often on adsorbents other than activated carbon.

The aim of this study was to investigate the effect of several adsorption factors (adsorbate initial concentration, pH and IS) on the adsorption of three amino acids belonging to the major AAs commonly identified in natural waters containing AOM and also in treated water after coagulation/flocculation – aromatic *phenylalanine* (Phe), basic *arginine* (Arg) and acidic *aspartic acid* (Asp). The AAs were adsorbed in laboratory scale operation on two types of commercially applied granular activated carbon (GAC) with different textural and charge properties to clarify which mechanisms govern their adsorption.

2. Materials and methods

2.1. Characterization of adsorbents

GAC Picabiol 12 × 40 (PIC) and Filtrasorb TL 830 (FTL) were used for the adsorption of AOM amino acids based on the results of our previous adsorption study with AOM peptides [15]. Both GACs are microporous and designed for drinking water treatment including adsorption of natural organic matter, taste and odour compounds, cyanobacterial toxins and other organic matter with a low molecular weight. Textural and charge properties of the GACs are summarized in Table S1 (see Supplementary material). Details of the performed characterization methods can be found in our previous study [16].

The characterization of surface functional groups was made by Boehm titration [28]. Carbon suspensions were prepared with 1 g of GAC and 50 mL of 0.05 M NaOH and HCl solutions, equilibrated for 48 h at room temperature (22 ± 0.5 °C). Twenty mLs of these solutions were filtered through a 0.22 μm membrane filter (Millipore, USA) and then titrated either with 0.05 M HCl or 0.05 M NaOH. The amount of acidic and basic functional groups was calculated from the uptake of titration agent according to the methodology in literature [29].

2.2. Adsorbates

Three amino acids with different molecular structure and chemical properties were selected as the adsorbates in this study: L-*aspartic acid*, L-*arginine* and L-*phenylalanine* (Sigma-Aldrich, USA). They represent the dominant amino acids identified in natural waters [9]. The characteristics of selected AAs are shown in Table S2 (see Supplementary material).

2.2.1. DOC analysis

Concentrations of AAs in the samples were quantified before and after the adsorption as the concentration of DOC (Dissolved Organic Carbon) measured by a total organic carbon analyser TOC-V$_{CPH}$ (Shimadzu Corporation, Japan) according to the methodology described in our previous studies [1,3]. Each sample was performed in triplicate with the relative error <3%. The dependence of the DOC content on the concentration of AAs in mg L^{-1} is depicted in Fig. S1 (see Supplementary material).

2.2.2. Quantitative analysis of natural amino acids in cellular organic matter

The quantitative analysis of free AAs was performed to verify the proportional representation of the studied AAs in cyanobacterial cellular organic matter (COM). COM produced by cyanobacterium *Microcystis aeruginosa* of MW <500 Da was used for this analysis. The cultivation of the cyanobacterium and the preparation of COM samples were done according to the methodology described in our previous studies [1,3]. Free amino acids included in COM were determined after derivatization by fluorenylmethyl chloroformate (FMOC) by the HPLC system [9] (see Section S1 in Supplementary material).