



Adsorption of 3,4-dihydroxybenzoic acid onto hematite surface in aqueous medium: Importance of position of phenolic –OH groups and understanding of the same using catechol as an auxiliary model

Nabanita Saikia, Jyotirmoy Sarma, Jayanta M Borah, Sekh Mahiuddin *

Materials Science Division, CSIR-North East Institute of Science and Technology, Jorhat 785 006, Assam, India

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ABSTRACT

A comparative adsorption kinetics, isotherms, dissolution and surface complexation of 3,4-dihydroxybenzoic acid (3,4-DHBA) and 1,2-dihydroxybenzene (catechol) at the hematite/electrolyte interface were investigated. The kinetics at pH 10 and 298.15 K suggested that the adsorption behaviour of 3,4-DHBA and catechol onto hematite surface is similar and attain same equilibration time of 60 min. The adsorption kinetics data of 3,4-DHBA and catechol fit the pseudo-second-order kinetic equation of nonlinear form best. The adsorption density of 3,4-DHBA at pH ≥ 9 increases and thereby mimics the behaviour of catechol. The solubility of hematite depends on both pH of the suspension and concentration of adsorbate. The inner-sphere complex is formed by 3,4-DHBA and catechol onto hematite surface but the mode orientation is likely to be different in the pH range 5–8 and 9–10. The advance microscopic scanning in conjunction with the vibration spectroscopy would provide better pictorial presentation of the mode of orientation of 3,4-DHBA and catechol onto hematite surface at different pH.

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1. Introduction

Phenolic compounds possessing –COOH and –OH functionalities are distributed in the aquatic ecosystems. They are discharged as industrial effluents from rubber, chemical, dye, photographic, pharmaceuticals and oil industries [1–8]. They are also ubiquitous in the ecosystem from the primary and the secondary sources [9–15]. More specifically, they are well known natural organic matter (NOM) analogues and exhibit surface-active properties but not like a typical surfactant [16]. The interactions of these analogues at the mineral oxide/water interface contribute knowledge for understanding the mineral dissolution, beneficiation of ores and minerals using surface-active agents, soil remediation, wetting and dispersion of particles in a suspension and its stability [17–24].

The adsorption and subsequent surface complexation of dihydroxybenzoic acids (DHBA), examples of phenolic compounds, onto metal oxides and (oxy)hydroxides surface in aqueous medium occur through –COOH and/or phenolic –OH groups depending on the experimental conditions [25–31]. It is interesting to note that the position of –COOH and phenolic –OH groups in the benzene ring significantly governs the adsorption behaviour of DHBA onto mineral oxides surface in aqueous medium. The phenolic –OH group at the *ortho* and/or *para* positions in a DHBA remarkably

increases the magnitude of the adsorption density onto an adsorbent [27–30], and subsequent increase in electron density in the benzene ring is responsible for the higher magnitude of the adsorption density of an adsorbate. Further, the replacement of one of the phenolic –OH groups of catechol by –NH₂ group decreases the adsorbed amount by ~ 3 –8 times (4-nitrocatechol vs. 4-nitro-2-aminophenol) at pH 6 with 1 g/L oxide loading [23].

The adsorption of DHBA and 1,2-dihydroxybenzene (catechol) onto different adsorbents (metal oxides, (oxy)hydroxides, clays, activated carbon) surface with a special emphasis for removal and the surface complexation have been reported in the literature [7,8,23,27–35]. The surface complexation of DHBA and catechol onto minerals surface and subsequent mineral dissolution is largely pH specific of the medium and the mode of complexation onto the mineral surface. Nevertheless, adsorbents also play an important role for surface complexation with a particular adsorbate. More specifically, catechol predominantly forms an outer-sphere complex onto MnO₂ and an inner-sphere complex onto Fe₂O₃, TiO₂, Cr₂O₃, Al₂O₃, and Fe(O)OH in aqueous medium [7,15,28]. Therefore, the literature results indicate that the pH of the medium in conjunction with mode surface complexation (inner-sphere) of NOM surrogates onto mineral surface promotes mineral dissolution [7,36–43].

The adsorption behaviour of 3,4-DHBA and catechol onto α -alumina surface as a function of pH was found to be opposite in nature [28]. The results showed that contrary to decrease, the magnitude

* Corresponding author. Fax: +91 (0)376 2370011.

E-mail addresses: mahirrljt@yahoo.com, mahiuddin@rrljorhat.res.in (S. Mahiuddin).

of adsorption density of catechol increases with the increase in pH of the medium, which found to be ~ 5.6 times more as the pH increases from 5 to 10 and comparable (~ 2.6 times) with the literature for the pH range 5–8 [43]. However, at pH 10, the adsorption behaviour of both the 3,4-DHBA and the catechol is found to be equivalent. Nevertheless, the adsorption profile of catechol and DHBA onto different adsorbents exhibits monolayer adsorption and Langmuirian in nature [8,15,28,32,34]. Surprisingly, in the present studies, catechol and 3,4-DHBA exhibit double- and monolayer adsorption behaviour, respectively, onto hematite surface. The double layer adsorption behaviour is not surprising and reported for carboxylate as well as surfactant onto mineral surfaces [44,45].

In the framework of removal of pollutants (both organic and inorganic) from water use of different adsorbents (processed and unprocessed agriwaste and natural and synthetic minerals), following adsorption technique is invariably reported in the literature. In the scope of adsorption of NOM surrogate, we report adsorption of 3,4-DHBA and catechol onto hematite as a function of pH. The reason for choosing hematite as an adsorbent follows: the reactivity of mineral surface for accounting the adsorption process in aqueous medium depends on the surface atomic and electronic structure [46,47]. Hematite is most stable ubiquitous oxide in the nature due to the fact that it has less hydrolysis constant than the corresponding (oxy)hydroxide and alumina [47–49]. Details reactivity of different oxides and (oxy)hydroxides are beyond the scope of this paper and discussed elsewhere [47,50–52]. It is apparent that the adsorption behaviour of a simple organic acid onto different metal oxides and (oxy)hydroxides would be different. Therefore, in this paper, our main aim is to compare the adsorption behaviour of 3,4-DHBA and catechol onto hematite surface. In addition, surface complexation and mineral dissolution have also been addressed.

2. Experimental

2.1. Materials

Hematite (> 99.7 %, Aldrich, Germany) was activated at ~ 120 °C before use. The surface area of hematite was determined by BET method and was found to be $4.88 \text{ m}^2 \text{ g}^{-1}$. Catechol (99%, HiMedia Laboratories, India), 3,4-DHBA (97%, Alfa Aesar, USA), sodium chloride (>99%, s.d. fine-chem, India), hydrochloric acid (A.R grade, NICE chemicals, India) and sodium hydroxide (A.R grade, Merck, India) were used as received. Freshly prepared double-distilled water, to avoid CO_2 contamination, was used for solution preparation and adsorption studies.

2.2. Adsorption kinetics

A series of sample tubes containing suspension of 0.5 g hematite in 15 mL water were equilibrated at a desired temperature for one hour in a shaking-water-bath (PersonallT-10F, Japan), and calculated amount of adsorbate (3,4-DHBA or catechol) was added to each sample tube. Adsorption kinetics of 3,4-DHBA and catechol onto hematite surface in aqueous medium were investigated by batch method in the presence of 0.05 mM NaCl at pH 5 and four temperatures (288.15, 298.15, 303.15 and 313.15 K), and at pH 10 and 298.15 K. The initial concentration of 3,4-DHBA and catechol and other experimental conditions for kinetics run are noted in the respective figure captions. At different intervals of time, the suspension was filtered through a membrane of $0.2 \mu\text{m}$ pore size. The pH of the suspension was adjusted to six using either dilute NaOH or HCl solution with digital pH metre-335 (Systronics, India). The residual concentrations of 3,4-DHBA

and catechol in the suspension were estimated at $\lambda_{\text{max}} = 282$ and 192.2 nm (absorption maximum) [28], respectively, using UV-visible spectrophotometer (Specord 200, Analytikjena, Germany). The adsorption densities (amount adsorbed per unit surface area), Γ , of 3,4-DHBA and catechol onto hematite surface were estimated by mass balance equation.

$$\Gamma = \frac{(C_0 - C_e)V}{ma} \quad (1)$$

where C_0 and C_e are the initial and residual, at different interval of time, concentrations in mM of an adsorbate in the suspension, V is the total volume of the suspension, and m and a are the mass and surface area of the adsorbent, respectively.

2.3. Adsorption isotherms

Adsorption isotherms of 3,4-DHBA and catechol onto hematite surfaces in the pH range 5–10 were carried out at 298.15 K in screw-capped glass tubes by batch method. A suspension containing 0.5 g hematite and 0.05 mM NaCl solution was agitated using a vortex mixer. The pH of the suspension was adjusted to a desired value. The resultant suspension was equilibrated for 1 h in a shaking-water-bath. The required amount of an adsorbate (3,4-DHBA or catechol) was added and the pH was adjusted, whenever necessary. The suspension was then equilibrated for another 2 h (adsorption equilibration time), and after the reaction time elapsed, the suspension was filtered through a membrane of $0.2 \mu\text{m}$ pore size. The residual concentration of 3,4-DHBA and catechol in the supernatant liquid was estimated as outlined in Section 2.2.

2.4. Dissolution of hematite

The effect of pH and the concentration of 3,4-DHBA and catechol on the dissolution of hematite was studied in the presence 0.05 mM NaCl(aq) at 298.15 K following the adsorption process. The exact concentration of 3,4-DHBA and catechol is noted in the respective dissolution plots. The amount of dissolved Fe^{3+} in the supernatant liquid was estimated with an Atomic Adsorption Spectrophotometer (Aanalyst 100, Perkin-Elmer, USA) using iron flame and oxyacetylene gas at 248.3 nm.

2.5. Diffuse reflectance infrared Fourier transform (DRIFT) spectra

0.5 g hematite was equilibrated individually with 0.5 mM of 3,4-DHBA and catechol for 2 h in the presence of 0.05 mM NaCl at different pH 5–10 and 298.15 K. The suspension was filtered through a membrane of $0.2 \mu\text{m}$ pore size, and the residue was washed once with double-distilled water and dried in a vacuum desiccator over fused calcium chloride. The DRIFT spectra with a resolution of 4 cm^{-1} were recorded with 200 scanning using a FTIR-Spectrum-100 (Perkin Elmer) and KBr as the background.

3. Results and discussion

3.1. Adsorption kinetics of 3,4-DHBA and catechol

Adsorption densities of 3,4-DHBA and catechol onto hematite (0.5 g) surface in the presence of 0.05 mM NaCl(aq) as a function of time at pH 5 and four temperatures are shown in Fig. 1. The adsorption equilibration time for 3,4-DHBA/hematite system was 90 min, whereas it was 120 min for the catechol/hematite system except at 313.15 K. The equilibration time for the catechol/hematite system is ~ 1.3 times higher than the catechol/goethite system, and this difference is expected due to the different surface proper-

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