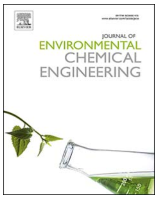
Journal of Environmental Chemical Engineering 5 (2017) 2976–2985

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece



Research paper

Adsorption of substituted benzoic acids onto α-Al_2O_3 surface in mixed-adsorbate mode: 2,4-Dihydroxybenzoic acid, 2,6-dihydroxybenzoic acid and 1,2,4-benzenetricarboxylic acid (trimellitic acid)

Jyotirmoy Sarma[1], Sekh Mahiuddin[2,*]

Materials Science Division, CSIR-North East Institute of Science and Technology, Jorhat 785006, Assam, India

ARTICLE INFO

Keywords:
Competitive and co-operative adsorption
α-Al_2O_3
2,4-DHBA
2,6-DHBA
Trimellitic acid
Adsorption kinetics
Adsorption isotherms

ABSTRACT

Influence of position and type of functional groups (—COOH and phenolic —OH groups) in a benzene ring on the adsorption of three natural organic matter (NOM) analogues e.g. 2,4-dihydroxybenzoic acid (2,4-DHBA), 2,6-dihydroxybenzoic acid (2,6-DHBA) and trimellitic acid (1,2,4-benzenetricarboxylic acid) onto α-alumina surface are explored in terms of adsorption kinetics and isotherms in single- and mixed-adsorbate mode. Focusing at the positional functional groups, adsorption profile of 2,4-DHBA and 2,6-DHBA is compared in single- and mixed-adsorbate mode. 2,4-DHBA produces higher adsorption density than 2,6-DHBA in both single- and mixed-adsorbate mode, governing factor is the *ortho-para* position of phenoilc —OH group in 2,4-DHBA for higher adsorption density. Concerning type of functional groups, adsorption profile of 2,4-DHBA is also compared with trimellitic acid. Here again 2,4-DHBA produces higher adsorption density than trimellitic acid in single-adsorbate mode. In contrast, in mixed-adsorbate mode both adsorbates exhibit roughly equal adsorption densities indicating competition of co-operative nature, which is also supported by their activation energy values in mixed-adsorbate mode. Nevertheless, there exists a competition for the same surface sites of α-alumina that results in reduction of adsorption densities in mixed-adsorbate mode than that of the single-adsorbate mode.

1. Introduction

In the natural aquatic eco-system, the mass concentration of soluble natural organic matter (NOM) is in the range of 0.5–100 mg/L of organic carbon [1]. Generally, NOM undergoes continuous biological, chemical and photochemical transformations and produces low molecular weight carboxylic and dihydroxybenzoic acids (DHBAs) [2–4]. The DHBAs are also produced by degradation of vegetative matters [5,6] and by ozonation of fulvic acids [7]. Nevertheless, DHBAs are important intermediates of many industrial synthetic products [8,9] and are undesirable pollutants, beyond some concentration, in the biosphere and in the aquatic eco-system [10,11]. The concentration of these acids varies depending on the source and locations [12,13]. Simple organic compounds with —COOH, —OH and > C═O functional groups are significant since these functional groups are responsible for controlling some important properties and processes such as, metal complexing capacity, surface activity, adsorption onto metal oxide surface, stability of mineral colloids and mineral dissolution [14–20].

The adsorption of simple aromatic organic acids onto model mineral oxide surface helps in understanding the complex NOM-mineral oxide interactions in aquatic eco-systems because experimental sorption with very complex molecules with —COOH and —OH groups are difficult to understand and interpret for many geochemical processes [21,22].

Adsorption of simple and well-defined NOM analogues in single-adsorbate mode with varying numbers and position of functional groups in the benzene ring onto mineral oxides surface is well documented in the literatures [22–28], only some important and relevant references are cited, readers may see cited references in these literatures. The *ortho* and *para* substituted mono-hydroxybenzoic acids were found to produce higher adsorption density than *meta* substitued one [27]. However in comparison *ortho*-hydroxybenzoic acid produces higher adsorption density than the *para* isomer onto α-alumina surface [29]. Examining the effect of —COOH vs. —OH group at pH 5 and 298.15 K, it is observed that all the isomers of DHBA showed higher adsorption density than the corresponding benzenecarboxylic acids. Examples are, 2,4-DHBA produced (~2.1 times) higher adsorption density than trimellitic acid, 2,3-DHBA (~1.2 times) higher than hemimellitic acid and 3,5-DHBA (~1.7 times) higher than trimesic acid

---

* Corresponding author.
E-mail address: mahirrljt@yahoo.com (S. Mahiuddin).

[1] Department of Chemistry, School of Basic Sciences, Kaziranga University, Koraikhowa, NH 37, Jorhat 785006, Assam, India.

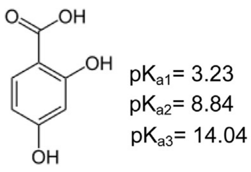
[2] Village & PO: Lokabati, Dhaniakhali, Hooghly, West Bengal 712302, India.

http://dx.doi.org/10.1016/j.jece.2017.05.049
Received 1 February 2017; Received in revised form 22 April 2017; Accepted 29 May 2017

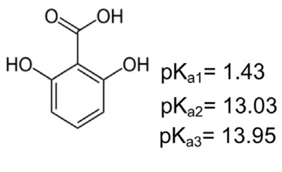
[23]. The comparison of adsorption between salicylic and phthalic acids at pH 5 and 298.15 K onto alumina surface [30,31] also demonstrates the importance of phenolic −OH group in adsorption process. Interestingly, amongst DHBA isomers, 3,4-DHBA was found to produce higher adsorption density onto α-Al_2O_3 surface at alkaline pH (pH ≥ 9) and behaves like catechol due to the presence of two adjacent phenolic −OH groups but none of the −OH group is adjacent to −COOH group as in the case of 2,3-DHBA [32]. The importance of adjacent phenolic −OH group is also demonstrated in a recent publication [28] wherein both 3,4-DHBA and 3,4,5-THBA (tri-hydroxybenzoic acid) shows similar adsorption behavior, indicating negligible effect of the third phenolic −OH group in THBA and similar observation has also been reported earlier [22].

In the natural aquatic eco-system, the existence of multi-adsorbates is expected to be more common than the single adsorbate. In multi-adsorbate mode, competition amongst two or more adsorbates exists for a common surface site of an adsorbent [33]. Hence, the adsorption behavior of single- and mixed-adsorbate systems is likely to be different.

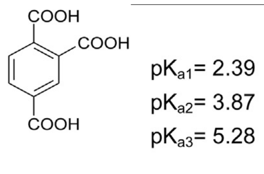
In the scope of competitive adsorption, especially organic adsorbents, we have recently compared the position of phenolic −OH group of a pair of monohydroxybenzoic acid onto α-alumina surface [29]. Results showed reduction of adsorption densities for both the adsorbates in their mixed-adsorbate mode than the respective single-adsorbate mode, which was concluded as a sign of competitive adsorption. Nevertheless, *ortho*-hydroxybenzoic acid produced higher adsorption density than the *para* isomer due to the presence of phenoloic −OH group at *ortho* position, which enhanced the adsorbate/adsorbent interaction. Now, for better understanding of the influence of phenolic −OH groups in DHBA adsorption, replacement of two phenolic −OH groups by carboxylic −COOH groups and finally adsorption comparison of the corresponding acids onto α-alumina surface would be better choice. Further the role of carboxylic −COOH and phenolic −OH groups in simple aromatic organic acids on the adsorption is an essential proposition for understanding the complex adsorption phenomena occurring in the natural aquatic eco-system [22,34], which is basically a mixed-adsorbate/mineral system. So, keeping in mind about the natural aquatic eco-system, in this paper, the influence of carboxylic −COOH and phenolic −OH groups on the adsorption of 1,2,4-benzenetricarboxylic acid (trimellitic acid), 2,4-DHBA and 2,6-DHBA onto α-Al_2O_3 surface is compared both in single- and mixed-adsorbate mode. 2,4- and 2,6-DHBAs are part of the series of DHBA isomers, differentiated by the position of one of the phenolic −OH groups. The novelty of this study is the qualitative assessment of adsorption parameters amongst the three emerging NOM analogues in mixed-adsorbate mode, which was found lacking in the literature.



2,4-DHBA



2,6-DHBA



Trimellitic acid

The pK_a of the adsorbates are collected from the reference [22].

2. Experimental

2.1. Materials

α-Alumina (> 99%, Aldrich, Germany) was washed twice with double-distilled water, dried and finally reactivated at 700 °C for 3 h and was kept in a vacuum desiccator. The surface area of α-alumina was found 13.12 $m^2\,g^{-1}$. 2,4-Dihydroxybenzoic acid, (97%, Alpha Aesar, UK), 2,6-dihydroxybenzoic acid (98%, Alpha Aesar, UK), 1,2,4-benzenetricarboxylic acid (99%, Alpha Aesar, UK), sodium hydroxide (> 99%, s.d. fine-chem, India), sodium chloride (> 99.5%, Merck, India) and HCl (AR grade, NICE Chemicals, India) were used without further purification. Detailed experimental procedures are given elsewhere [29] and some are recapitulated below.

2.2. Adsorption kinetics

Adsorption kinetics of 2,4-DHBA and 2,6-DHBA, as single- and mixed-adsorbate, onto α-alumina in aqueous medium (suspension concentration, 0.5% w/v) were performed in the pH range, 5–8 at one unit interval and at different temperatures (exact temperature is noted in the figure caption). For the pair 2,4-DHBA and trimellitic acid adsorption kinetics were also carried out in the mixed-adsorbate mode onto α-alumina (suspension concentration, 0.5% w/v) in the pH range 6–9 at one unit interval and at different temperatures (exact temperature is noted in the figure caption). The suspension was stirred by using a magnetic stirrer and the temperature was maintained by circulating liquid through the jacketed receptacle from the thermostat (Julabo F32HP, Germany) with an accuracy of ± 0.1°. The initial concentration of the adsorbates was (i) 0.15 mM for 2,4-DHBA and 2,6-DHBA pair and (ii) 0.03 mM for 2,4-DHBA and trimellitic acid pair. The concentration of NaCl was 0.05 mM for both adsorbate pairs. As the reaction proceeds ~10 mL of suspension was withdrawn at different intervals of time and filtered through a membrane of 0.2 μm pore size. Organic acids being surface-active may sorb onto the filtering material and to avoid the uncertainty of the adsorbate concentration in the supernatant liquid, first few mL of the filtrate (~3 mL out of ~10 mL) was discarded and the middle fraction was collected for the analysis. The residual concentrations of the adsorbates were estimated at the respective absorption maxima, 291.8 nm (2,4-DHBA), 246 nm (2,6-DHBA), 204.3 nm (trimellitic acid) by using an UV–vis spectrophotometer (Specord 200, AnalytikJena, Germany). The adsorption density, Γ, of the respective acid onto α-alumina surface was estimated by mass balance equation

$$\Gamma = \frac{(C_o - C_e)V}{ma} \tag{1}$$

where, C_0 and C_e are the initial and residual concentration of the respective acids in the suspension, V is the volume of the suspension and m and a are the mass and surface area of the α-alumina, respectively.

2.3. Adsorption isotherms

Adsorption isotherms for (i) 2,4-DHBA and 2,6-DHBA/α-alumina and (ii) 2,4-DHBA and trimellitic acid/α-alumina systems in aqueous medium in single- and mixed-adsorbate mode were studied at different pH and at a fixed temperature by batch method. A suspension of 15 mL containing 0.2 g α-alumina and 0.05 mM NaCl in a screw-capped glass vial was mixed thoroughly with the help of a vortex mixer. The pH of the suspension was adjusted to a desired value within ± 0.1 unit using