

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

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Received 2 July 2004; accepted 26 November 2004

Available online 30 December 2004

## 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 ( $I = 1 \times 10^{-4} \text{ mol dm}^{-3}$ ). 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  $I = 5 \times 10^{-4} \text{ mol dm}^{-3}$  NaCl and at different temperatures. The adsorption isotherms for both the adsorbates were Langmuir type up to pH 8. The  $\Gamma_{\text{max}}$  for benzoate is  $\approx 2.7$ – $13.7$  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  $\approx 4$  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  $\Gamma_{\text{max}}$ .

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**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 chem-

ical 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  $\alpha\text{-Fe}_2\text{O}_3$ , unlike  $\alpha\text{-Al}_2\text{O}_3$ , is relatively inert and no oxy (hydroxides) like goethite ( $\alpha\text{-FeOOH}$ ) and lepidocrocite ( $\gamma\text{-FeOOH}$ ) 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  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>–salicylate system was obtained after 2.5 h [36] in comparison to the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–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  $\approx 700^\circ\text{C}$  and assayed 99% Fe<sub>2</sub>O<sub>3</sub>, 0.68% SiO<sub>2</sub> and 0.29% Al<sub>2</sub>O<sub>3</sub>. 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  $\approx 3.0$  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  $25^\circ\text{C}$  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  $1.67\text{ m}^2\text{ g}^{-1}$ .

### 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,  $I = 5 \times 10^{-4}\text{ mol dm}^{-3}$  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 =  $28\,790 \times g$ ). The residual concentration of benzoate and salicylate was estimated at  $\lambda_{\text{max}} = 224.6$  and  $296\text{ nm}$  (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  $5 \times 10^{-4}\text{ mol dm}^{-3}$  NaCl solution was mixed thoroughly with the help of a vortex mixer. The pH of the suspension was adjusted to a desired value within  $\pm 0.1$  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 ( $\approx 0.25\%$ ) at around  $500^\circ\text{C}$ . The FTIR spectra show a broad band at  $3436\text{ cm}^{-1}$  corresponds to the lateral hydrogen bonding with the hydroxyl group. The two bands at 545 and

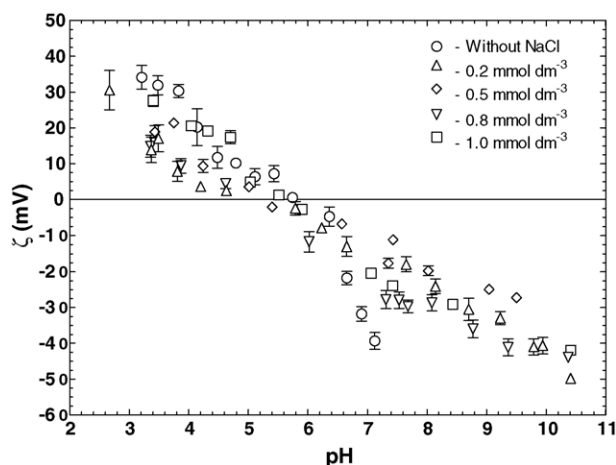


Fig. 1. The zeta potential of natural hematite as a function of pH at different concentrations of sodium chloride.

466 cm<sup>-1</sup> represent the asymmetric and symmetric Fe–O stretching vibration. The bands at 904 and 631 cm<sup>-1</sup> are due to the Al–O stretching vibration and are in agreement with reported values [38]. The  $d$ -values from XRD pattern of the natural hematite are: 3.684, 2.699, 2.520, 1.695, 1.600, 1.486, 1.454, 1.312, 1.259, 1.189, 1.162, 1.141 and 1.103 Å, which are comparable with the reported values of hematite [39]. The  $d$ -values correspond to silica observed at 16.14 Å having relative intensity of 4.4%. For quartz and minerals like aluminosilicate, the  $d$ -values are found at 1.841 and 2.207 Å [39], which also correspond to hematite. The results show that the ore contains predominantly hematite.

### 3.2. Zeta potential

The zeta potential of the natural hematite as a function of pH at different ionic strengths is depicted in Fig. 1. The isoelectric point (IEP) of the natural hematite without adding sodium chloride is 5.80, which is in good agreement with the reported value [40–42]. The IEP of the natural hematite used in the present study is around 3–4 pH units less than the reported value of synthetic hematite [28,41,42]. Such a difference in the IEP is expected due to the presence of impurities like silica (0.08%) [43] and aluminosilicate minerals in iron ore [44]. For example, synthetic hematite at an ionic strength,  $I = 0.01$  mol dm<sup>-3</sup> NaCl has an IEP at pH 7.5 but the mixtures of hematite–montmorillonite and hematite–kaolinite at 1:1 ratio exhibit lower IEP [26], which is due to the interaction with an oppositely charged aluminosilicate minerals and the hematite. On increasing the ionic strength (NaCl) the IEP of the natural hematite decreases by  $\approx 0.8$  pH units, which may be accounted for the weak and specific adsorption of chloride ions. A similar decrease in the IEP of synthetic and commercial hematite has been reported [45], which was accounted for adsorption of chloride ions and release of H<sup>+</sup> due to storage medium.

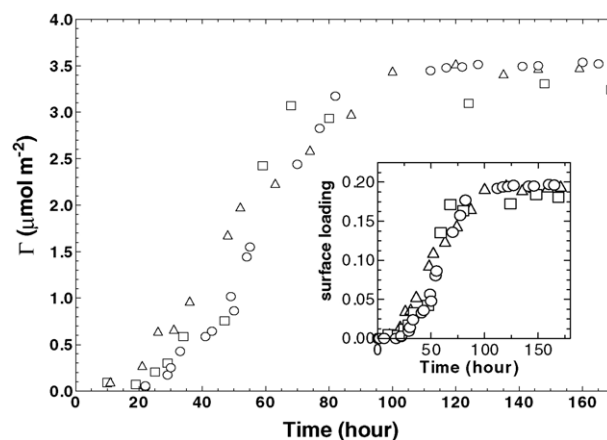


Fig. 2. Effect of temperature on the adsorption of benzoate onto the natural hematite surfaces as a function of time at a fixed initial concentration of sodium benzoate,  $C_0 = 2 \times 10^{-4}$  mol dm<sup>-3</sup>, natural hematite = 0.5 g,  $I = 5 \times 10^{-4}$  mol dm<sup>-3</sup> NaCl,  $V = 15$  mL, pH 5, 27 °C (○), 35 °C (△) and 45 °C (□). Inset: surface loading vs. time at 27 °C (○), 35 °C (△) and 45 °C (□).

### 3.3. Kinetics of adsorption of benzoate and salicylate

The changes in adsorption density with time for benzoate and salicylate on natural hematite for pH 5 and  $I = 5 \times 10^{-4}$  mol dm<sup>-3</sup> NaCl and at three temperatures are shown in Figs. 2 and 3. It is apparent that the state of equilibrium in the case of benzoate is 144 h, whereas it is 70 h for salicylate. To our best knowledge, only one cited work on the kinetics of adsorption of oleate onto the natural hematite (assay 99.3%) [31] is available wherein the state of equilibrium was obtained after 36 min. On the other hand, the equilibration time for synthetic hematite-adsorbates like polyacrylamide [32] and dodecyl benzene sulfonate [30] is 80 and 150 min, respectively. The difference in equilibration time for

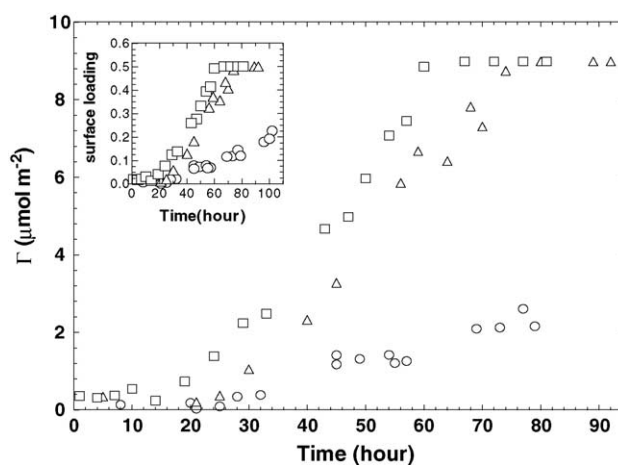


Fig. 3. Effect of temperature on the adsorption of salicylate onto the natural hematite surfaces as a function of time at a fixed initial concentration of sodium salicylate,  $C_0 = 5 \times 10^{-4}$  mol dm<sup>-3</sup>, natural hematite = 0.5 g,  $I = 5 \times 10^{-4}$  mol dm<sup>-3</sup> NaCl,  $V = 15$  mL, pH 5, 20 °C (○), 30 °C (△) and 40 °C (□). Inset: surface loading vs. time at 20 °C (○), 30 °C (△) and 40 °C (□).

Table 1  
Values of adsorption coefficient (from Eq. (3)) and kinetics parameters (from Eq. (2)) for benzoate and salicylate adsorbed onto natural hematite

Temperature (°C)	$K_s$	$K_1$ (h <sup>-1</sup> )
Benzoate		
27	54.4	$2.08 \times 10^{-2}$
35	46.7	$4.53 \times 10^{-2}$
45	34.0	$6.37 \times 10^{-2}$
Salicylate		
20	188.9	$5.94 \times 10^{-3}$
30	38.1	$1.44 \times 10^{-1}$
40	37.8	$2.37 \times 10^{-1}$

the present system is attributed to difference in surface loading. For comparison, increase in surface loading with time for the present systems are shown as an inset in Figs. 2 and 3.

The kinetics of adsorption of benzoate and salicylate on the natural hematite were affected differently by temperature. Benzoate adsorption did not change significantly with temperature from 27 to 40 °C. The extent of adsorption of salicylate, however, was markedly different at 20, 30 and 40 °C and the adsorption density at 40 °C was approximately four times more than that at 20 °C for similar adsorption periods.

The kinetic parameter,  $K_1$  is the rate constant for adsorption, was estimated using the following equation:

$$\frac{1}{C(t)} = \frac{K_1 t}{C_0} + \frac{1}{C_0} \quad (2)$$

where  $C_0$  and  $C(t)$  are the initial concentration and the concentration at time  $t$  of the adsorbate. The derivation of Eq. (2) from the rate expression is reported elsewhere [46] in detail. The estimated value of the parameter  $K_1$  is given in Table 1. The rate constant for adsorption,  $K_1$  for salicylate is greater than that of benzoate and it increases (up to  $\approx 4$  times) with the increase in temperature. The higher value of  $K_1$  for salicylate is due to the difference in functionality of the two adsorbates used in the present study.

The kinetic parameters for adsorption of small anions as used in the present system, onto hematite are not available in the literature. However, the rate constant for adsorption,  $K_1$  for the synthetic hematite–polyacrylamide system [32] at room temperature is  $\approx 2.6 \times 10^{-5} \text{ s}^{-1}$ . From the reported kinetics of the adsorption data for the natural hematite–oleate system [31], the value of the parameter  $K_1$  is estimated to be  $6.0 \times 10^{-4} \text{ s}^{-1}$ .

### 3.4. Adsorption isotherm

Adsorption density of benzoate and salicylate onto natural hematite surfaces at  $I = 5 \times 10^{-4} \text{ mol dm}^{-3}$  and varying the concentration of adsorbate from 0.026 to 1.0 mmol dm<sup>-3</sup> versus equilibrium concentration at 27 and 20 °C is shown in Figs. 6 and 7, respectively. The adsorption isotherms show that the adsorption increases with the increase in concentration of adsorbate even at higher temperature (Figs. 4 and 5). For benzoate, as an adsorbate, the isotherm exhibits two types

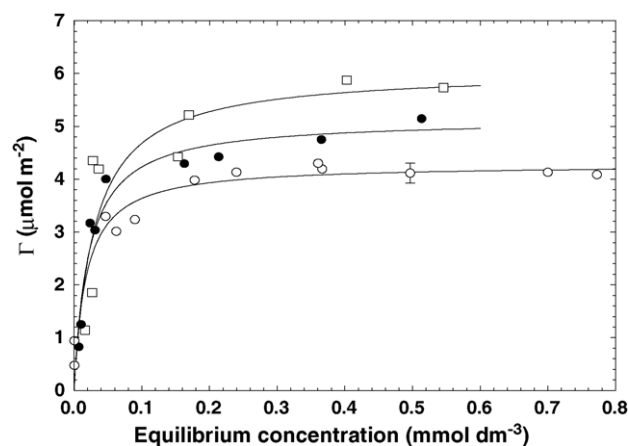


Fig. 4. Adsorption isotherm of sodium benzoate onto the natural hematite at 27 °C (○), 35 °C (●) and 45 °C (□). Natural hematite = 0.5 g,  $I = 5 \times 10^{-4} \text{ mol dm}^{-3}$  NaCl,  $V = 15 \text{ mL}$ , pH 5. The data points are the average of triplicate experiments and an error bar is shown for reference.

of adsorption, up to pH 8 it is Langmuir type and beyond pH 8, the adsorption of benzoate increases with the increases in concentration and no surface saturation could be observed. Whereas, the adsorption in the case of salicylate exhibits Langmuir type up to pH 7 and from pH 8 onwards unlike benzoate there is no adsorption.

The Langmuir adsorption isotherm equation of the following form was used to estimate the adsorption coefficient,  $K_s$

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_{\max}} + \frac{1}{\Gamma_{\max} K_s C_e} \quad (3)$$

where  $C_e$  is the equilibrium concentration of adsorbate (mmol dm<sup>-3</sup>), and  $\Gamma$  and  $\Gamma_{\max}$  are the adsorption density of adsorbate ( $\mu\text{mol m}^{-2}$ ) at equilibrium and after saturation of the natural hematite surfaces, respectively. The estimated values of the  $K_s$  and  $\Gamma_{\max}$  parameters for both the systems

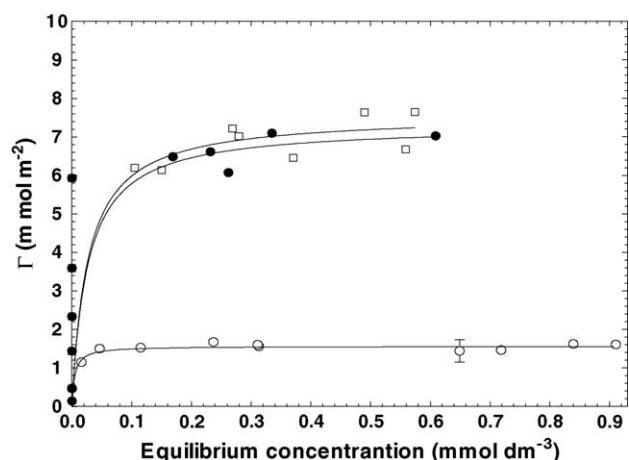


Fig. 5. Adsorption isotherm of sodium salicylate onto the natural hematite at 20 °C (○), 30 °C (●) and 40 °C (□). Natural hematite = 0.5 g,  $I = 5 \times 10^{-4} \text{ mol dm}^{-3}$  NaCl,  $V = 15 \text{ mL}$ , pH 5. The data points are the average of triplicate experiments and an error bar is shown for reference.

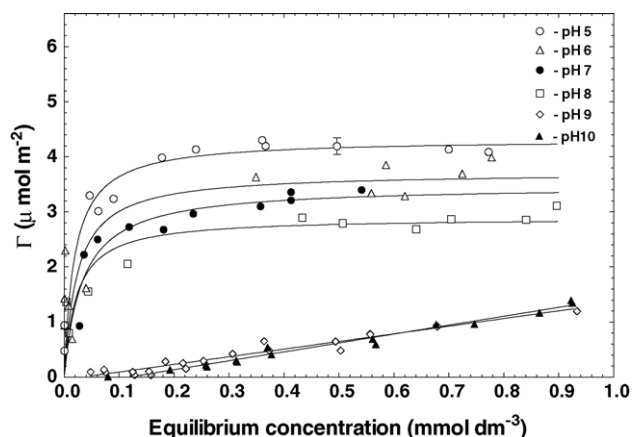


Fig. 6. Adsorption isotherm of sodium benzoate onto the natural hematite at different pH, fixed  $I = 5 \times 10^{-4} \text{ mol dm}^{-3}$  NaCl and at  $27^\circ\text{C}$ . Symbols are the experimental values and the solid lines are theoretical values (Eq. (3)), respectively. The data points are the average of triplicate experiments and an error bar is shown for reference.

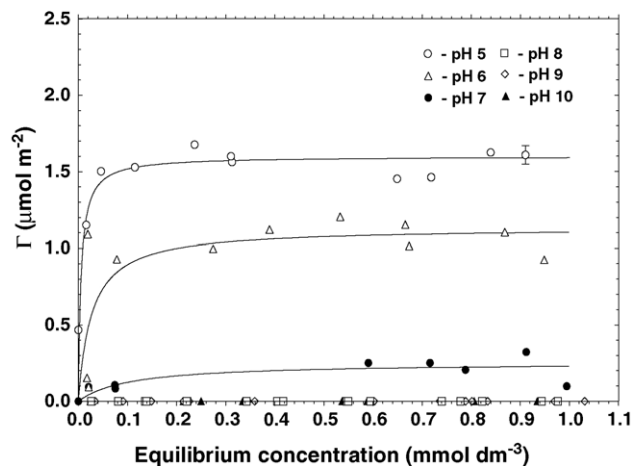


Fig. 7. Adsorption isotherm of sodium salicylate onto the natural hematite at different pH, fixed  $I = 5 \times 10^{-4} \text{ mol dm}^{-3}$  NaCl and at  $20^\circ\text{C}$ . Symbols are the experimental values and the solid lines are theoretical values (Eq. (3)), respectively. The data points are the average of triplicate experiments and an error bar is shown for reference.

using an alternative form of Eq. (3) as  $\Gamma = \Gamma_{\max} C_e / (K + C_e)$ , where  $K = 1/K_s$  are presented in Tables 2 and 3. It is interesting to note that the adsorption density at saturation ( $\Gamma_{\max}$ ) of benzoate onto natural hematite is  $\approx 2.7$ – $13.7$  times more up to pH 7 than that of salicylate in spite of the fact that the salicylate has additional  $-\text{OH}$  group. The reasons could be: the site density of the natural hematite is estimated to be  $10.82 \text{ site nm}^{-2}$ .

Table 2

Values of adsorption parameters as a function of pH for benzoate adsorption on natural hematite

Langmuir parameters	pH			
	5	6	7	8
$\Gamma_{\max}$ ( $\mu\text{mol m}^{-2}$ )	4.307	3.715	3.473	2.895
$K_s$	54.4	42.5	30.2	45.3
S.D.	0.32	0.90	0.37	0.37

Table 3  
Values of adsorption parameters as a function of pH for salicylate adsorption on natural hematite

Langmuir parameters	pH		
	5	6	7
$\Gamma_{\max}$ ( $\mu\text{mol m}^{-2}$ )	1.594	1.133	0.253
$K_s$	188.9	37.2	9.6
S.D.	0.16	0.26	0.06

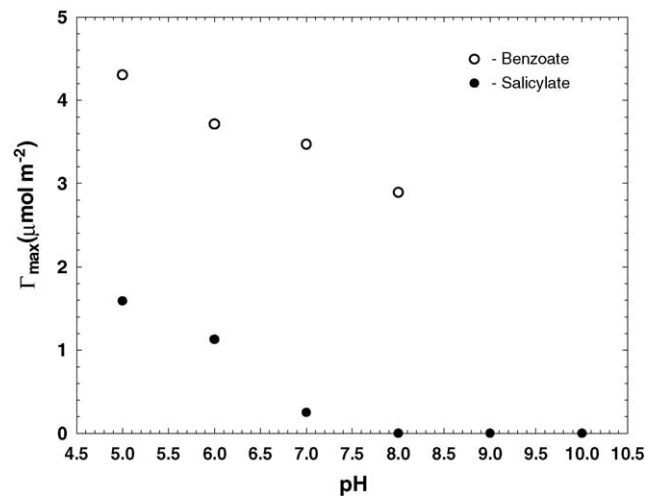


Fig. 8. Effect of pH on  $\Gamma_{\max}$ .

The salicylate is comparatively larger than the benzoate. The salicylate covers around three or more surface sites [47] or the salicylate requires higher activation energy than that of benzoate to cross the energy barrier.

The variation of  $\Gamma_{\max}$  with pH is shown in Fig. 8. The  $\Gamma_{\max}$  for both the systems decreases linearly up to pH 8 due to charge reversibility. The natural hematite for the present study has IEP at pH 5.26 at  $I = 0.5 \text{ mmol dm}^{-3}$  NaCl, it means that the  $\Gamma_{\max}$  should have decreased after pH 5.26. It implies that the hydrogen bond between the surface hydroxyl of the neutral surface and  $-\text{COO}^-$  of the adsorbate plays an important role in the present system [48,49].

### 3.5. Thermodynamic parameters

The activation energy for adsorption,  $E$  for both the systems were estimated using Arrhenius equation,  $K = A e^{-E/RT}$ , where  $K$  is the rate constant for adsorption,  $A$  the frequency factor,  $R$  the gas constant and  $T$  temperature (K). The estimated value of  $E$  and other thermodynamic parameters for the adsorption process are listed in Tables 4 and 5. The results show that the adsorption of benzoate and salicylate on to natural hematite is exothermic, which is more for salicylate system. The activation energy for adsorption of salicylate on to natural hematite is 2.9 times more than that of benzoate, which is accountable for the lower  $\Gamma_{\max}$  (Figs. 6 and 7).

Table 4

Values of the thermodynamic parameters for adsorption of benzoate onto the natural hematite surfaces

Temperature (K)	$E$ (kJ mol <sup>-1</sup> )	$-\Delta H$ (kJ mol <sup>-1</sup> )	$-\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )
300.15			10.0	36.7
308.15	48.6	21.0	9.8	36.2
318.15			9.3	36.7

Table 5

Values of the thermodynamic parameters for adsorption of salicylate onto the natural hematite surfaces

Temperature (K)	$E$ (kJ mol <sup>-1</sup> )	$-\Delta H$ (kJ mol <sup>-1</sup> )	$-\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )
293.15			12.8	168.1
303.15	141.8	62.0	9.2	174.4
313.15			9.4	168.0

#### 4. Conclusions

The present study highlights the following points:

- (1) The time for the state of equilibrium for the natural hematite–benzoate system is  $\approx 2$  times more than that of natural hematite–salicylate system.
- (2) The rate constant for adsorption of salicylate at the natural hematite–water interface is  $\approx 4$  times greater than that of benzoate at a fixed temperature.
- (3) The adsorption isotherms for both the systems are Langmuir type up to  $\approx \text{pH } 8$ .
- (4) The adsorption density of benzoate at the saturation point onto the natural hematite is around 2.7–13.7 times more than that of salicylate up to pH 7.
- (5) The activation energy for adsorption of salicylate at the natural hematite–water interface is higher in comparison to benzoate.
- (6) The lower value of  $\Gamma_{\text{max}}$  for the natural hematite–salicylate system is due to the activation energy and coverage of more than one surface site by salicylate.

#### Acknowledgements

The authors are grateful to the Department of Science and Technology, New Delhi, for the grant-in-aid. The authors are also thankful to the Director, Regional Research Laboratory, Jorhat, for the facilities and interest in the work. The authors are also grateful to the anonymous reviewers for the suggestions for revision.

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