

Adsorption of *N*-hydrocinnamoyl-*N*-phenylhydroxylamine on pure minerals

Ramanathan Natarajan · Jatin Sharma ·
Inderjit Nirdosh

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Abstract Equilibrium adsorption studies of *N*-hydrocinnamoyl-*N*-phenylhydroxylamine (HCNPHA) on galena, sphalerite, pyrite, chalcopyrite and quartz at pH 9 and 10 are reported. All adsorption isotherms followed Langmuir model, however, Freundlich type was observed for quartz. As HCNPHA is a strong chelating agent, formation of monolayers by chemisorption appeared to be the most probable mechanism of adsorption on the base-metal sulphide minerals. Specific adsorption of HCNPHA on iron containing minerals, namely, chalcopyrite and pyrite, was about three times that on galena and sphalerite, and specific adsorption on quartz was the lowest amongst the minerals studied. Specific adsorptions (in $\mu\text{mol/g}$) of HCNPHA on the minerals at pH 9 are: sphalerite: 30.5; galena: 26.9; chalcopyrite: 112.3; pyrite: 145.4; quartz: 2.9. Compared to pH 9, specific adsorption of HCNPHA on the minerals decreased at pH 10, indicating hydroxylation of mineral sites due to higher hydroxide ion concentration at pH 10. A spectral-colorimetric procedure was developed for the quantitative estimation of HCNPHA. Due to deprotonation of hydroxamic acids direct estimation using UV absorption was not possible. Hence, complexation of HCNPHA with Fe^{3+} was used to develop a purple coloured complex that absorbs in the visible region with $\lambda_{\text{max}} = 500$ nm. Change in concentration of HCNPHA was measured from absorbance of the HCNPHA- Fe^{3+} complex at 500 nm.

Keywords Hydroxamic acids · Pure minerals · Adsorption · UV spectra · Mineral processing

1 Introduction

Hydroxamic acids are *N*-acyl derivatives of hydroxylamine (NH_2OH) and act as bi-dentate ligands to complex with several metal ions (Fig. 1). Their ability to form stable complexes with transition, lanthanide and actinide metal ions extends their application in different areas such as analytical chemistry, spectral-colorimetric analyses, solvent extraction and mineral processing (Agrawal 1979; Agrawal and Tandon 1974; Barocas et al. 1966; Baroncelli and Grossi 1965; Chatterjee 1978; Inoue et al. 2000; Lutwick and Ryan 1954; Natarajan and Nirdosh 2006; Pradip and Fuerstenau 1983; Saha et al. 2002; Shendrikar 1969; Yale 1943)). A large number of articles are published on the chemistry of hydroxamic acids and their metal chelates (Agrawal 1977, 1979; Agrawal and Kapoor 1977; Agrawal and Tandon 1974; Chatterjee 1978; Majumdar 1972; Verma et al. 1977; Yale 1943).

Hydroxamic acids have higher pK_a than those of the corresponding carboxylic acids and consequently are more selective than carboxylic acids (Agrawal 1979). As shown in Fig. 1, hydroxamates are O-O type ligands and the amine nitrogen is not involved in chelation. *N*-alkylhydroxamates have been tested as non-thiol chelating collectors for the

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R. Natarajan · J. Sharma · I. Nirdosh (✉)
Department of Chemical Engineering, Lakehead University, 955
Oliver Road, Thunder Bay, Ontario, P7B 5E1, Canada
e-mail: inirdosh@lakeheadu.ca

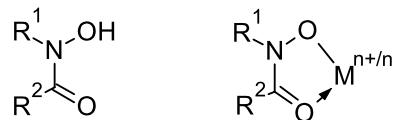


Fig. 1 Generic structures of hydroxamic acids and their metal chelates

flotation of non-sulphidic ores such as oxidized copper minerals and rare earth minerals (Barbaro et al. 1997; Pradip and Fuerstenau 1983; Raghavan and Fuerstenau 1975a, 1975b; Urbina 1985). They were also used in the beneficiation and purification of clay (Yoon et al. 1992). Marabini (1993) tested *N*-phenylbenzohydroxamic acid (NBPHA) for the flotation of rutile.

Various *N*-arylhydroxamic acids were synthesized and tested in the flotation of sphalerite from a Cu-Zn ore as well as Pb-Zn ore by Natarajan et al. (2001, 2006). Sphalerite was floated without the addition of copper sulphate for surface activation. Though this is a very attractive finding, concomitant flotation of pyrite and silica placed a major limitation on the commercial application of these reagents. Out of the 31 hydroxamic acids tested, *N*-hydrocinnamoyl-*N*-phenylhydroxylamine (HCNPHA) gave the best results (80% zinc recovery into 27% weight of the feed). In the current mill practice using xanthates as collectors, addition of copper sulphate for sphalerite activation is very essential. Elimination of copper sulphate addition in the beneficiation of zinc ores is very attractive as it reduces the manufacturing cost, equipment corrosion, and toxicity of the mill effluents.

In order to find the optimum conditions for selective flotation of sphalerite without co-flotation of pyrite, HCNPHA was selected as a model compound to study the adsorption of *N*-arylhydroxamic acids on pure minerals namely chalcopyrite, galena, pyrite, quartz and sphalerite. The results of adsorption equilibrations of HCNPHA on pure minerals are reported in this paper. A spectral-colorimetric method was standardized for the quantitative estimation of HCNPHA using its coloured Fe^{3+} complex.

2 Materials and methods

2.1 Adsorbate: HCNPHA

HCNPHA was synthesized following the reported procedure (Tandon and Priyadarshini 1967) and crystallized from ethanol-water mixture (3:1 v/v). Purity of synthesized chemical was ascertained by C, H, N elemental analysis and spectroscopic methods ($^1\text{H-NMR}$ and mass spectral analyses). Stock solutions of HCNPHA were prepared by dissolving appropriate amounts in de-ionized water at pH 9 and 10 adjusted with sodium hydroxide.

2.2 Adsorbents: minerals

Pure minerals, namely, chalcopyrite (CuFeS_2), galena (PbS), pyrite (FeS_2), quartz (SiO_2) and sphalerite (ZnS) were bought from the Ward's (Ward's Natural Science Establishment, Inc., St Catharines, Ontario, Canada). Big pieces of each mineral sample were crushed with hammer and the

smaller pieces, handpicked under light microscope, were grinded using a mechanical mortar and pestle with an agate medium. Mineral particles of size $< 75 \mu\text{m}$ were used for adsorption studies. Purities of the grinded mineral samples were obtained from the *d*-spacing of the powder X-ray diffraction. The minerals were found to be more than 90% pure and the percentage purity of the minerals used in the study were: sphalerite: 92% (with 8% quartz); galena: > 99%; pyrite: 95% (with 2% quartz and, 3% bornite); chalcopyrite: 98% (with 2% pyrite).

Before conducting the adsorption tests, 1 g each of the five minerals was agitated overnight with 35 mL of distilled and de-ionized water to verify whether any compounds formed due to surface oxidation of the minerals during storage leached out into water. The solution was filtered and analysed by Inductively Coupled Argon Plasma Atomic Emission Spectrometry (ICAP). No detectable amounts of any metal ions were found in filtrates. However, pyrite was an exception to this observation. The filtrate obtained after agitating in water overnight with pyrite was detected to have 20 ppm iron. This might be due to the dissolution of any oxidation product such as iron sulphate formed on the surface of pyrite due to weathering. Because the adsorbate, HCNPHA, would complex with any metal ion in solution and this would interfere with the adsorption study, pyrite was washed with 0.1 N hydrochloric acid several times and then washed thoroughly with water before use. The wet pyrite thus obtained was used immediately without drying and the percentage of moisture in the sample was determined by drying a weighed portion. Freshly cleaned pyrite was used for all equilibrium adsorption studies.

2.3 Procedure for adsorption

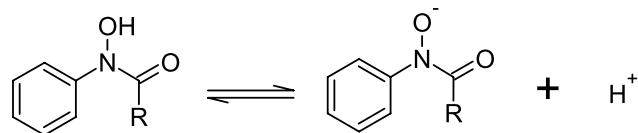
Adsorption tests were conducted at pH 9 and 10 to be consistent with the pH values used in the flotation studies conducted by Natarajan et al. (2001, 2006). Several solutions of HCNPHA were prepared at appropriate concentrations and pH values with distilled, de-ionized water. Aliquots of 30 mL of each of the HCNPHA solutions were added individually to 50 mL conical flasks that contained the same mass of adsorbent (galena, chalcopyrite, quartz, sphalerite or pyrite). A blank test was run with the same mass of the adsorbent and the same volume of deionized water, and the supernatant from the blank was used in the reference cell of the UV spectrometer during colorimetric analysis. All the flasks were stoppered and shaken at room temperature for 4 h at 200 rpm in a table top shaker (Max 2000, Barnstead Lab-Line). The solutions were allowed to stand overnight for settling and also to ensure equilibrium had been established (please see Sect. 3.2 for equilibration time). From each of the HCNPHA stock solutions, 10 mL aliquots were pipetted into conical flasks (50 mL capacity) which were stoppered and left undisturbed on the bench at room temperature

for the same duration for which the adsorption tests were conducted on the shaker. This was followed to take into account any thermal or photochemical decomposition of HCNPHA that might have taken place during experimentation. It was also confirmed that 500 ppm HCNPHA solution at pH 9 did not decompose to detectable levels by recording the UV spectrum at various time intervals up to 72 h. Each equilibrated solution was filtered through a 0.45 μm Millipore filter paper and then analyzed following the spectral-colorimetric procedure explained in Sect. 3.1. Concentrations of the feed solution and the filtrate (equilibrated solution) after adsorption were obtained from the absorbance of the coloured iron(III) complex at 500 nm. Thus, depletion in concentration of HCNPHA was determined by the difference between the initial and the residual equilibrium concentrations of the solutions. This gave the amount of HCNPHA adsorbed on the adsorbent.

3 Results and discussion

3.1 Spectral-photometric procedure for the quantitative estimation of HCNPHA

Dissociation equilibrium of *N*-phenylhydroxamic acids is given below:



The relative concentration of the species in solution is pH dependant and this was indicated by the UV spectrum of HCNPHA recorded for different buffered solutions from pH 3.6 to 13 and 1 N NaOH (Fig. 2a). In order to verify the deprotonation equilibrium, UV scans of *N*-benzoyl-*N*-phenylhydroxylamine (NBPHA) were recorded. A typical set of UV scans of NBPHA is given in Fig. 2b to illustrate the shift in λ_{max} and the pH at which the transition takes place. A shift in λ_{max} was observed beyond pH 8 indicating the complete shift in the dissociation equilibrium to the right hand side. The bathochromic shift (red-shift) indicated the formation of the hydroxamate ion which absorbed at lower energy due to the availability of non-bonding electron in the anion. The pH corresponding to the change was around 9 and this is near the pK_a of several *N*-arylhydroxamic acids (Agrawal 1979). The UV spectroscopic studies showed the pH dependence of the absorption band. Hence, direct estimation of HCNPHA using UV absorption (as carried out by Muthuswami et al. 1985 for a similar study using cupferron) appeared to be unsuitable in the present study. Hydroxamic acids are known to form highly coloured complexes

with metal ions such as copper(II), iron(III), vanadium(V) (Agrawal 1979; Chatterjee 1978). This was taken advantage of and HCNPHA was estimated spectral-colorimetrically using its complexation with Fe^{3+} ion based on an earlier report (Armour and Ryan 1957) The iron(III) complex of the model compound, HCNPHA, used in the adsorption study was found to have a strong absorption band in the visible region (λ_{max} at 500 nm). For comparison four other *N*-arylhydroxamic acids were tested (UV spectra of iron(III) complexes of five *N*-arylhydroxamic acids are given (Fig. SI-1 to Fig. SI-5) in the supplementary information freely available at the journal website) and in all the cases the λ_{max} was found to be around 500 nm. However, a slight shift from 500 nm was observed (see Fig. SI-6 in supplementary information) due to the electronic nature of substituents in the aryl groups. These results are given in supplementary material, entitled *UV spectra of iron(III) complexes of N-arylhydroxamic acids*. UV-spectra of HCNPHA- Fe^{3+} complex for various concentrations of HCNPHA are shown in Fig. 3. Based on the above, absorbance of the coloured complex at 500 nm was used for quantitative estimation of HCNPHA. Solutions of HCNPHA- Fe^{3+} complex for spectrالcolorimetric analyses were prepared as described below:

To 10 mL HCNPHA solution (a standard solution for calibration or the filtrate of an equilibrated solution after adsorption), 5 mL ethyl alcohol (85%) and 10 mL FeCl_3 solution (1000 ppm) at pH 2.0 were added. Ethanol was added to keep hydroxamic acid in solution without getting precipitated due to the change in pH from basic to acidic range. The calibration curves obtained on several repeated trials had R^2 value (variance) > 0.99 . The calibration was repeated several times for concentrations ranging from 10 ppm to 500 ppm, and was found to give highly reproducible results.

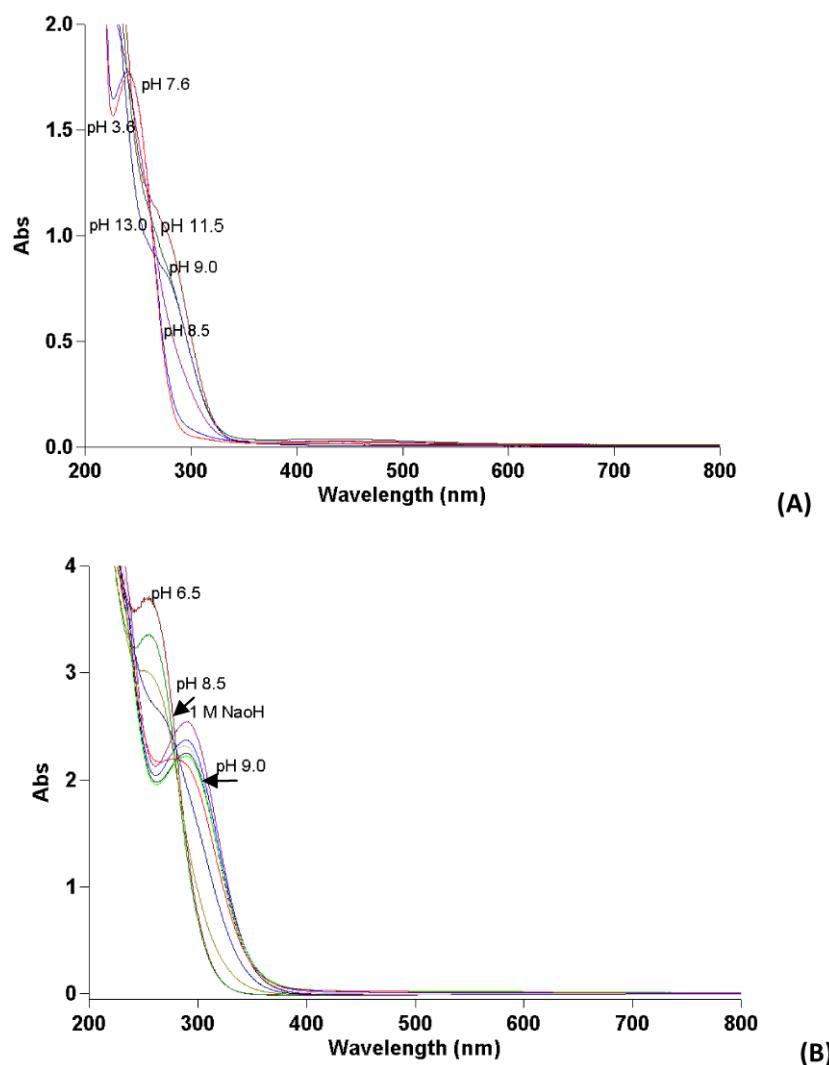
3.2 Equilibration time for adsorption

It is important to know the time needed for adsorption to attain equilibrium. Specific adsorptions of HCNPHA (adsorption densities in mg/g) on different minerals were plotted against time (Fig. 4). It was found that the minimum equilibration time was less than 30 min for minerals used in the study. However, pyrite was an exception and it required about 100 min to attain equilibration. In the current study, solutions were agitated on a shaker at ambient room temperature for 4 hours and left overnight assuming that this time was sufficient to attain equilibrium.

3.3 HCNPHA adsorption on minerals

Specific adsorption of HCNPHA on different minerals is given in mg of adsorbate (HCNPHA) adsorbed per g of adsorbent (mineral). Figure 5 shows the adsorption isotherms

Fig. 2 Effect of pH on UV absorption of HCNPHA (a) and NBPHA (b)



at pH 9. It may be noted that each trial (datum) was repeated twice to ensure reproducibility. If the error between two trials was more than 2%, then the experiment was duplicated to get a data point in an adsorption isotherm such that the error was $\leq 2\%$ with the duplicate. The adsorption isotherms were obtained by curve fitting the adsorption data using the software Origin Pro 8.0. Different adsorption models were used for curve fitting and the model that gave the best fit (highest correlation coefficient, r) was considered the adsorption model followed by the experimental data. Except for the adsorption data for quartz, all the other were fitted well using Langmuir equation and the correlation coefficients were the highest for the Langmuir model ($r > 0.9$).

Adsorption isotherm for quartz fitted better using Freundlich ($r > 0.9$) model than with Langmuir model ($r < 0.75$). Specific adsorption of HCNPHA on different minerals decreased in the order pyrite > chalcopyrite > sphalerite \geq galena > quartz. Chelating agents adsorb on

mineral surfaces by three possible mechanisms namely- chemisorption, surface reaction and bulk precipitation. Chemisorption involves bonding of the chelate molecules with the metal cations that do not move from their crystal lattice position. On the other hand, surface chemical reaction leads to displacement of metal cations from the lattice positions due to the bonding with the chelating agent. If the solution conditions of the mineral system are such as to promote dissolution of mineral surface, the chelating agent would react with the metal ions in solution to form a metal chelate complex that would precipitate at the interface. Hydroxamic acids are strong chelating agents and are almost completely ionized near the pH of their pK_a (~ 9). Hence, at pH 9 or 10 they can adsorb on mineral surfaces by any of these mechanisms. Chemisorption seems to be the most probable mechanism of adsorption of HCN-PHA on galena, sphalerite, chalcopyrite and pyrite because dissolution of metal ions from mineral surfaces is significantly low at pH 9 and 10. In chemisorption, each surface

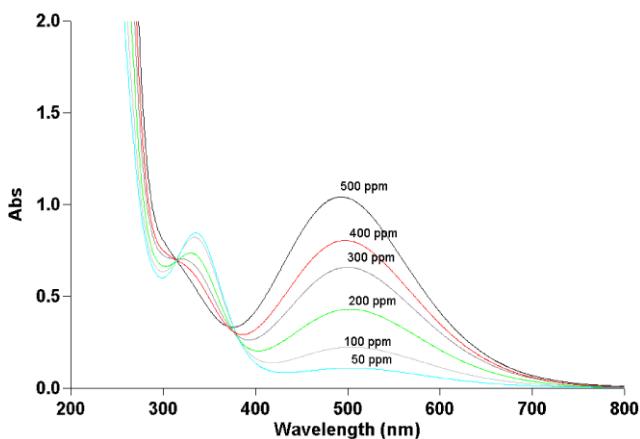


Fig. 3 UV spectra of HCNPHA-Iron(III) complex at various concentrations of HCNPHA (the band at 329 nm is due to FeCl₃). 10 mL HCNPHA solution (at concentration mentioned on each of the spectra) was complexed with 10 mL of 1000 ppm iron(III) chloride and 5 mL alcohol was added

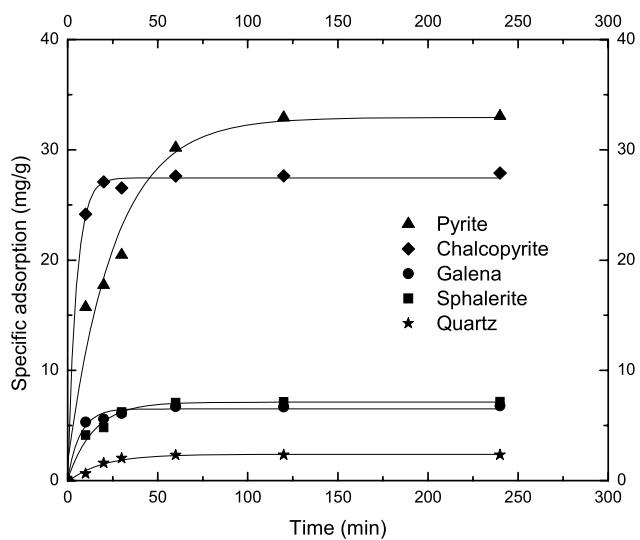


Fig. 4 Equilibration time for different minerals

metal ion site chelates to a single chelating reagent molecule (HCNPHA) leading to the formation of a monolayer of adsorption. This was further confirmed by the L-type curves (Giles et al. 1960) which again indicated the formation of monolayers. Hence, surface reaction and bulk precipitation which lead to the formation of multilayers seemed to be least probable. It is worthwhile to refer to the classification of isotherms by Giles and coworkers. They classified the adsorption isotherms based on the initial slope and the shape of the upper parts of the curves into four types namely, S, L (Langmuir type), H (high affinity) and C (constant partition) isotherms. As hydroxamate ions are very strong ligands and are known to form stable complexes with transition metal ions, surface chelation on the cations of the minerals lead to monolayer formation. Hy-

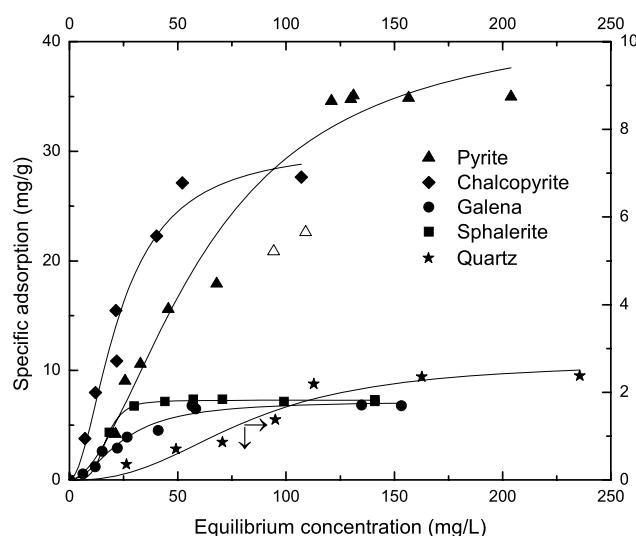


Fig. 5 Adsorption isotherms at pH 9 (for pyrite the two data points (Δ) were not included in curve fitting)

droxylation of mineral cation is an intermediate step that controls the overall mineral-hydroxamate interaction. Unlike other minerals, there are no metal ions in quartz and therefore, only weak interactions between HCNPHA and quartz might have led to the adsorption of HCNPHA. Such weak interactions could not lead to close packed configuration of hydroxamate groups on the surface and thus, the mechanism of adsorption of HCNPHA on quartz appears to be different from that of the other sulphide minerals.

In the case of pyrite and chalcopyrite, no reasonable amount of adsorbate was left in solution at low concentrations indicating very strong adsorbate interaction. The data points in their isotherms were obtained by using reduced masses of the adsorbent. Based on this, it may be concluded that the isotherms for iron containing minerals belonged to the classification H-type rather than L-type (Giles et al. 1960). As mentioned above the L-type isotherm stands for Langmuir type where the adsorption follows Langmuir model and is governed by monolayer formation. H-type is a special case of L-type, in which the solute has high affinity for adsorbate and in dilute solutions it is completely adsorbed and there is no measurable residual amount left in the solution. Hence, the initial part of the isotherms is vertical. During the equilibration studies using pyrite and chalcopyrite for low concentrations of HCNPHA no detectable amount of HCNPHA was left behind. Hence, the experiments were repeated by using smaller amount of solids. This clearly indicated high affinity of HCNPHA for iron containing minerals. The results also indicated highest specific adsorption for pyrite and chalcopyrite among the minerals studied (see Table 1).

Table 1 Comparison of specific adsorption ($\mu\text{mol/g}$) / adsorption density ($\mu\text{mol/m}^2$) of octylhydroxamates and cupferron on minerals with the results of the present study

Adsorbent	Adsorbate	pH	Conc. (mmol/L)	$\mu\text{mol/g}$	Reference
Hematite ($0.5 \text{ m}^2/\text{g}$)	Octylhydroxamate	7.5	1.0	5	Raghavan et al. (1975a, 1975b)
Malachite ($< 3 \mu\text{m}$)	Octylhydroxamate	6.6	0.11	113	Lenormand and Salman (1979)
Chrysocolla ($< 75 \mu\text{m}$)	Octylhydroxamate	9.0	0.17	415.0	Urbina (1985)
			1.13	685.0	
Calcite ($2.15 \text{ m}^2/\text{g}$)	Octylhydroxamate	9.0	0.6*	1.7 ($\mu\text{mol/m}^2$)	Pradip and Fuerstenau (1983)
Barite ($2.4 \text{ m}^2/\text{g}$)	Octylhydroxamate	9.0	1.0*	1.3 ($\mu\text{mol/m}^2$)	Pradip and Fuerstenau (1983)
Chalcopyrite ($< 37 \mu\text{m}$)	Cupferron	7.0	1.0	1.8	Prabhakar and Khangaonkar (1982)
Pyrite ($< 37 \mu\text{m}$)	Cupferron	7	1.1	50	Muthuswami et al. (1985)
			10	225	
Quartz ($< 37 \mu\text{m}$)	Cupferron	7	1.0	0.13	Muthuswami et al. (1985)
			10	1.3	
Sphalerite ($< 75 \mu\text{m}$)	HCNPHA	9	0.24	30.5	
		10	0.25	10.0	
Galena ($< 75 \mu\text{m}$)	HCNPHA	9	0.24	26.9	
		10	0.27	8.8	
Pyrite ($< 75 \mu\text{m}$)	HCNPHA	9	0.54	145.4	Present Work
		10	1.45	119.5	
Chalcopyrite ($< 75 \mu\text{m}$)	HCNPHA	9	0.22	112.3	
		10	0.22	90.4	
Quartz ($< 75 \mu\text{m}$)	HCNPHA	9	0.20	2.9	
		10	0.24	0.7	

*Feed concentration

3.4 Effect of pH

Adsorption isotherms at pH 10 are given in Fig. 6 and they were similar to those obtained at pH 9 for each of the corresponding minerals. Similar to results obtained at pH 9, isotherms corresponding to adsorption on sphalerite, galena, chalcopyrite and pyrite followed Langmuir type plot while that for quartz followed Freundlich type plot. Specific adsorptions of HCNPHA on different minerals at pH 9 and pH 10 are given in Table 1. Specific adsorptions were lower at pH 10 owing to the hydroxylation of cations of the minerals at ten-fold higher OH^- concentration.

3.5 Comparison of various specific adsorptions

Specific adsorptions of HCNPHA obtained in the present study are compared (Table 1) with those of octylhydroxamates on copper and iron minerals (see Table 1). Specific adsorption of cupferron on chalcopyrite, pyrite and quartz

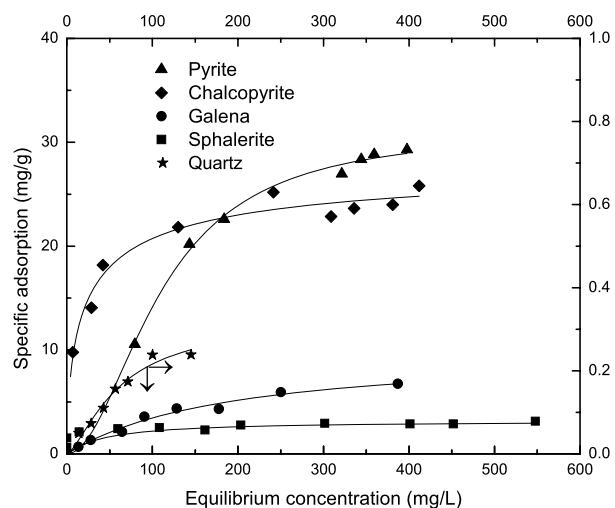


Fig. 6 Specific adsorption of HCNPHA on minerals at pH 10

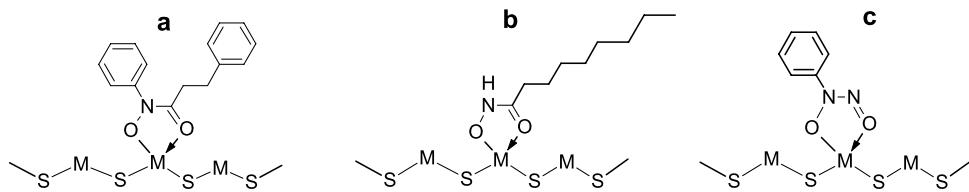


Fig. 7 Schematic representation of chemisorption on a sulfide mineral ($M = \text{metal}$; $S = \text{sulphur}$) surface by chelating collectors (crystal structure of the mineral is not included): (a) HCNPHA, (b) octylhydroxamic acid, (c) cupferron

are also included because cupferron is also an O-O type chelating agent and was found to float sphalerite without copper sulphate activation of the surface (Natarajan 1995; Natarajan et al. 1997; Nirdosh and Natarajan 2002). Specific adsorption of octylhydroxamate on copper minerals such as malachite (at pH 6.6) and chrysocolla (at pH 9) reported in literature (Table 1) are comparable to the specific adsorption of HCNPHA on chalcopyrite observed in the present work. Adsorption of HCNPHA on quartz was found to be the least in the current study and this is similar to the adsorption of cupferron on quartz (at pH 7, Muthuswami et al. 1983) and that of octylhydroxamate on calcite and barite (at pH 9, Pradip and Fuerstenau 1983). This observation is of great importance in the flotation of base-metal sulphide ores because they usually contain barite, calcite and quartz as gangue minerals. The orders of magnitudes of specific adsorptions are comparable among the results obtained in the present study and those reported in the literature. In the case of hydroxamates (octylhydroxamates and HCNPHA), low concentration of adsorbate was enough to attain specific adsorption almost equal to that of cupferron. In the case of octylhydroxamate and HCNPHA, several mineral cation sites might be masked for any adsorption to take place owing to the bigger hydrocarbon part of their molecules. On the other hand, chemisorption of cupferron on a mineral surface leaves most of the mineral sites available for adsorption. This is schematically shown in Fig. 7, and while depicting the chemisorptions on sulphide minerals coordination number the metal sites (M) and the crystal structure are not considered. Relatively smaller size of cupferron was attributed to the large consumption of cupferron in floating a uranium ore (Muthuswami et al. 1983, 1985).

4 Conclusions

HCNPHA was found to adsorb on base-metal sulphides via chemisorptions. This may be due to the almost complete deprotonation of the hydroxamic acid at pH 9 and 10 which are near the pK_a . Specific adsorptions of HCNPHA on all minerals studies were found to be lower at pH 10 than that at pH 9. This might be due to hydroxylation of mineral sites at higher OH^- ion concentration. Among the sulphide minerals studied, iron containing minerals were found to have

very high specific adsorption and this appeared to be due to the high affinity between iron and hydroxamates. Adsorption of HCNPHA on quartz was nearly one-tenth of that on sphalerite and galena. These observations indicate that in the flotation of galena or sphalerite using HCNPHA, pyrite needs to be suppressed and no silica suppressant would be required. Consumption of HCNPHA as a flotation collector will be low as high specific adsorptions were obtained at lower adsorbate concentrations.

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