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Kinetics and adsorption of benzoate and salicylate at the natural hematite–water interface

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Abstract

Kinetics of adsorption of benzoate and salicylate onto the natural hematite surfaces have been carried out at pH 5 and at a fixed ionic strength ($I = 1 \times 10^{-4}$ mol dm^{-3}). The state of equilibrium was attained at 144 and 70 h for benzoate and salicylate, respectively. Adsorption behaviour of benzoate and salicylate onto the natural hematite was studied over a wide range of pH at a fixed $I = 5 \times 10^{-4}$ mol dm^{-3} NaCl and at different temperatures. The adsorption isotherms for both the adsorbates were Langmuir type up to pH 8. The $\Gamma_{\max}$ for benzoate is ≈2.7–13.7 times more than that of salicylate depending on the pH of the suspension. Unlike benzoate, salicylate is not only adsorbed at one surface site but also covers around three or more surface sites of hematite surface. The rate constant for adsorption, K_1 for salicylate onto the natural hematite is greater than that of benzoate and increases with the increase in temperature and ≈4 times greater at a fixed temperature. The activation energy for the adsorption of salicylate onto the natural hematite is 2.9 times more than that of benzoate on the same adsorbent resulting in lower $\Gamma_{\max}$.

Keywords: Adsorption; Benzoate; Kinetics; Natural hematite; Salicylate; Zeta potential

1. Introduction

In the mineral processing industries the use of ionic or non-ionic polymers, surfactant and polyelectrolytes is an essential proposition to liberate and separate minerals from the ore [1–7]. The humic acid or its alkali salt finds application for beneficiation of iron ore fines and slimes [1,7–10]. The interaction between humate and mineral surfaces are not well understood due to its polydispersity, polyfunctionality, polyelectrolytic characteristics and the positioning of the different functional groups [11,12]. Humic substances are supramolecular species composed of humin, humic and fulvic acids, which can be separated according to their solubility in different pH values. The structural investigation using pyrolysis–gas chromatography/mass spectroscopy showed that there are no significant differences between the chemical composition of fulvic and humic acids except fulvic acid has more functional groups [13]. The results also indicated that fulvic and humic acids are built up of aromatic rings with predominately carboxylic and phenolic groups. The simple and well-defined acids like benzoic, salicylic and phthalic acid are the constituting models of the functional groups occurring in humic acid. Therefore, depending on the structure, functionality and the conformational factors, the adsorption profile and the surface complexation are different [14,15].

It is reported that α-Fe_2O_3, unlike α-Al_2O_3, is relatively inert and no oxy (hydroxides) like goethite (α-FeOOH) and lepidocrocite (γ-FeOOH) are formed when exposed to air, humid air and water for 3 months [16]. On the other hand, scanning tunnelling microscopic studies of hematite [17] showed that the uppermost Fe is partially hydrated when exposed in water or humid air due to the chemisorption of water vapour [18]. Therefore, adsorption profile of small organic acids having carboxylic and phenolic groups onto hematite is different

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[14,19] due to increased acidity or for the formation of surface complexes involving all the functional groups [14].

A good amount of work related to adsorption of small organic acids of different polydispersity and functionality [14,15,19–25], humic acid [20,26,27] and polymers [28,29] onto synthetic hematite and goethite is reported. In those papers, the equilibrium time for adsorption was varied from 0.5 to 72 h mostly at room temperature without the kinetic study. The dynamic aspect of adsorption process preferably of small organic molecules onto hematite is not rich [30–32] in the literature in comparison to metal ions on the oxide minerals surfaces [33–35] and the static aspects of adsorption. The adsorption of a metal ion or an organic anion at the oxide water interface depend on the surface loading (ratio of adsorbate to adsorbent), surface site of adsorbent (external edges or interlayer sites), pH of the suspension and background electrolyte. Adsorption of small organic acid is also depends on the functionality and conformational factors. Earlier, it has been reported that the state of equilibrium for α-Al_2O_3–salicylate system was obtained after 2.5 h [36] in comparison to the γ-Al_2O_3–salicylate system where it was 6 h [37]. Further, the adsorption of benzoate and salicylate onto the natural hematite over a wide range of ionic strength and pH have not been studied in detail. In this communication we report the zeta potential of the natural hematite, kinetics of adsorption and adsorption isotherms of benzoate- and salicylate–natural hematite systems.

2. Experimental

2.1. Materials

Natural hematite was washed several times with distilled water, dried and finally activated at ≈700 °C and assayed 99% Fe_2O_3, 0.68% SiO_2 and 0.29% Al_2O_3. Sodium benzoate (>99.5% E. Merck, India), sodium salicylate (>99.5% E. Merck, India), sodium hydroxide (LR grade, S.D. Fine-Chem., India), sodium chloride (AR grade, E. Merck, India) and hydrochloric acid (AR grade, NICE Chemicals, India) were used without further purification.

2.2. Adsorbent

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) (SDT 2960, TA Corporation, USA), X-ray diffraction (XRD) (X'pert Pro, Philips, The Netherlands) and Fourier transform infrared (FTIR) (model-2000, Perkin-Elmer, USA) Spectra of activated natural hematite were recorded. The zeta potential of adsorbent at different pH and ionic strengths was measured using Zetasizer-3000HS (Malvern Instruments, UK). The pH of the suspension of the adsorbent at a fixed ionic strength was initially adjusted at ≈3.0 and the zeta potential was measured with increasing pH of the suspension by adding dilute sodium hydroxide with a multipurpose titrator (DTS 5900, Malvern, UK). The zeta potential was measured at 25 °C and controlled by a PCS software provided by Malvern Instruments, UK. The specific surface area was determined by BET method and was found to be 1.67 $m^2\,g^{-1}$.

2.3. Adsorption kinetics

Kinetics of adsorption of benzoate and salicylate separately onto the natural hematite (0.5 g) in a 15 mL suspension at pH 5 and ionic strength, $I = 5 \times 10^{-4}$ mol dm^{-3} in a batch process were measured at three temperatures. The suspensions at different intervals of time were cooled and centrifuged at 12 500 rpm for 15 min (relative centrifugal force = 28 790 × g). The residual concentration of benzoate and salicylate was estimated at λ_{max} = 224.6 and 296 nm (absorption maximum), respectively, with a Specord 200 (Analytic Zena, Germany). The amount of adsorbate adsorbed per unit surface area of the adsorbent (adsorption density) was estimated by mass balance using the following relation:

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

where C_0 and C_e are the initial and residual concentration of the adsorbate in the suspension; V is the volume of the suspension and m and a the mass and surface area of the adsorbent, respectively.

2.4. Adsorption isotherm

Adsorption of benzoate and salicylate onto the natural hematite was carried out at room temperature in a screw-capped glass tube. A suspension of 15 mL containing 0.5 g natural hematite and 5×10^{-4} mol dm^{-3} NaCl solution was mixed thoroughly with the help of a vortex mixer. The pH of the suspension was adjusted to a desired value within ±0.1 units using either NaOH or HCl solution and then allowed to equilibrate for 1 h. The required amount of sodium benzoate or sodium salicylate was added and the pH of the suspension was readjusted if necessary. The suspension was then allowed to equilibrate with intermittent mixing for 70 and 144 h (duration of equilibrium adsorption test for salicylate and benzoate, respectively). After the reaction period, the suspension was then centrifuged and the residual concentration of benzoate and salicylate was estimated as explained in the previous section.

3. Results and discussion

3.1. Adsorbent

The thermogram (DTA and TGA) of the natural hematite sample shows that there is a small change in the weight (≈0.25%) at around 500 °C. The FTIR spectra show a broad band at 3436 cm^{-1} corresponds to the lateral hydrogen bonding with the hydroxyl group. The two bands at 545 and