



Adsorption of tetradecylamine on quartz and its implication on flotation

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Abstract

The paper in hand deals with the adsorption characteristics of tetradecylamine on quartz surface that was investigated using Fourier transform infrared spectroscopy/energydispersive spectroscopy (SEM-EDS) analyses. The spectroscopic data were correlated with adsorption and flotation results. UV–Visible analysis was applied on a clear supernatant solution attained after solid–liquid separation at the end of adsorption, while FTIR and SEM–EDS were implemented to the dried adsorbent quartz. Moreover, in order to collate enough data on carbonate fluorapatite thermal stability with respect to chemical composition and structural parameters, the carbonate fluorapatite ore was subjected to a detailed thermogravimetry/differential scanning Calorimetry (TG-DSC) analysis. The TG-DSC analysis displays an exothermic pic at 700 °C attributed to the decomposition of carbonates, such as dolomite and calcite, and an endothermic pic at 780 °C indicating the beginning of formation of a new phase. The results indicate that the state of adsorbed tetradecylamine at quartz surface varies significantly at weak pH values. The adsorption was found to be prominent within a pH range of 8–8.5. The qualitative adsorption results were validated by quantitative analysis on quartz. The findings revealed better correlations with quartz and fluorapatite flotation tests. The overall results proved that tetradecylamine is an efficient quartz collector with resilient performance.

Keywords Quartz · Tetradecylamine adsorption · UV–Visible spectrometry · FTIR and SEM–EDS spectroscopy · TG-DSC · XRD diffraction · Flotation

Introduction

Quartz is considered as an impurity in many ores; hence, its removal can solve a lot of quartz supply problems in various fields. Reverse flotation is the utmost renowned approach for the treatment of phosphate ore containing quartz gangue minerals. According to the literature, long chain primary amines and particularly their salts are considered as furthestmost important for the quartz separation by flotation, especially in the separation of silicates from phosphate ores. This process was studied by electrokinetic, contact angle,

and flotation recovery measurements (Kou et al. 2010; Chernyshova et al. 2000; Fuerstenau and Jia 2004; Lubisi et al. 2017). Cationic collectors act on the mineral surface of quartz to form a thin nonpolar film that does not react with the water dipoles and can be only formed either physically or chemically through the combination of reagents ions with the unsaturated mineral.

Recently published studies of amine adsorption compartment were undertaken using atomic force microscopy (Zhang et al. 2007), Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) (Lima et al. 2005; Chernyshova and Hanumantha 2001; Bijsterbosch 1974), frequency vibration spectroscopy, UV–Visible spectrometry (Wang et al. 2010; Zhong and Jang 2011) and SEM–EDS spectroscopy (Bu et al. 2017). Density functional theory (DFT) is computational method can be used to study the adsorption behavior of amines on quartz surface and can provide valuable information about the chemical properties of adsorbate-surface systems in flotation process. DFT calculations can be used to predict the energies of interaction

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between the amine molecules and the quartz. Additionally, DFT calculations can also be used to explore the mechanism of adsorption, including the orientation of the adsorbate molecules on the surface (Wang et al. 2018; Rath et al. 2014).

Our earlier study of the two-stage reverse flotation process to remove dolomite and quartz from phosphate ore using fatty acids and mixed amines found that an optimum balance in terms of grade and recovery could be achieved. The first stage includes fatty acids for dolomite flotation; the second stage includes a mixture of amines such as dodecylamine, tetradecylamine and hexadecylamine for quartz flotation (Amirech et al. 2018). Carbonate flotation followed by quartz flotation is an effective way to remove carbonates and quartz minerals from phosphate ores, but calcination of phosphate ores followed by quartz flotation is an important process for the production of high-quality phosphate products. The removal of carbonates and separation of quartz minerals from phosphate ore can improve the purity and value of the final product. Calcination is a process that removes carbonates from phosphate ore.

Carbonate flotation followed by quartz flotation is an effective way to separate carbonate and quartz minerals from phosphate ores (Amirech et al. 2018); however, the calcination of phosphate ores followed by quartz flotation is an important process for producing high-quality phosphate products. By removing carbonates and separating the quartz minerals from phosphate, this process can improve the purity and the value of the final product. Carbonates such as calcite and dolomite are common impurities in phosphate and can reduce the quality of the final product. Calcination of phosphate ore followed by flotation can result in several benefits compared to flotation only. Some of these benefits include higher purity, increased recovery of the phosphate minerals by reducing the interference of carbonates with flotation process, and reduced reagent consumption and higher purity of phosphate concentrate. After calcination of phosphate ore, the next step is quartz flotation, which separates the quartz from phosphate. Quartz flotation is carried out using cationic collectors as amines, which selectively adsorb onto the surface of the quartz particles allowing them to be separated from the phosphate ore by flotation.

The current investigation concentrated mainly on the study of the adsorption of tetradecylamine on quartz and its application in reverse flotation process in order to remove quartz from phosphate ore. The adsorption mechanism at pH range 7.6 – 8.5 was studied using FTIR, UV–Visible and SEM–EDS spectroscopy so as to obtain complementary results. The clear supernatant solution obtained after solid–liquid separation at the end of adsorption was investigated using UV–Visible analysis, while FTIR and SEM–EDS spectroscopy were applied to the dried adsorbent quartz. The identification of the carbonate apatite

mineral was achieved by means of XRD Bruker diffractometer (AXS-8D) functioning at 45 kV with CuK α radiation (1.5406 Å). Moreover, thermal analysis of carbonate fluorapatite ore was performed by thermogravimetry/differential scanning calorimetry (TG-DSC) using NETZSCH STA 449 F3 JUPITER.

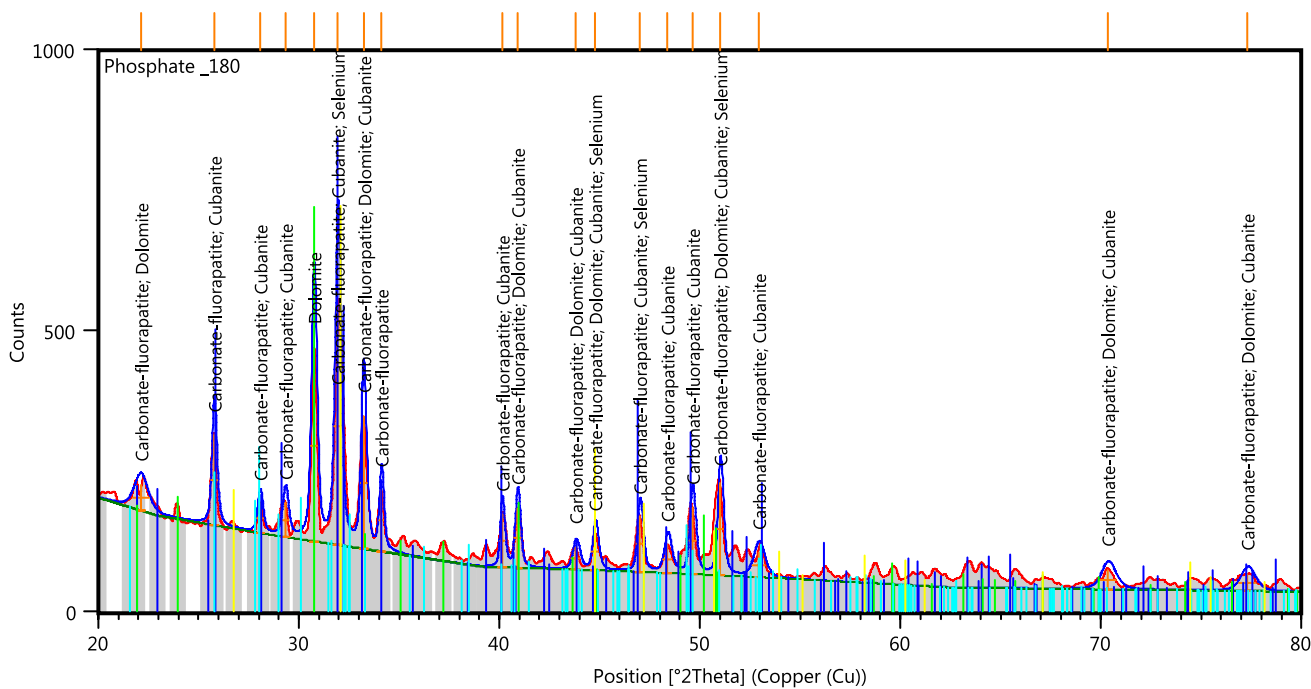
The results of tetradecylamine adsorption on quartz were confirmed by flotation and showed a better selectivity compared to what was reported with dodecylamine. So as to elucidate the sensitivity of the flotation response of quartz and fluorapatite with pH changes, the minerals were set to float over a wide-range of pH values (5 to 11.5) by adding Tetradecylamine as collector at 15–30 mg/L. The results showed an increase in quartz recovery higher than that of apatite which means that quartz is more floatable than apatite. Accordingly, reverse flotation by depression of apatite and flotation of quartz from apatite ore after calcination was studied as a separation process of quartz from carbonate apatite ore.

Experimental

Materials and reagents

A 75% fraction quartz-apatite samples were dry-ground, sieved to a particle size of 0.160 + 0.074 mm and used in flotation tests and adsorption mechanism study. The quartz sample was purchased from fluka analytical and apatite ore was obtained from Somiphos plant located in Djebel Onk Algeria (Fig. 1). The X-ray diffraction patterns of the carbonate fluorapatite ore sample presented in Fig. 1 show a noteworthy variance between phases. The five most intense peaks were shown in 2 Theta ranges that is 30.75° for dolomite and 25.8°; 31.94°; 33.22°; 34.1° for carbonate fluorapatite using Xpert highscore software based on Search-Match function which enables the search of the reference database for patterns matching the data and/or peak data of the anchor scan. The best matching patterns were examined in details and ranked according to their score for both standard and automatic phase identification. The list of candidate minerals is filled with patterns by the phase analysis function. After accepting a pattern by dragging it from the candidates list, during automatic identification, the software approves candidates.

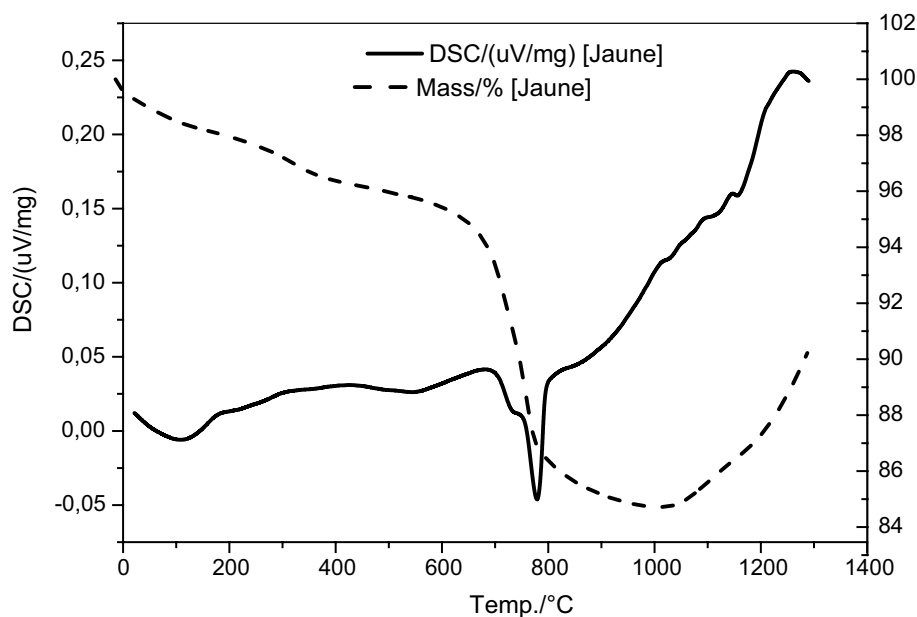
In order to collect enough data on thermal stability based on chemical composition and structural parameters, the carbonate fluorapatite ore was subjected to a detailed DSC-TG analysis which displayed an exothermic pic at 700 °C attributed to the decomposition of carbonates, such as dolomite and calcite, and an endothermic pic at 780 °C indicating the beginning of formation of a new phase (Fig. 2). Moreover, the carbonate apatite was characterized by X-ray diffraction



N°	Peak Height (%)	Position 2 Theta (°)	d-spacing (Å)	Mineral
1	100	31.94	2.801	Carbonate fluorapatite
2	80	30.75	2.907	Dolomite
3	55.4	33.22	2.696	Carbonate fluorapatite
4	37.8	25.80	3.455	Carbonate fluorapatite
5	25.7	34.11	2.628	Carbonate fluorapatite

Fig. 1 XRD patterns of carbonate fluorapatite ore

Fig. 2 DSC-TG of carbonate fluorapatite ore



using HighScore software and FTIR spectroscopy before and after calcination process (Figs. 1, 3).

Figure 3 shows the accepted XRD patterns of identified ore that underwent heating at 700 °C to burn the organic matter, oxidize the residual carbon and remove dolomite and calcite present in the carbonate fluorapatite ore. The most intense peaks in Fig. 3 show only carbonate fluorapatite at 2 Theta 31.94°; 33.22°; 34.1° used in flotation tests.

The tetradecylamine C14: $\text{CH}_3(\text{CH}_2)_{12}\text{CH}_2\text{-NH}_2$ with 95% purity was supplied by Sigma Aldrich. Calcium oxide (CaO) of analytical grade was purchased from Riedel de Haën. The tetradecylamine was prepared by mixing the necessary quantities of the corresponding amine and hydrochloric acid as a consequence of the weak solubility and dispersion in water. The concentration was 1% in weight. Calcium oxide and phosphoric acid were used as regulators and depressant, and distilled water was used in the flotation tests.

UV visible spectrometry and FTIR spectroscopy

The ultraviolet spectra of the studied compounds were determined on Specord 200 Plus spectrophotometer. Water and water-chloroform were used as solvent systems: The solvent system spectrum was eliminated as it is in the comparison cell in all cases. The spectral studies were performed with double beam spectrophotometer for solutions and dried adsorbent quartz. In a stepwise approach, the formation of methyl orange-amine complex in buffered solution using sodium acetate was maintained at constant pH. The absorbance was recorded at wavelength scan from 1100 to 200 nm.

The wavelength range of UV–Visible spectral data was 1 nm. The FTIR measurements were accomplished on Jasco FTIR 4700 series and all spectra were recorded at a resolution of 2 cm^{-1} .

Scanning electron microscopy and energy-dispersive X-ray microanalysis (SEM-EDS)

The apparent morphology and elemental composition were determined using a scanning electron microscope (TESCAN-VEGA 3 model) equipped with an EDS (energy-dispersive X-ray spectroscopy) detector (Bruker model) and operating at 20 keV. All the samples were observed from SEM, with elemental compositions being analyzed by EDS. The use of a high vacuum scanning electron microscope is therefore preferable in X-emission micro spectrometry.

Flotation tests

All flotation tests were performed over pH range from 4 to 12 in a Plexiglas cell pH containing 500 mL of solution, and 4 g of the sample. The samples were conditioned with collectors for 2 mn over a flotation time of 3 mn. Tetradecylamine and dodecylamine were neutralized using hydrochloric acid. All tests were conducted in the existence of phosphoric acid, under acidic pH to check its depressant effect on the apatite floatability and calcium oxide, and under alkaline pH to check the quartz floatability. The generated bubble Reynolds number is more than 385 reflecting a near turbulent flow (Kouachi et al. 2010; Drzymala 1994).

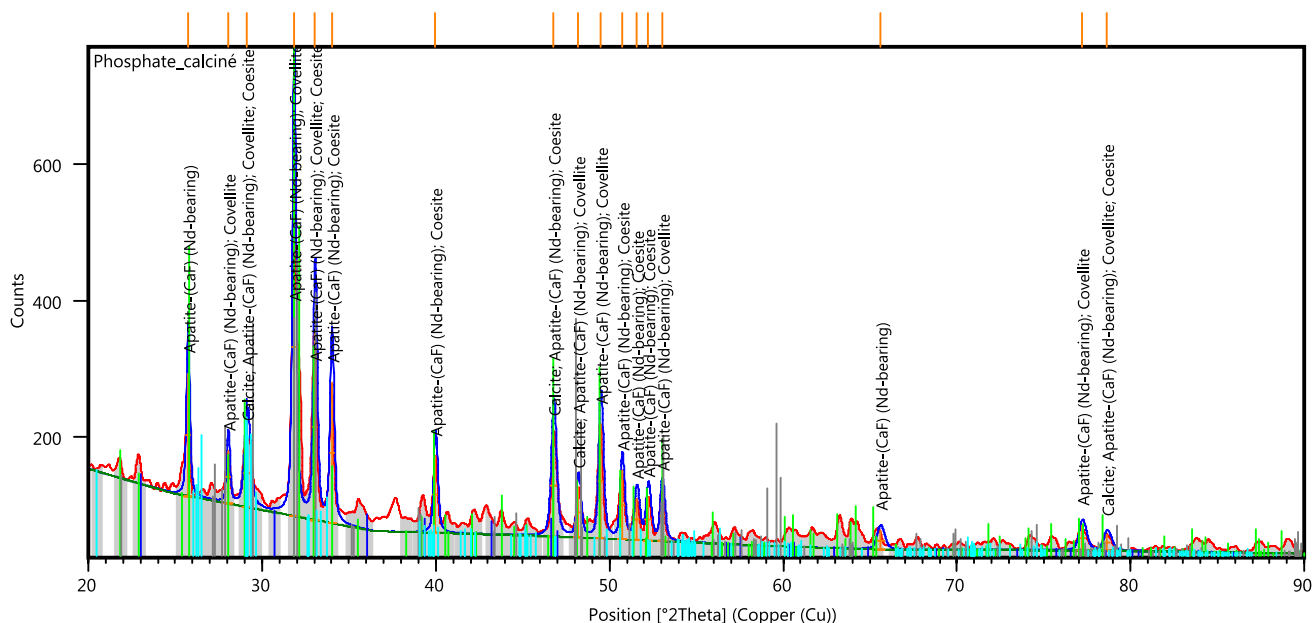


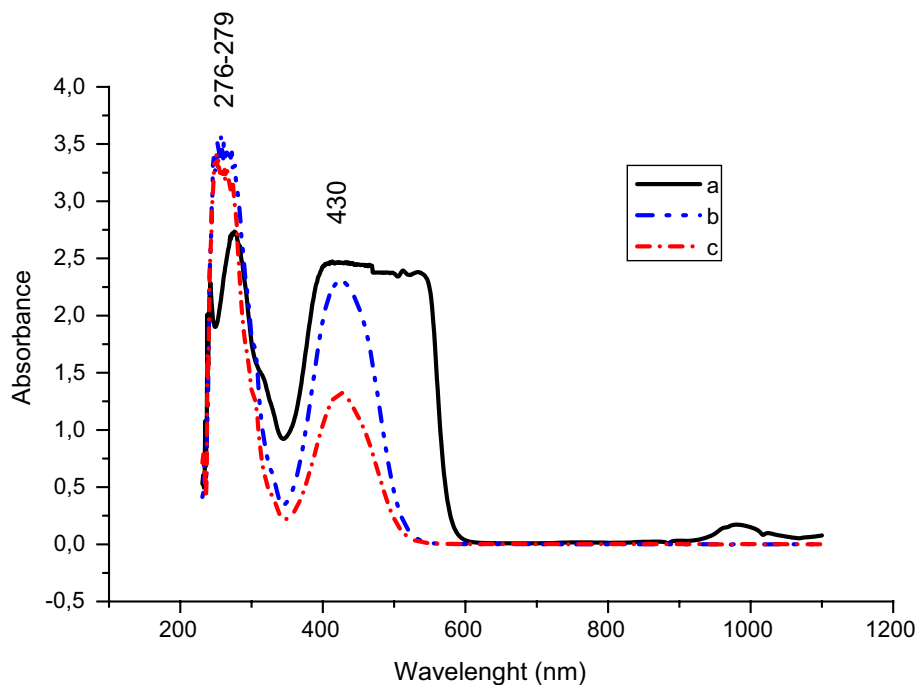
Fig. 3 XRD patterns of heated carbonate fluorapatite ore

The flotation experiments were conducted in a laboratory GTEK XFD Single flotation cell D12 at 1300 rpm.

Results and discussion

Spectrometric results (UV, FTIR) revealed that the adsorbed tetradecylamine state onto quartz varies significantly over various pH levels. It is proposed that at low concentrations, the amine is adsorbed via electrostatic interaction (Wang et al. 2016; Alexandrova and Rao, 2009). However, hemimicelles are formed when amine cations are adsorbed at the quartz surface at high concentration. At this concentration, the amine molecules are packed closely together and their hydrophobic tails interact with each other to minimize their exposure to the aqueous phase. This leads to the formation of a monolayer of amine molecules on the quartz surface, with their hydrophilic (water-attracting) heads facing the liquid phase and their hydrophobic tails facing the surface resulting in a monolayer physically adsorbed on the quartz surface. On quartz surface, for neutral and weakly acidic pH, tetradecylamine is practically wholly ionized owing to its $pK_a = 4.2$; dissociation constant: 6.3×10^{-5} and solubility: 1×10^{-6} mol/L at 25 °C, while the quartz surface is negatively charged. The variation of pH considerably affects the quantity of amine adsorbed because pH determines the magnitude of the surface potential. The analysis of amine adsorption was performed at pH range 7.6–8.5 in order to study the quartz surface with the presence of hydrophobic and hydrophilic conditions.

Fig. 4 UV–Visible spectra of methyl orange solution **a**; amine–methyl orange solutions at tetradecylamine concentration of 1.4×10^{-4} mol/L using 10 ml of chloroform **b** and 15 ml of chloroform **c** for amine extraction



Spectral properties and amine adsorption mechanism on quartz

UV-Visible spectrometric studies

A well-known theory used for analysis of experimental results is the hemimicelles approach as described by many reports (Fuerstenau and Jang 1991; Somasundaran and Fuerstenau 1966). This approach recommends that amine adsorption primarily takes place via coulombic transport of singular amine cations in the diffuse layer and in stern plane at the surface with their polar heads oriented. During attachment, at pH of 7.64; 8.0 and 8.5, the quartz surface is charged negatively and at low concentrations, tetradecylamine ions are adsorbed as separate ions at low density. According to Wang and Miller (2018), the restricted adsorption at amine solution/silica interface is accompanied by a quite improved dodecylamine adsorption at air bubble/amine solution. During adhesion, dodecylamine is transmitted to quartz surface and the adsorption density increases significantly with the establishment of an ordered monolayer at the air bubble quartz/quartz interface. Figure 4 demonstrates that the contact of methyl orange with tetradecylamine causes the development of shifted peak situated nearby 430 nm. An increase in the chloroform quantities (Fig. 4b, c) causes an evolution of the peak at 276–279 nm and at 430 nm proving a better complexation with methyl orange at 10 ml of chloroform.

Methyl orange is an orange-colored synthetic dye, whose color changes depending on the solution pH. It essentially displays a red or yellow color with respect to acidity or basicity of solutions, respectively. Optical properties of red

combined solution containing methyl orange, sodium acetate and KCl were described by the absorbance spectrum as follows: Methyl orange has a maximum absorbance at 430 nm (Klotz et al. 1969; Takagishi and Klotz 1972; Sato et al. 2009; Vleugels et al. 2017). Moreover, the presence of a sharp peak at 276–279 nm generally highlights the presence of tetradecylamine, whereas larger aggregates, held together by Van Der Waals interactions, display an absorption peak at 430 nm (Hatano et al. 1973). The methyl orange added to tetradecylamine exhibits its peak at 430 nm prevails at low concentration with concurrent increase in the spectral region 250–300 nm (Figs. 1b, 4a). At low concentrations, tetradecylamine showed an increase in the intensity of the adsorption peak at 276–279 nm vs. increasing amine concentration (Fig. 5). pH is a key factor, particularly that of reagents that is why it is so important to define the favored pH range for flotation as stated by Liu et al. (2015). For all amine collector solvents, the adsorption abilities of the collector are larger at pH = 8.0 compared to pH = 4.0 and 10.0. Knowing that amine forms dependent on the pH; thus cationic form is the dominant molecule species at pH < 10. At low pH (pH = 4), the quartz negative charge is significantly reduced, and the cationic amine RNH_3^+ adsorption capacity decreases. On this basis, a pH range of 7.6–8.5 was chosen to carry on the amine adsorption on quartz. The adsorption of ions upsurges with pH until the amine solubility limit is reached in the quartz-solution interface. Once surface precipitation arises resulting in an increased surface hydrophobicity and flotation which may occur when a pH = 8–8.5 is reached such that the CMC is exceeded locally at the quartz surface through adsorption of amine ions, then flotation decreases for further increasing pH up to the point where

the CMC is exceeded in the bulk of the solution (Smith and Scott 2007). The spectra of clear supernatants solution obtained at the end of adsorption at pH 7.6; 8.0 and 8.5 show the absence of characteristic bands of amines (Fig. 6) proving a complete tetradecylamine adsorption on quartz. These results correlate well with those stated by Liu et al. (2015).

The UV–visible data analysis of tetradecylamine adsorption on quartz at pH = 8.0 and 8.5 adjusted with calcium oxide is presented in Fig. 6. Calcium ion has particularly a sturdy affinity to quartz. Some research reports indicated that the principal activation procedure is the surface dumping of calcium species on silica. Ozkan et al. (2009) and Wang et al. (2018) explained the adsorption mechanism of calcium ion at high pH values and ended up with the fact that less hydrated Ca(OH)(I) was adsorbed on negatively charged quartz surface assuming that the CaOH^+ complexes formed upon increasing pH do not have a greater impact than Ca^{2+} (Somasundaran 1968; Zhu et al. 2020), and this is because an increase in pH decreases negative surface charge of the quartz.

IR spectroscopy

In tetradecylamine ATR/FTIR spectrum, the typical bands in the range $2800\text{--}3000\text{ cm}^{-1}$ are attributed to the $\nu(\text{C-H})$ symmetrical and asymmetrical stretching. Amines demonstrate characteristic $\nu(\text{N-H})$ absorption band in the region $3300\text{--}3500\text{ cm}^{-1}$. In dilute solutions, primary amines display two sharp bands due to symmetrical and asymmetrical stretching. However, in pure amines, the N–H bands appear in the range $3250\text{--}3330\text{ cm}^{-1}$ and $3330\text{--}3400\text{ cm}^{-1}$ due to intermolecular hydrogen bonding. For the pure crystalline

Fig. 5 UV–Visible spectra of chloroform as reference **a**, methyl orange solution **b** and methyl orange-tetradecylamine solutions at respective concentrations: 2.34×10^{-5} mol/L **c**; 6.09×10^{-5} mol/L **d**; 9.37×10^{-5} mol/L **e** and pH = 4

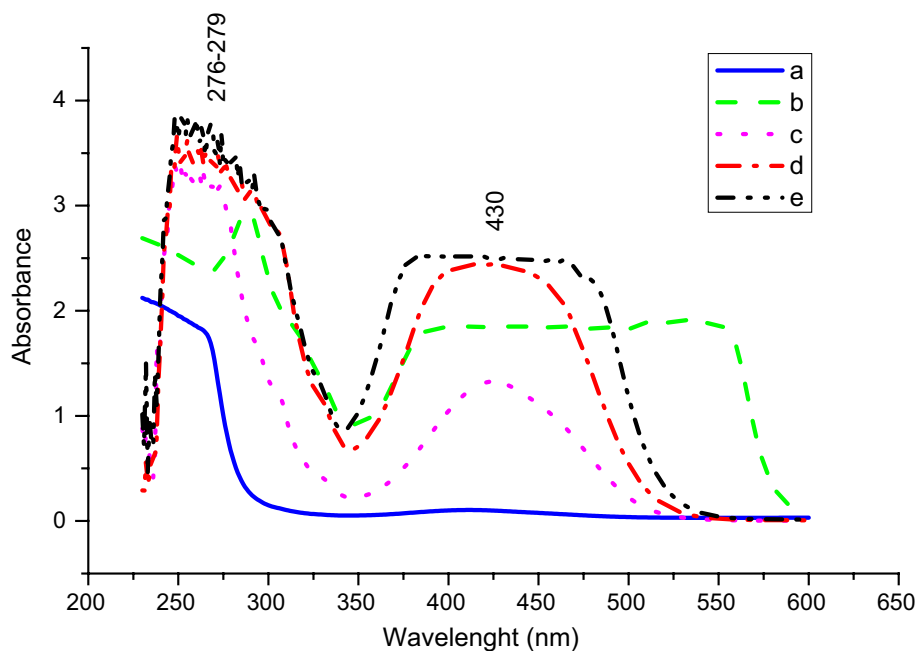
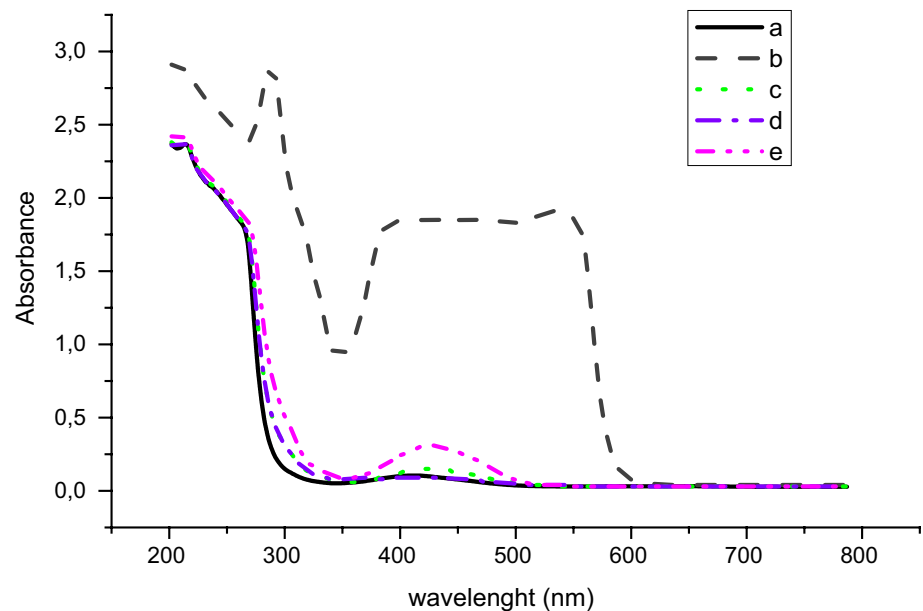


Fig. 6 UV spectra of chloroform as reference **a**; methyl orange solution **b** and clear supernatants solutions after the tetradecylamine adsorption on quartz at pH 7.6 **c**; pH 8 **d**; pH 8.5 **e** at 1.4×10^{-4} mol/L



tetradecylamine, doublets can be observed at 1471.4 and 1461.8 cm^{-1} for the scissoring modes and 719.3 cm^{-1} for the rocking mode (Li and Ishida 2003) (Fig. 7). The C–N stretching during medium to weak absorption appears in the range of 1250–1020 cm^{-1} (Fig. 7).

The characteristic absorbance band of the quartz appears as a strong band at 1080 cm^{-1} , which can be assigned to the stretching vibration of Si–O. The bands at 799.3, 780 and 695 cm^{-1} are also attributed to the silica structure and the absorption at 799.3 cm^{-1} is assigned to Si–O–Si symmetrical stretching vibration. The 780 cm^{-1} band could be a complement of 799.3 cm^{-1} (Fig. 8a). Infrared spectra of quartz after tetradecylamine adsorption were as well investigated so as to confirm the adsorption process (Fig. 8). An increase in tetradecylamine concentration to 1.4×10^{-3} mol/L gave

rise to a quartz spectrum including a number of characteristic amine bands. The spectra show the absorption bands from 2800 to 3000 cm^{-1} attributed to alkyl chain of amines because they are consistent with tetradecylamine spectra shown in Fig. 7.

Figure 8 shows the significant FTIR spectra for tetradecylamine adsorption on quartz surface at 1.4×10^{-3} mol/L with respect to pH. Two typical pH values (8.0 and 8.5) were chosen to distinguish the quantitative adsorption results and flotation. The characteristic absorption band of calcium oxide appears at 1421 cm^{-1} and CH stretching appears on the spectra of quartz after adsorption. The stretching CH range in Fig. 8c and d shows two CH_2 stretching at 2852.5 cm^{-1} due to symmetric stretching mode and at 2919.7 cm^{-1} due to CH_2 asymmetric stretching mode. It is evident that the

Fig. 7 IR spectrum of pure crystalline tetradecylamine

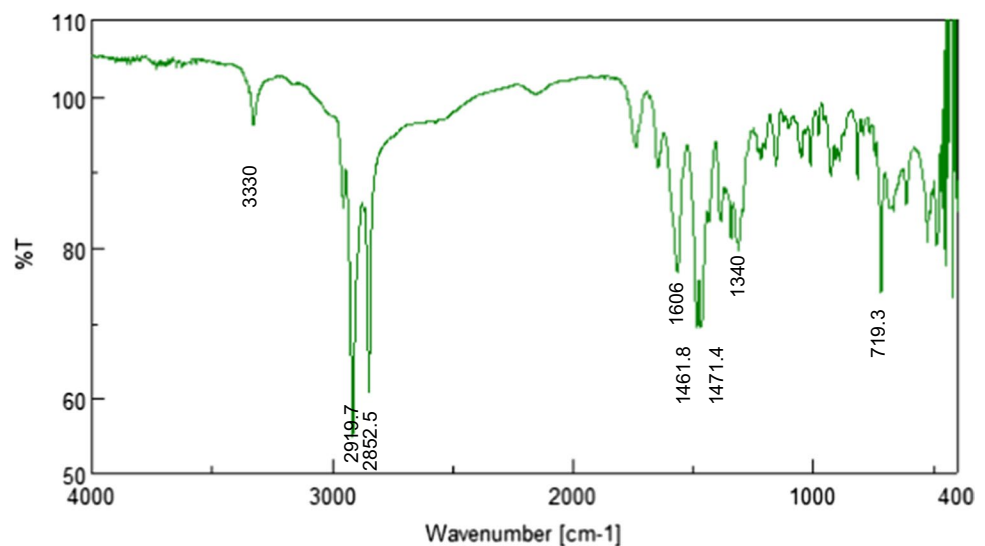
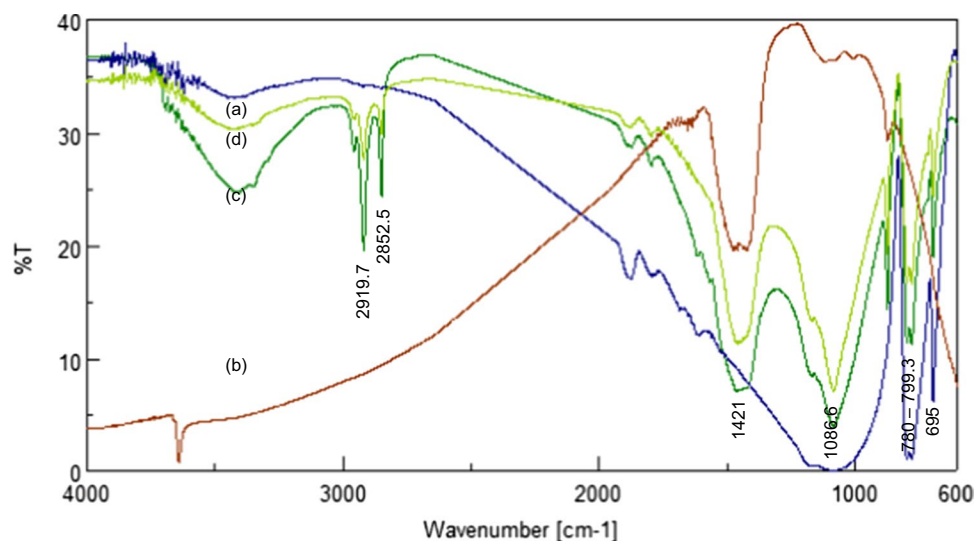


Fig. 8 IR spectra of quartz **a**, calcium oxide **b**, quartz after tetradecylamine adsorption at pH 8.0 **c**, at pH 8.5 **d** at 1.4×10^{-3} mol/L



tetradecylamine is adsorbed on quartz surface in the presence of calcium oxide. These results are in good arrangement with quantitative tetradecylamine adsorption on quartz and flotation tests (Figs. 13, 14).

Scanning electron microscopy and energy-dispersive X-ray microanalysis (SEM-EDS) results

For the purpose to characterize the surface morphology of quartz, a collection of SEM-EDS probe analyses were alongside implemented to come up with the type and distribution of tetradecylamine and calcium oxide on quartz surface. The elemental composition and quartz morphology, as in Fig. 9b, and calcium oxide, as in Fig. 9a, were determined using scanning electron microscope equipped with energy-dispersive X-ray spectroscopy (SEM-EDS), where the photomicrographs from the SEM study shown in Fig. 9 exposed that the surface of pure quartz (Fig. 9b) displayed the oxygen and silicon elements distributed on the surface.

Energy-dispersive X-ray analysis was performed to assess the quartz surface after adsorption and desorption of tetradecylamine, where the surface morphology was monitored using SEM/EDS microscope TESCAN – VEGA3. The SEM images at 1.4×10^{-4} mol/L (30 mg/L) and pH of 8.5 acquired at 20 kV accelerator voltage are shown in Fig. 9. Figure 9c displays the micro-chemical maps of the selected area revealing the presence of calcium, carbon, chlorine and nitrogen, which confirmed the adsorption of tetradecylamine. The influence of chlorine on tetradecylamine collector is clearly perceived.

On the collected spectra, the detected elements are successively Si, O, Ca, C, N, Cl. The elements: C, N, O, are less detectable. After tetradecylamine adsorption onto

quartz at concentration 1.4×10^{-4} mol/L and pH = 8.5, the SEM-EDS analyses carried out on samples of quartz and quartz containing tetradecylamine are shown in Fig. 9.

EDS detected the emission of silica element (Si), oxygen (O) for quartz (a) and calcium (Ca), oxygen (O) for calcium oxide (b). The distinctive signals, characteristics of Si, O, and Ca are observed at energy values of 1.7, 0.5, 3,7 and 4.0 keV, respectively (Fig. 10).

The distinctive signals, characteristics of Si, O, Ca, C, N and chlorine are, respectively, observed at the energy values of 1.7; 0.5; 3.7 and 4.0; 0.3; 0.4 keV and can be unveiled in Fig. 11 of the EDS spectra of adsorbed tetradecylamine on quartz. Comparing the spectrum of adsorbed quartz with desorbed one, the absence of tiny peaks of N, C and Cl signaled the desorption process and the confirmation of binding of the amines onto the quartz is further palpable from SEM images. Figures 9, 11 corresponding to the surface of quartz-tetradecylamine at concentration 1.4×10^{-4} mol/L and pH = 8.5 adjusted with calcium oxide discloses significant morphological changes compared with desorbed case which corresponds to that of quartz surface alone. Energy-dispersive X-ray (EDS) pattern of Fig. 11a shows a distinct increase in percentage of C, N and chlorine from that of Fig. 11b.

The EDS mapping highlighted in adsorbed quartz sample confirms the presence of 1.29% of nitrogen, 0.30% of chlorine, 16.05% of carbon and 8.74% of calcium endorsing the adsorption of tetradecylamine at pH = 8.5 adjusted with calcium oxide and the presence of chlorine indicates that tetradecylamine was pre-treated with hydrochloric acid (Table 1). The EDS mapping highlighted in desorbed quartz sample confirms only the presence of calcium (4.53%) and carbon (19.22%).

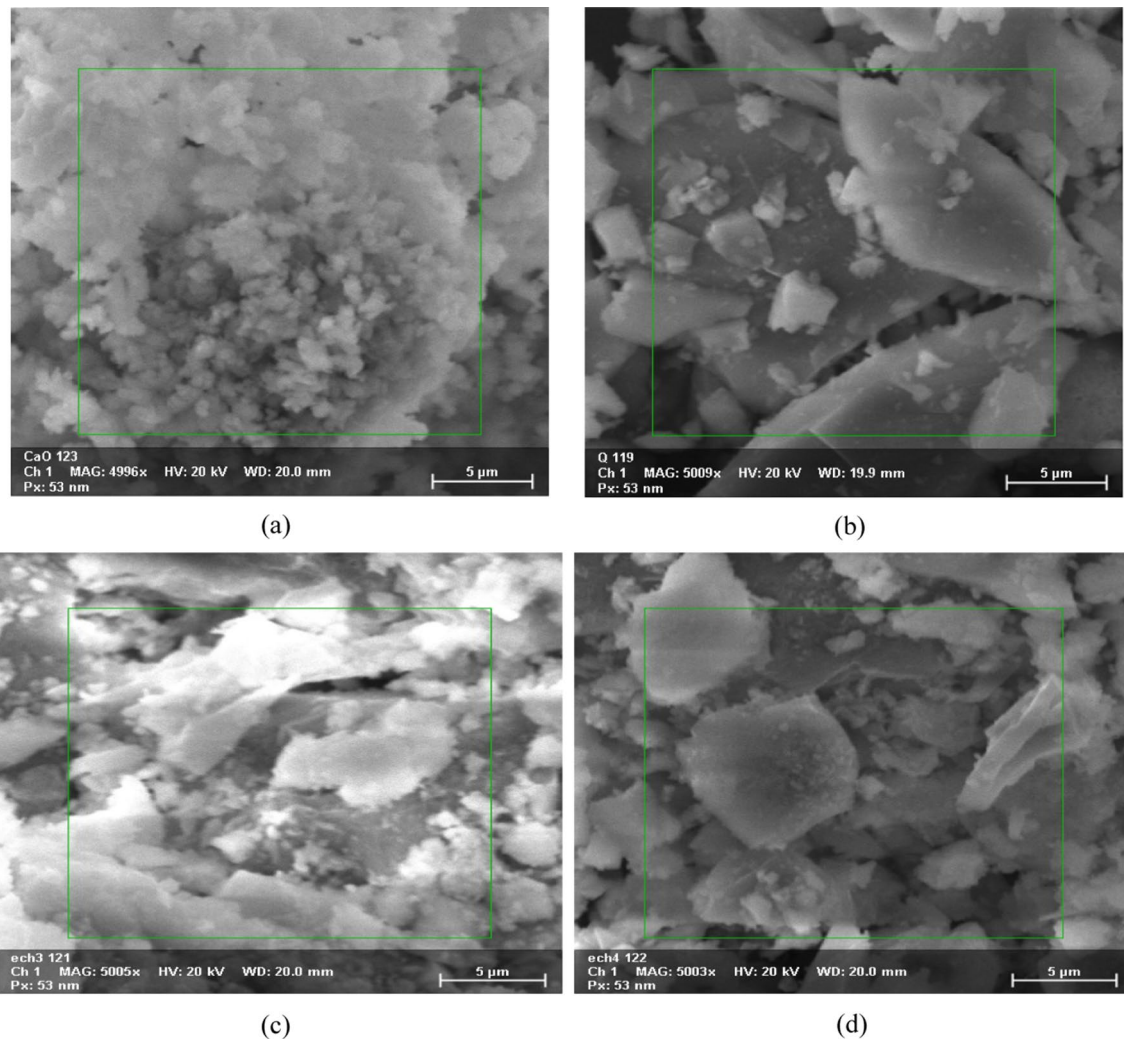


Fig. 9 SEM image of calcium oxide **a**, quartz before **b** and after **c** adsorption and desorption **d** of tetradecylamine at concentration 1.4×10^{-4} mol/L and pH 8.5 adjusted with calcium oxide

Quantitative adsorption

The amine adsorption study is an important step in selecting the appropriate collector for quartz flotation, as it helps determine the optimal conditions for amine adsorption surface. The results of this study can then be used to optimize the flotation conditions and obtain a higher quality phosphate product. Tetradecylamine and dodecylamine are both alkylamines that are commonly used as collectors in the flotation process of quartz minerals. The selection of the appropriate collector for phosphate ore containing quartz depends on several factors, including the chemical composition of the ore, the pH of the pulp, and the surface properties of the minerals. Tetradecylamine and dodecylamine are similar in chemical structures with difference in length of their alkyl chains. This difference can have a significant impact on their performance as cationic collectors.

Figure 12 presents the quantitative adsorption results of tetradecylamine and dodecylamine where the adsorption increased with increasing concentration at pH range of 8–8.5. From these curves, it can be clearly seen that both tetradecylamine adsorption capacities are greater compared to dodecylamine. This was attributed to the longer alkyl chain of tetradecylamine, which provided a stronger hydrophobic interaction between tetradecylamine and the quartz.

Flotation tests

The quartz and apatite flotation tests were carried out within the pH range from 5.5 to 11.5 at amine concentration of 15; 30 mg/L and the effect of pH on quartz recovery is plotted in Fig. 13. It is worth observing that with increasing pH, the overall quartz recovery decreased. At pH above 9.5, calcium oxide reduces the quartz floatability significantly. Better

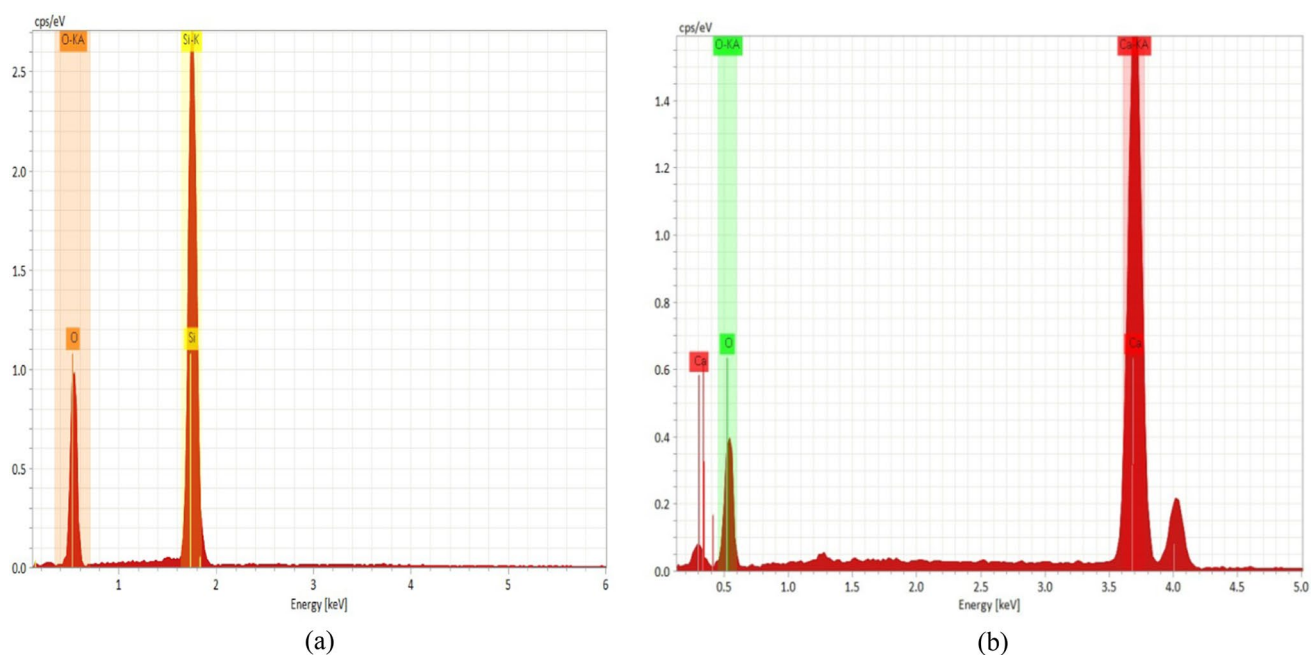


Fig. 10 EDS data of quartz **a** and calcium oxide **b**

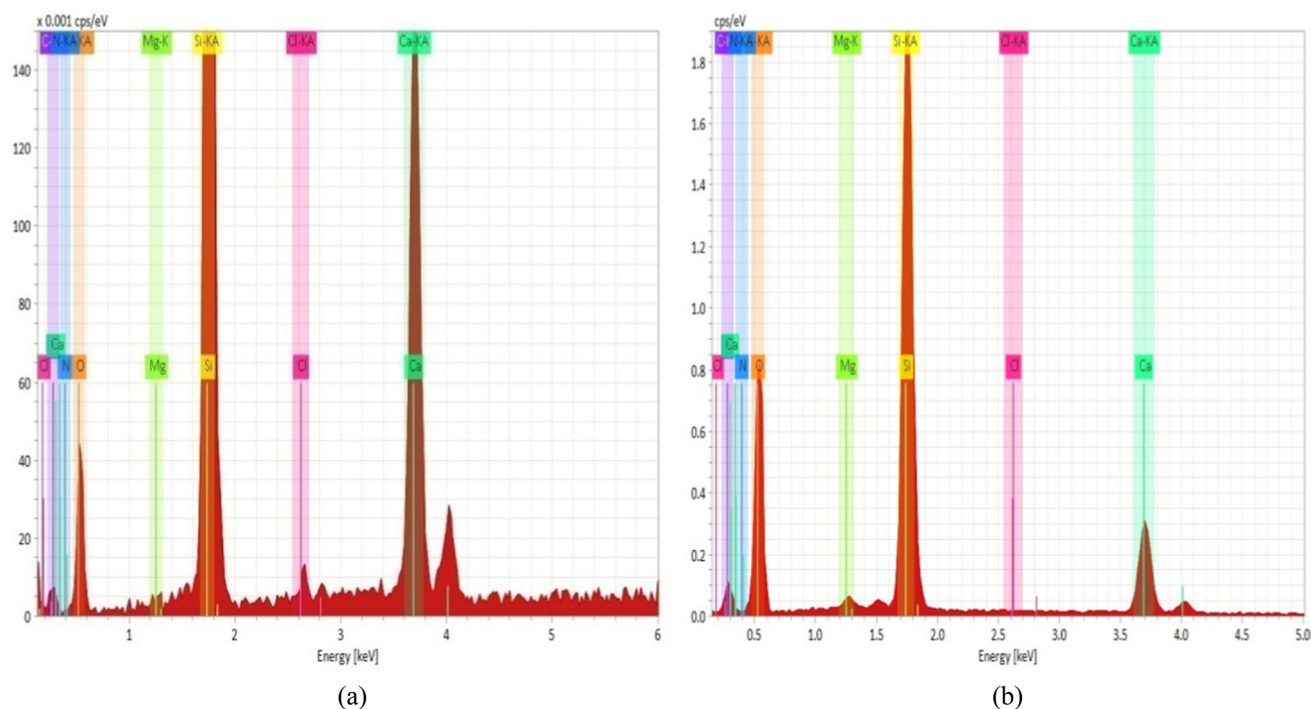


Fig. 11 EDS data of quartz after adsorption **a** and desorption **b** of tetradecylamine at concentration 1.4×10^{-4} mol/L and pH=8.5 adjusted with calcium oxide

results are realized with pH from 6.5 to 8.5 in the presence of calcium oxide and quartz recovery reached up to 98%. These findings are consistent with the results obtained by Yoon and Ravishankar (1996), where in the pH range from

5.7 to 9.5, no momentous alterations are observed. As the pH augmented to 10.1, the adhesion force diminishes sharply to less than 50 mN/m (Table 2), which is possibly because of the presence of separated amine phase on the mineral

Table 1 Elemental composition of calcium oxide (a) and quartz before (a) and after adsorption (b) and desorption (c) at tetradecylamine concentration 1.4×10^{-4} mol/L and pH=8.5 adjusted with calcium oxide

Elemental composition of calcium oxide (a) and quartz before (b) and after (c) adsorption and desorption (d) of tetradecylamine

Element	Calcium oxide (a)	Quartz before adsorption (b)	Quartz after adsorption (c)	Quartz before desorption (d)
Oxygen	75.14	70.22	42.33	61.37
Silicon		29.78	31.28	14.88
Carbon			16.05	19.22
Calcium	24.86		8.74	4.53
Nitrogen			1.29	0.00
Chlorine			0.30	0.00

surface. The precipitates might decline the hydrophobicity and generate substantial roughness on the surface, and hence contribute to the weakening of adhesion forces.

The flotation experiment illustrated in Fig. 13 was conducted to investigate the flotation ability of tetradecylamine (C14) and dodecylamine (C12) on apatite to achieve good separation of quartz from apatite. The results specify that the recovery of apatite increased with increase in concentration, and $1.5 \cdot 10^{-4}$ mol/L with a recovery rate of 15–20% was maximum allowed to minimize losses of P_2O_5 in the phosphate concentrate. In addition, suitable depressants such as phosphoric acid and calcium oxide must be added to achieve good flotation ability of C14 and C12 on both apatite and

quartz, and to ensure effective separation of quartz from apatite in reverse flotation. The concentration effect of C14 and C12 on apatite is shown in Fig. 13, where the maximum allowable concentration is $1.5 \cdot 10^{-4}$ mol/L, with pH range of 7.4 to 8.5.

As shown below, different floatabilities of quartz were exhibited when tetradecylamine was used as collector, phosphoric acid as depressant for apatite and calcium oxide as regulator for quartz. Recoveries of quartz and apatite, were 91.5–98% and 20–39%, respectively, and could be obtained with tetradecylamine concentrations between $0.7 \cdot 10^{-4}$ mol/L and $1.4 \cdot 10^{-4}$ mol/L (15 mg/L–30 mg/L) at pH 8.5.

The results of pure quartz and quartz contained in calcined apatite ore floatability in the presence of tetradecylamine are presented in Fig. 14. The maximum floatability of pure quartz at 1.4×10^{-4} mol/L in tetradecylamine solution was 98%, achieved at pH=8.5. The tetradecylamine acts as an effective collector for pure quartz, as can be perceived in Fig. 14a, b. The floatability of pure quartz was 98–85% in pH range from 6.5 to 9.5, showing the strong dependency of the collector on chain length. On the other hand, the recovery of pure quartz decreased manifestly, together with a decreasing values of 50 to 20% at tetradecylamine concentrations of 1.4×10^{-4} and 0.7×10^{-4} mol/L, respectively, when pH was fixed at 11.0–11.5 using calcium oxide.

The experimental findings suggest that the addition of tetradecylamine can enhance the floatability of quartz from calcined apatite ore. The results reveal that the highest flotation of quartz was achieved at pH 8.5, adjusted with calcium oxide, and at tetradecylamine concentrations of

Fig.12 Quantitative adsorption of dodecylamine **a** and tetradecylamine **b** on quartz as a function of concentration at pH=8–8.5 using calcium oxide

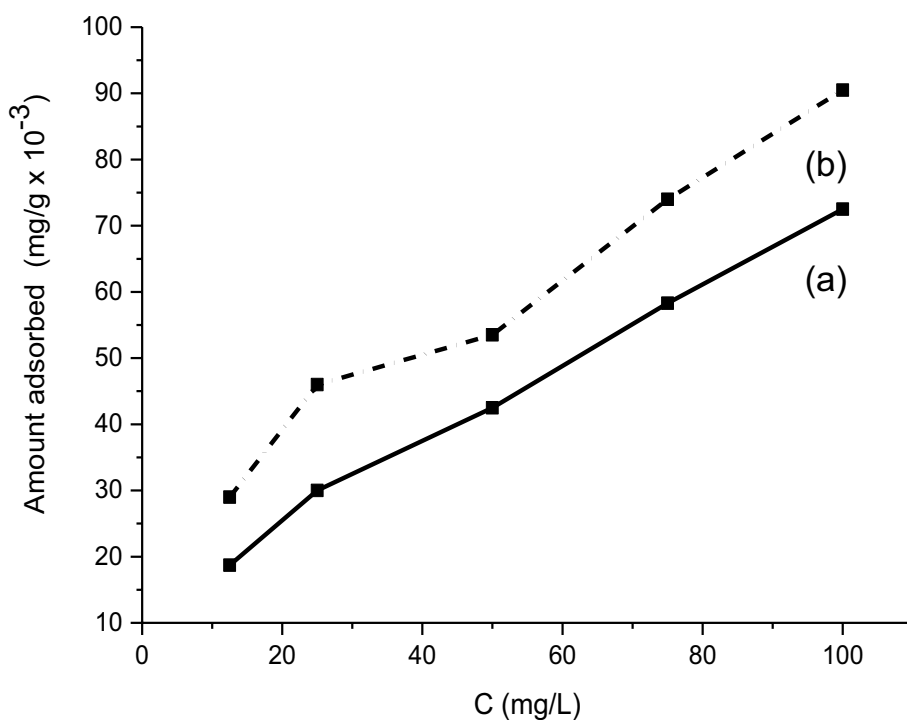


Fig. 13 Concentration effect on flotation of apatite at pH 7.8–8.5 using tetradecylamine **a** and dodecylamine **b**

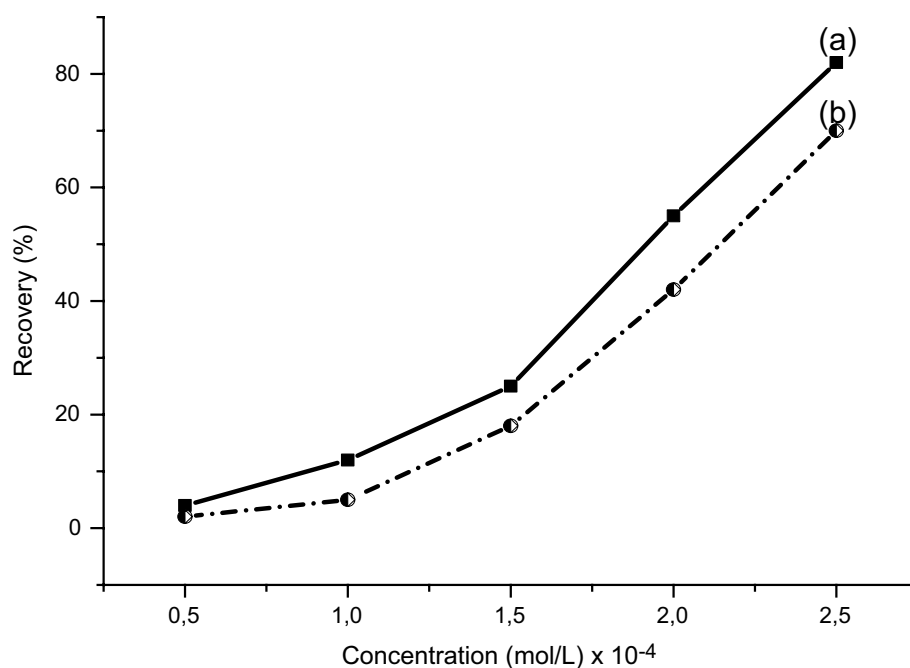


Table 2 Results of Surface Force Measurements Conducted with Mica Surfaces in DAHCl Solutions at different pH values (Yoon and Ravishankar 1996)

pH	Amine concentration	Pull of force (mN/m) ± 25	Adsorbed layer thickness (nm)
5.7	1×10^{-6}	170	0.6
8.0	1×10^{-6}	170	0.6
9.5	1×10^{-6}	170	0.6
5.7	3×10^{-6}	190	0.6
9.5	3×10^{-6}	190	0.6
10.1	1×10^{-7}	50	0.5
10.1	1×10^{-6}	40	0.6
10.1	2×10^{-6}	0	1.5–2.0
10.1	5×10^{-6}	0	3.5–4.0

1.4×10^{-4} mol/L and 0.7×10^{-4} mol/L, resulting in maximum flotation of 39.4% and 20.7%, respectively. To enhance the flotation of quartz from apatite ore and prevent the loss of P_2O_5 in the floated quartz, it is recommended to conduct flotation at a tetradecylamine concentration of 0.7×10^{-4} mol/L, which yielded a flotation of 20.7%. This information can be valuable in mineral processing applications to increase quartz recovery while minimizing P_2O_5 losses.

It could be observed that the beneficiation of carbonate apatite ore was accomplished through the two stage: calcination of apatite ore at temperature 750 °C in the first stage and flotation of quartz contained in apatite ore in the second stage at pH ranging from about 8 to 8.5. The flotation of quartz from calcined apatite ore using tetradecylamine shows a significant increase in P_2O_5 in the concentrate and

decrease in MgO and SiO_2 . The apatite concentrate as sink product analyzing 33.1% P_2O_5 , 0.30% MgO and 2.9% SiO_2 could be produced from a sample of 25.02% P_2O_5 , 2.78% MgO and 10.68% SiO_2 (Table 3). Quartz flotation with tetradecylamine as a collector was found to be possible; however, a small addition of collector is required for selective removal of quartz.

Conclusion

Calcination of phosphate ores followed by quartz flotation is an important process for producing high-quality phosphate products. By removing carbonates and separating the quartz minerals from calcined phosphate ore, this process can improve the purity and the value of the final product. Calcination is process that removes carbonates from the phosphate ore. Carbonates such as calcite and dolomite are common impurities in carbonate phosphate ore. Some of these benefits include higher purity, increased recovery of the phosphate minerals by reducing the interference of carbonates with flotation process, and reduced reagent consumption and higher purity of phosphate concentrate. After calcination of phosphate ore, the next step is quartz flotation, which separates the quartz from phosphate. Understanding the adsorption behavior of the collector onto mineral surface is necessary for developing an effective and efficient flotation process for the separation of minerals from ores. The results of this study indicated that the adsorption behavior of tetradecylamine onto quartz varied at different pH values. The findings suggest that the weak range of pH values

Fig. 14 pH effect on pure quartz **a, b** and quartz from calcined apatite ore **c, d** flotation using phosphoric acid, calcium oxide as regulators and tetradecylamine as cationic collector at concentrations 0.7×10^{-4} mol/L **a, c** and 1.4×10^{-4} mol/L **b, d**

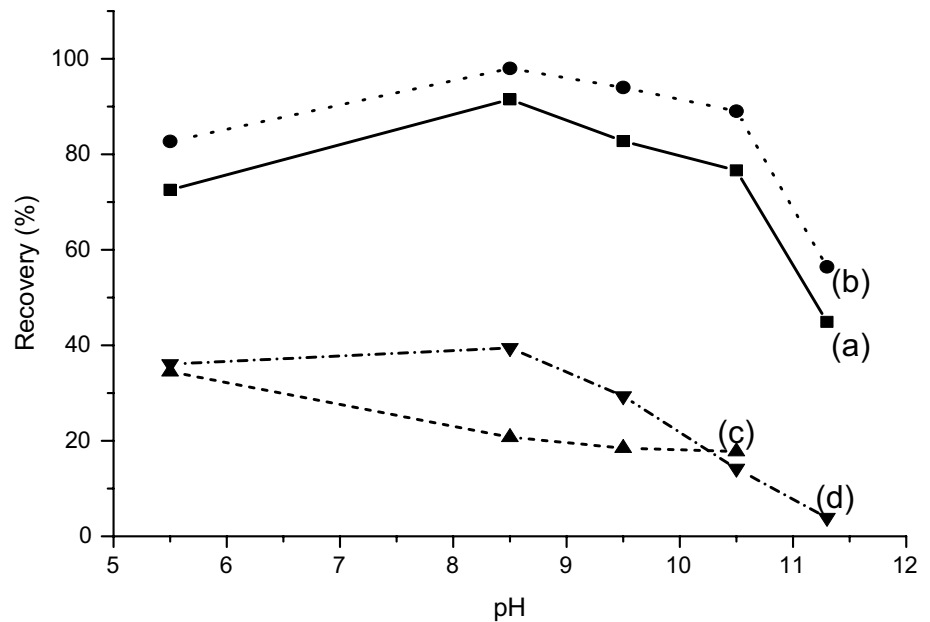


Table 3 Results of heated and floated carbonate apatite ore

Product	Grade (%)			
	P ₂ O ₅	MgO	SiO ₂	CO ₂
Feed	25.02	2.78	10.68	8.71
Calcined apatite at 750 °C	31.62	1.30	9	0.60
Float product-quartz	16.23	0.80	49.5	–
Sink product (apatite concentrate)	33.10	0.30	2.9	–

(8.0–8.5) is the preferred pH range for the flotation of quartz using tetradecylamine as a collector, as it results in significantly higher flotation recovery.

Reverse flotation is common method used to separate minerals, and it involves selectively depressing the valuable mineral while floating the gangue mineral. In this case, reverse flotation of quartz by depression of apatite involves adding a depressant reagent to the flotation process that selectively adsorbs onto apatite surface, rendering it less floatable. Meanwhile, the quartz remains floatable and can be recovered as a separate product. Reverse flotation of quartz by depression using phosphoric acid of apatite has been investigated as a potential method for separating quartz from phosphate rock. This study was led to inspect the sensitivity of the flotation response of quartz and apatite to changes in pH. The minerals were floated over a wide pH range of 5 to 11.5, and tetradecylamine was added as a collector at concentrations of 15 and 30 mg/L. The results indicate that the pH range of 8 to 8.5 is optimal for the flotation of phosphate ore using tetradecylamine as collector. pH is a critical factor in mineral flotation, as it

can influence the surface chemistry of the mineral and its interaction with collector. Identifying the ideal pH range for the flotation of phosphate ore is essential for optimizing the flotation process and improving mineral recovery. The results of the phosphate ore analysis given in Table 3 indicate a high concentration of phosphorus pentoxide (P₂O₅) in the sample, as well as low levels of magnesium oxide (MgO) and silicon dioxide (SiO₂) in the concentrate. The P₂O₅ content is of particular interest in the analysis of the mineral, as it is an essential nutrient for plant growth and a key component of fertilizers. In addition to its use as fertilizer, phosphorus is also used in the production of a range of products; including phosphoric acid is a key industrial chemical that is used in a wide range of practices, covering the manufacture of fertilizers, food additives, and detergents. The low MgO and SiO₂ contents in the concentrate are also noteworthy and the fact that the sample is relatively low in these minerals could have positive implications for the potential use of the mineral.

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Declarations

Conflict of interest The authors state that there is no conflict of interest in publishing this article.

Informed consent All the authors mentioned in the manuscript have agreed for authorship, read and approved the manuscript, and given consent for submission and subsequent publication of the manuscript

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