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Mass spectrometric analysis of bisphenol A desorption from ceria nanoparticles: L-histidine versus L-lysine as biochemical desorption co-agents

Seyed Mohammad Majedi, Edward P.C. Lai*

Ottawa-Carleton Chemistry Institute, Department of Chemistry, Carleton University, Ottawa, ON K1S 5B6, Canada

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ABSTRACT

Mass spectrometry (MS) was used to investigate desorption of bisphenol A (BPA) bound on the surface of ceria (CeO_2) nanoparticles in water. Two amino acids, L-lysine and L-histidine were evaluated as biochemical agents for their desorption capability as a result of their competitive adsorption on CeO_2 nanoparticle surface through their α-carboxyl, α-amino and side chain amine groups, either on their own or in synergy with formic acid or ammonium acetate (NH_4Ac). The recovery, adsorption, and desorption percentages were calculated from the abundances of target adduct ions determined by direct-infusion MS without requiring any prior separation of nanoparticles from the BPA sample solution. MS analysis demonstrated the efficient desorption of BPA by L-histidine and NH_4Ac at neutral pH. Various influential factors on desorption efficiency were investigated. A desorption efficiency of (78 ± 3)% was achieved for a 10 µg/mL BPA pre-mixed with 20 µg/mL CeO_2 nanoparticles for 3 h in the dark under the following experimental conditions: 1 mM L-histidine, 5 mM NH_4Ac, pH = 7.2, and desorption time of 1 h at room temperature. Further evaluation of various CeO_2 nanoparticle concentrations up to 100 µg/mL (10-fold higher than BPA concentration) confirmed no significant decrease in the desorption efficiency. The desorption method is efficient, simple, robust, fast, environmentally friendly, and MS compatible. It would lead to more accurate determination of both the free and bound forms of BPA with co-existing nanoparticles in water.

List of symbols and abbreviations

BPA	bisphenol A
CeO_2	ceria
MS	mass spectrometry
M.W.	molecular weight
NH_4Ac	ammonium acetate

1. Introduction

Bisphenol A (BPA) is one of the widely produced and consumed chemicals with an annual production of near 8 million tons in 2016 that is projected to reach 10.6 million tons by 2022 [1]. It has found a wide range of applications in polycarbonate plastics and epoxy resins as food and beverage can coatings, medical and electronic devices, toys and sport equipment, cosmetics and detergents, thermal paper receipts, and water pipes and tubings [2]. In some personal and home care products, the BPA content may go up to 100 µg/g [3]. The global release of BPA into the environment has reached 100 tons per year. It has been detected in aquatic environments such as surface water, groundwater, runoff, wastewater, landfill leachate, soil, and atmosphere [4]. BPA shows acute toxicity to aquatic organisms. European Union in a risk assessment report has suggested predicted no effect concentrations (PNEC) of BPA in fresh water to be 1.6 µg/L (for chronic toxicity) and 11 µg/L (for acute toxicity) [5]. A PNEC of 3700 µg/kg dry weight in soil has chronic toxicity as well [6, 7]. As an endocrine disruptor, BPA shows estrogenic activity even at concentration levels below 1 ng/L in water [8]. The United States Environmental Protection Agency estimated an oral reference dose (RfD) of 50 µg of BPA/kg of body weight/day [9]. The residual/unreacted monomers of BPA in polycarbonate and also free BPA released under alkaline conditions such as by applying strong alkali detergents or during microwave heating from polycarbonate plastics and coatings have made this chemical ubiquitous for human exposure [10], as detected in the urine of 90% of a school children population [11]. BPA has been proven to significantly

* Corresponding author.
E-mail address: edward.lai@carleton.ca (E.P.C. Lai).

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disrupt thyroid [11] and male reproduction functions [12, 13], cause diabetes mellitus [14], and increase the chance of developing cardiovascular diseases [15].

A very recent measurement of BPA concentrations in the province of Quebec in Canada has shown that the levels of BPA in both water and solid matrices were significantly higher than those of other emerging contaminants [16]. The average BPA concentration for a period of five months was reported to be 356 and 593 ng/L for two municipal wastewater treatment plants and 60 ng/L in surface water while their respective solid fractions were much higher (3355–8045 ng/L, respectively), suggesting that BPA tends to partition in the solid phase such as suspended particulate matter of surface water.

Cerium oxide (CeO_x) is one of the most earth-abundant rare metal oxides, an n-type semiconductor with a wide bandgap, and a material of optical transparency [17, 18]. Ceria (CeO_2) nanoparticles are widely used in industrial applications as ultraviolet absorber for wood protection [19, 20], photocatalyst for dye abatement/degradation or ethanol conversion [21–23], catalytic oxidation of various organic compounds/substrates [24, 25], fuel cells [26, 27], gas sensors [28, 29], and polishing materials [30, 31]. Long-term exposure to CeO_2 nanoparticles can cause environmental stress, decreasing cell viability, reducing microbial diversity and shifting the microbial composition [32]. A recent study showed that CeO_2 nanoparticles had genotoxic potential on human peripheral blood lymphocyte cells after 3 to 24 h exposure [33]. There are a number of studies reporting cytotoxicity, dermal toxicity, environmental toxicity, hepatotoxicity, neurotoxicity, phytotoxicity, and respiratory toxicity of CeO_2 nanoparticles [34] on human hepatoma [35] and neuroblastoma cell lines [36]. A dose-dependent cyto-genotoxicity of CeO_2 nanoparticles inducing DNA damage has also been reported [37]. Photocatalytic degradation of BPA was enhanced using various CeO_2 nanocomposites with a $Bi_4Ti_3O_{12}$ heterojunction structure [38] and with reduced graphene oxide co-modified titania (TiO_2) nanotube arrays [39].

Interactions between nanoparticles and co-existing contaminants may cause synergistic effects on the distribution, transport, and biotransformation of contaminants which would lead to altered bioavailability and toxicity to organisms in the water environment [40]. BPA could adsorb onto metal oxide nanoparticle surface through π orbitals, hydrogen bonds and electrostatic interaction [41], thereby altering its bioaccessibility. A study on the adsorption of low concentration levels of BPA and TiO_2 nanoparticles demonstrated that the adsorption capacity did not change markedly in various media including cell cultures [42]. It was reported that the co-presence of BPA and TiO_2 nanoparticles resulted in increased bioavailability and uptake of BPA to zebrafish embryos cells [43]. Another study showed that the adsorption of BPA on TiO_2 nanoparticles caused adverse reproductive effects on zebrafish. The adsorbed BPA was translocated in various fish organs such as liver, brain, and gonad, resulting in a decreased reproductive hormones concentrations and enhanced endocrine disruption [44].

It is well known that amino acids interact with metal oxide nanoparticles [45]. Previously, chiral nanozymes were constructed by grafting a series of D- or L-amino acids onto the surfaces of CeO_2 nanoparticles to achieve stereo-selective oxidation of 3,4-dihydroxyphenylalanine [46]. Recently, our group developed a method for the electrophoretic separation and ultraviolet detection of zinc oxide nanoparticles in aqueous solution using a thiol-containing amino acid, L-cysteine, as an adsorbate [47]. The adsorption of gas-phase L-histidine (evaporated in the vacuum) on ceria nanoparticles was thoroughly studied using synchrotron radiation photoemission, resonant photoemission, and near edge X-ray absorption fine structure spectroscopies. It has been reported that histidine binds to CeO_2 via the carboxylate group and all three nitrogen atoms, and the imidazole ring orientates itself parallel to the nanoparticle surface. Both nitrogen atoms in the imidazole ring bind through π-orbitals, while the α-amino group interacts with the nanoparticle surface through hydrogen bonding to oxygen on the nanoparticle surface [48]. In another work, the adsorption of L-histidine on TiO_2 nanoparticles at the physiological pH of 7.4 was studied by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy that confirmed similar interactions between the oxide nanoparticle surface and the amino acid imidazole ring and α-amino group. It was further shown that the hydrogen bond between the amine groups and the oxide surface resulted in intramolecular proton transfer to the carboxylate group in the adsorbed histidine, which was called surface induced deprotonation of the amine group [49]. Magnetic iron oxide nanoparticles adsorbed aspartic acid and L-lysine. The adsorption was characterized by measuring ξ-potential, hydrodynamic size, and osmolality, and the amount of adsorption was determined by liquid chromatographic analysis of the amino acids in the supernatant. The mechanism of adsorption proposed was through single molecular layer for low amino acid concentrations (binding of carboxyl group) and formation of large molecular associates (binding of amino groups) for high amino acid concentration that was dominated by hydrogen bonding at acidic pH levels and electrostatic interactions at higher pH levels [50].

We have recently developed a method for desorbing BPA from TiO_2 nanoparticles by chemical desorption agents that are suitable for the acquisition of mass spectra with minimal spectral interference from photocatalytic product ions, namely acetate, fluoride, formate and hydroxide anions in combination with the ammonium cation [51]. In the present work, L-lysine and L-histidine were evaluated for their abilities to desorb BPA from CeO_2 nanoparticles. These amino acids contain both α-amine and α-carboxylic acid groups that could compete for the binding sites on the nanoparticles as a result of their chelating nature/ligand exchange, charge/proton transfer, and electrostatic attraction. Desorption pH level was selected based on the characteristic isoelectric point (IEP) of nanoparticles and logarithmic acid dissociation constants (pK_a) of amino acids. While the previous study on the desorption of BPA from titania nanoparticles mainly focused on the effect of desorption chemicals/modifiers on the sample pH (influencing electrostatic interactions between BPA and titania) and electrospray ionization (ESI) efficiency, the present study applied two amino acids as potential biochemical and biocompatible agents.

To the best of our knowledge, this is the first time that the application of biochemicals for the desorption of bound contaminants from nanoparticle surface is reported. The results of this study suggest that bound BPA carried by nanoparticles in biological matrices could be desorbed in the presence of amino acids (as ubiquitous biochemicals in biota). These results also proved the applicability of chemical/biochemical desorption as an important step in the sample preparation for samples containing BPA and CeO_2 nanoparticles. The proposed method can therefore be applied prior to preconcentration of trace BPA in environmental water samples for MS analysis. It can significantly enhance the recovery of adsorbed BPA to improve the accuracy of quantitative analysis. Furthermore, direct-infusion MS facilitated investigation of BPA adsorption/desorption without any prior separation of nanoparticles by ultracentrifugation or chromatography. It enabled selective detection of BPA with adequate sensitivity.

2. Experimental

2.1. Chemicals

All chemicals were acquired from commercial sources and were used as received. Bisphenol A (≥99% $C_{15}H_{16}O_2$, M.W. = 228.29), methanol (LC-MS grade), L-histidine (≥99% $C_6H_9N_3O_2$, M.W. = 155.15), L-lysine (≥98% $C_6H_{14}N_2O_2$, M.W. = 146.19), and CeO_2 nanopowder (99.95%, < 50 nm particle size) were purchased from Sigma-Aldrich (Oakville, ON, Canada). Ultrapure water was generated by a Milli-Q system (Millipore, Milford, MA, USA) for the preparation of all sample and standard solutions.