

Article

The Influence of Ca^{2+} and pH on the Interaction between PAHs and Molybdenite Edges

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Abstract: Nonpolar hydrocarbon oils are widely used as collectors for floating molybdenite. However, they can only adsorb on molybdenite faces and not on molybdenite edges, resulting in limited molybdenite recovery, especially in processed water containing a high amounts of Ca^{2+} . In this study, the influence of Ca^{2+} and pH on the adsorption of polycyclic aromatic hydrocarbons (PAHs), as part of composite collection on molybdenite edges, was studied. It was found that PAHs could only adsorb on molybdenite edges in the presence of Ca^{2+} . Ca^{2+} reacted with molybdenite edges to form CaMoO_4 precipitates. Then, CaMoO_4 precipitates interacted with PAHs to form a structure of π -cation- π by (1) the cation- π interaction, (2) the π - π interaction and (3) the electrostatic interaction. It was also found that CaMoO_4 precipitates on molybdenite edges promoted the adsorption of PAHs. The more the CaMoO_4 precipitates, the easier the PAHs adsorption occurred. As a result, the high amount of Ca^{2+} and low pH enhanced the adsorption of PAHs on molybdenite edges. This study provides insights into reducing the deleterious effect of Ca^{2+} on fine molybdenite flotation.

Keywords: polycyclic aromatic hydrocarbon; molybdenite edges; calcium ions

1. Introduction

Molybdenite is anisotropic due to its layered structure [1,2]. It exhibits two types of surfaces, namely face and edge, resulting from the break of S-S molecular bonds (nonpolar faces) and the rupture of the strong covalent Mo-S bonds (polar edges), respectively. The face is hydrophobic, while the edge is hydrophilic. The anisotropic property of crystalline molybdenite is given in Table 1 [3].

Some studies show that the floatability of molybdenite particles depends on the relative surface exposure of hydrophobic faces and hydrophilic edges [4,5]. A greater proportion of molybdenite edges corresponds to a lower flotation recovery. In other words, with the particles size decreasing, the proportion of molybdenite edges increases and molybdenite flotation recovery decreases.

Fine molybdenite particles have a low face/edge ratio with a high exposure of edges [5]. The hydrophilic edges have a deleterious influence on molybdenite floatability. Nonpolar hydrocarbon oils (saturated hydrocarbons) such as kerosene, diesel oil, transformer oil and solar oil are normally used as molybdenite flotation collectors [6–9]. However, they only adsorb on the nonpolar face of molybdenite by hydrophobic interactions and van der Waals forces [10–15], because the surface energy of nonpolar hydrocarbon oils is similar to that of molybdenite faces. Therefore, the hydrophobicity of molybdenite edges cannot be improved by nonpolar hydrocarbon oils [16,17]. Some studies show that molybdenite edges could interact with some metal ions existing in flotation pulp, which reduces

their hydrophobicity [17–21]. In particular, calcium ions were found to decrease the contact angle of molybdenite edges, and hence, exacerbate molybdenite flotation [17]. It has been documented that molybdenite edges are easily oxidized, but molybdenite faces are difficult to be oxidized in water at room temperature [4,21]. Therefore, the oxidation product (MoO_4^{2-}) will preferentially occur on molybdenite edges and make molybdenite negatively charged, enhancing the adsorption of calcium ions by electrostatic interactions. Calcium ions may also react with the oxidation product (MoO_4^{2-}) on molybdenite edges to form CaMoO_4 precipitates [4,21].

Table 1. The anisotropic property of crystalline molybdenite [3].

Property	Basal Plane [0001]	Edge [0100]
Cleavage	Perfect	None
Hardness	32 Kg/mm ²	900 Kg/mm ²
Surface energy	24 erg/cm ²	700 erg/cm ²
Contact angle	80°	35°

In the past, the surfactant or xanthate was mixed with a nonpolar hydrocarbon oil to increase the molybdenite flotation [2,22–26]. The surfactant or xanthate could adsorb on molybdenite edges to improve their hydrophobicity. However, they could also adsorb on other sulfide minerals, reducing the selectivity of molybdenite against other sulfide minerals in differential flotation. Studies to improve the hydrophobicity of molybdenite edges by other reagents are limited.

In this study, polycyclic aromatic hydrocarbons (PAHs) was used as a component of a composite collector to target molybdenite edges in a pure molybdenite system, based on the preliminary study showing that PAHs did improve the flotation of fine molybdenite particles at pH 7–8 when mixed with diesel. It should not work as an emulsifier of diesel since PAHs, a neutral, nonpolar molecule, only has a lipophilic group while Emulsifiers are surface-active, with both hydrophilic and lipophilic groups reducing oil–water interfacial tension [27]. In this study, the influence of Ca^{2+} and pH on the interaction between PAHs and molybdenite edges was studied by the ultraviolet-visible spectrophotometer measurement, zeta potential measurement and scanning electron microscopy and Energy Dispersive X-ray spectrometer (SEM–EDS) analysis. The adsorption of PAHs on molybdenite edges in the presence of Ca^{2+} was discussed.

2. Materials and Methods

2.1. Materials and Reagents

The pure molybdenite sample used in this study was obtained from the molybdenum–tungsten mine of Luanchuan in Henan Province, China. The molybdenite crystals were first selected by hand to obtain high-grade crystals for collectorless flotation, then crushed and ground in a porcelain ball mill before subjecting to collectorless flotation to further purify the molybdenite. Finally, the purified molybdenite was screened to obtain the $-38\ \mu\text{m}$ fraction for analyses. This material assayed 58 wt % Mo. The XRD result of the purified molybdenite sample shows 99 wt % molybdenite, as shown in Figure 1.

Diesel oil (DO) was used as a collector to target molybdenite faces. DO can only adsorb on the nonpolar face of molybdenite by hydrophobic interactions and van der Waals forces. DO cannot improve the hydrophobicity of molybdenite edges by adsorbing on the polar edge of molybdenite.

Polycyclic aromatic hydrocarbon (PAHs) which shows improved molybdenite flotation in the preliminary study when mixed with DO was examined in this study. It may adsorb on molybdenite edges. It has a general chemical formula of $\text{C}_n\text{H}_{2n-12}$ ($14 \geq n \geq 10$, $n = 11$ in this study). The typical molecule structure of PAHs is shown in Figure 2.

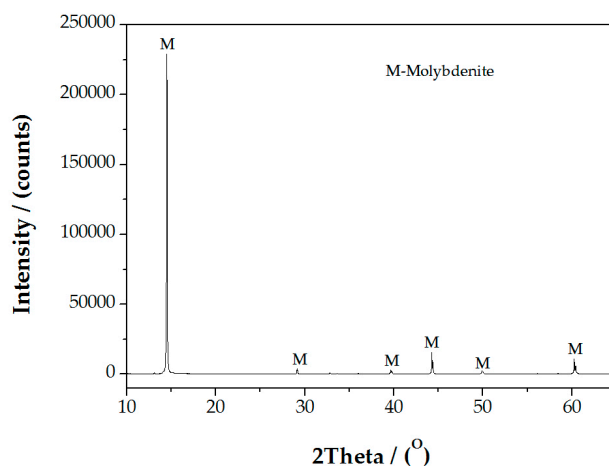


Figure 1. X-ray diffraction (XRD) analysis of the purified molybdenite sample.

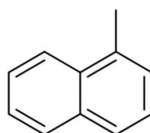


Figure 2. The typical molecule structure of polycyclic aromatic hydrocarbons (PAHs).

XLM is a mixture of DO and PAHs. It consists of 95 wt % DO and 5 wt % PAHs, the optimal DO and PAHs proportions identified in the previous study on molybdenite flotation. XLM produced a higher Molybdenite flotation recovery than DO or PAHs as a single collector. XLM was used in the whole experiment of this study to understand the adsorption of PAHs on molybdenite edges.

Calcium chloride and sodium chlorite were used for adjusting calcium and sodium concentrations. Na^+ was used for a comparison with Ca^{2+} . Sodium hydroxide was used to adjust solution pH. Distilled water and deionized water were also used in this study.

2.2. Ultraviolet-Visible Spectrophotometer Measurements

An ultraviolet-visible spectrophotometer (UV-2802S, Unico (Shanghai) Instruments Co., Ltd., Shanghai, China) was used to measure the concentration of PAHs remaining in the solution after the contact of molybdenite samples with XLM. The characteristic peak of PAHs appears at a wavelength of 220, 267, 275 and 283 nm [28,29]. Standard solutions of various concentrations of PAHs at 0.1, 0.2, 0.5, 1, 2, 4 and 10 mg/L were prepared to establish the standard absorption intensity of PAHs based on which the absorption intensity of the residual PAHs after adsorption on molybdenite was determined.

For the adsorption test, 0.2 g molybdenite and 100 mL Ca^{2+} solution were added to a 500 mL Erlenmeyer flask. They were mixed by a thermostatic oscillator for 5 min. Then, a 100 mL solution of 40 mg/L XLM was mixed by the thermostatic oscillator, and 2 mL solution was removed at a specified time interval. The supernatant was handled with ultrasonic treatment for 1 min after centrifugation. Then, the solution was analyzed by the UV-vis spectrophotometer. The adsorbed PAHs on molybdenite was calculated using the following equation:

$$q_t = (C_0 - C_t) V / m \quad (1)$$

where q_t is the adsorption quantity (mg/g); m is the mass of mineral sample (g); V is solution volume (L); C_0 and C_t are the solution concentration before and after the adsorption, respectively (mg/L). Five repeat adsorption tests were conducted and the average value was reported.

2.3. Zeta Potential Measurements

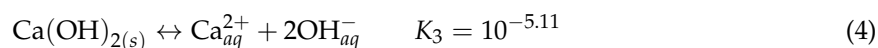
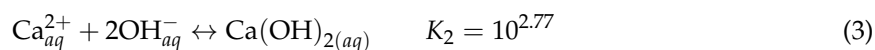
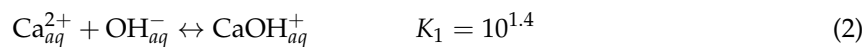
The suspension containing less than 5% molybdenite was dispersed for 15 min in the solution of Ca^{2+} at 0–2000 mg/L. The Ca^{2+} concentration of 0–2000 mg/L was only used in Zeta potential measurements in this study. Then, DO or XLM as a collector at a concentration of 20 mg/L was added after dispersing by a thermostatic oscillator for 3 min. The suspension was then transferred to a sample vessel for the zeta potential measurement at room temperature (20 °C). It should be noted that the purpose of this study was to understand the mechanism responsible for fine molybdenite flotation in the presence of a high amount of Ca^{2+} at pH 7–8, the optimum pH with PAHs, identified in the preliminary work. Therefore, the influence of the Ca^{2+} concentration on the zeta potential of molybdenite was only studied at pH 7 to be consistent with molybdenite flotation. Again, five repeat measurements were conducted and the average zeta potential value was reported.

2.4. Scanning Electron Microscopy and Energy Dispersive X-Ray Spectrometer (SEM-EDS) Analysis

The molybdenite sample 5 g was mixed in a Ca^{2+} solution of 800 mg/L for 10 min. The solids were then washed repeatedly by distilled water, dried and coated with carbon, and then analyzed by a Camscan CS44 scanning electron microscope (SEM) (Cam Scan CS44, Cam Scan Electron Optics, Ltd., Cambridge, UK) fitted with a Energy Dispersive X-ray spectrometer (EDS) (Cam Scan Electron Optics, Ltd., Cambridge, UK). SEM was used to map the surface topography, and identify molybdenite faces and edges, while EDS was used to provide elemental identification on molybdenite faces and edges.

2.5. Calcium Speciation

Calcium speciation was constructed to describe the chemical species that may be present over the range of experimental conditions. The following reactions were used to construct the calcium species diagram [27]:



3. Results and Discussion

3.1. Ultraviolet-Visible Spectrophotometer Measurements

Figure 3 shows the UV-vis absorption spectra of PAHs and XLM at concentrations of 10 mg/L and 1 mg/L. The crest of PAHs absorption wave was around 219 nm, 267 nm, 275 nm and 285 nm at 10 mg/L PAHs, but only around 219 nm at 1 mg/L PAHs. The crest of XLM absorption wave at both 10 mg/L and 1 mg/L was around 219 nm, which represents PAHs in the composite collector. Therefore, the 219 nm was chosen for measuring the wavelength of PAHs in PAHs solutions and remaining in the solution after XLM interacted with the molybdenite sample in the subsequent study.

Standard solutions of various concentrations of PAHs were prepared to establish the standard absorption intensity of PAHs. Figure 4 shows the absorbance of PAHs as a function of its concentration. A linear relationship was obtained between the PAHs absorbance and its concentration:

$$A = 0.01988 + 0.87672C \quad (\text{Correlation coefficient } R^2 = 0.99964) \quad (5)$$

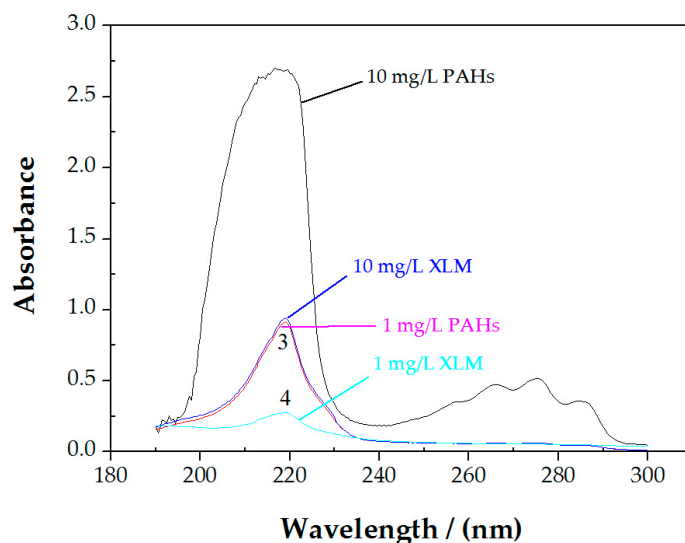


Figure 3. The UV-vis absorption spectra of PAHs and XLM at concentrations of 10 mg/L and 1 mg/L.

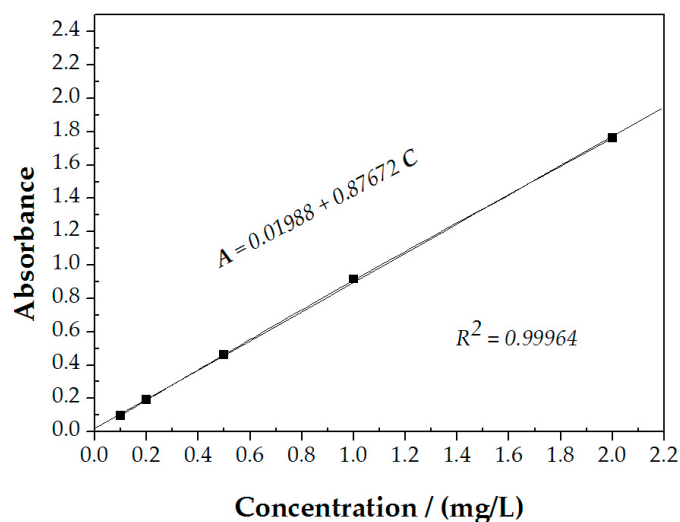


Figure 4. The absorbance of PAHs as a function of its concentration.

3.2. PAHs Adsorption on Molybdenite in the Presence of 800 mg/L Ca^{2+} or Na^{+}

The molybdenite sample was treated with 20 mg/L XLM in deionized water and in the presence of 800 mg/L Ca^{2+} or Na^{+} and then the adsorption of PAHs on molybdenite was measured. The results are shown in Figure 5. In general, PAHs adsorption from XLM increased rapidly when the adsorption time was less than 1 min. Then, the increase slowed down and an equilibrium was reached at about 3 min of adsorption. PAHs adsorption was also affected by the type of cations and pH. In deionized water, the maximum PAHs adsorption was 0.481 mg/g at pH 7. Since PAHs are a neutral, nonpolar molecule, it may adsorb on molybdenite surfaces as DO. Figure 5 also shows that at 800 mg/L Na^{+} , the maximum PAHs adsorption was 0.474 mg/g at pH 10 and 0.470 mg/g at pH 7. Compared with PAHs adsorption in deionized water, Na^{+} had little effect on PAHs adsorption. It is interesting to find that replacing Na^{+} by Ca^{2+} increased the maximum PAHs adsorption to 0.980 mg/g at pH 7 and 0.886 mg/g at pH 10, almost double the adsorption in deionized water. A higher pH decreased PAHs adsorption in the presence of Ca^{2+} .

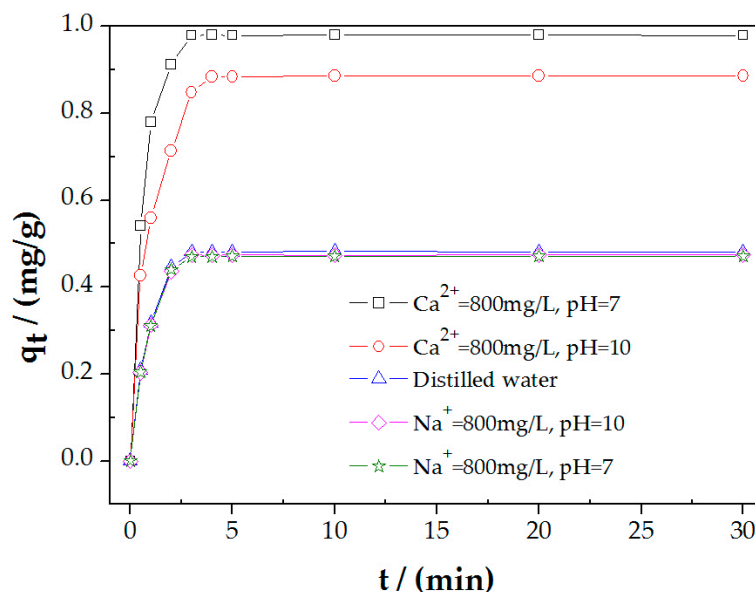
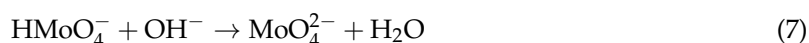
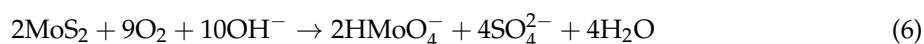


Figure 5. PAHs adsorption on molybdenite in the presence of 800 mg/L Ca^{2+} or Na^{+} at pH 7 and 10.

The adsorption test indicates that Ca^{2+} enhanced the adsorption of PAHs on molybdenite and the increased adsorption of PAHs was associated with the presence of Ca^{2+} .

Figure 6a,b show SEM images together with EDS of molybdenite faces and edges after treated with 20 mg/L XLM in the presence of 800 mg/L Ca^{2+} at pH 7. It was observed that the elemental composition was different on molybdenite faces and edges. As shown in Figure 6a, only Mo and S existed on molybdenite faces. This indicates that Ca^{2+} did not adsorb on molybdenite faces. However, Figure 6b clearly shows the presence of O and Ca besides Mo and S on molybdenite edges. Clearly, Ca^{2+} did adsorb on molybdenite edges. This is in agreement with previous studies [4,20] showing that the negative charge of molybdenite resulted from the oxidation of molybdenite edges, producing MoO_4^{2-} and HMoO_4^- . Ca^{2+} may adsorb on molybdenite edges by electrostatic interactions and spontaneously react with MoO_4^{2-} to form CaMoO_4 precipitates. The standard free energy of formation (ΔG_f°) is CaMoO_4 is $-1405.19 \pm 1.60 \text{ kJ mol}^{-1}$ [30]. CaMoO_4 is also slightly soluble with the solubility of $4.099 \times 10^{-3} \text{ g/100 g water}$ at 20°C . As a result, the formation of CaMoO_4 is possible on the oxidized molybdenite edges in the presence of Ca^{2+} . The following reactions are proposed to be responsible for the formation of CaMoO_4 :



The combination of Figures 5 and 6 suggests that the increased PAHs adsorption on molybdenite by Ca^{2+} compared to that in deionized water is related to Ca^{2+} that is only adsorbed on molybdenite edges. Obviously PAHs may adsorb on molybdenite edges through Ca^{2+} and the formation of CaMoO_4 precipitates may promote this adsorption. Since the presence of Ca^{2+} initiated PAHs adsorption on molybdenite edges, the influence of Ca^{2+} concentration and solution pH on PAHs adsorption was further studied.

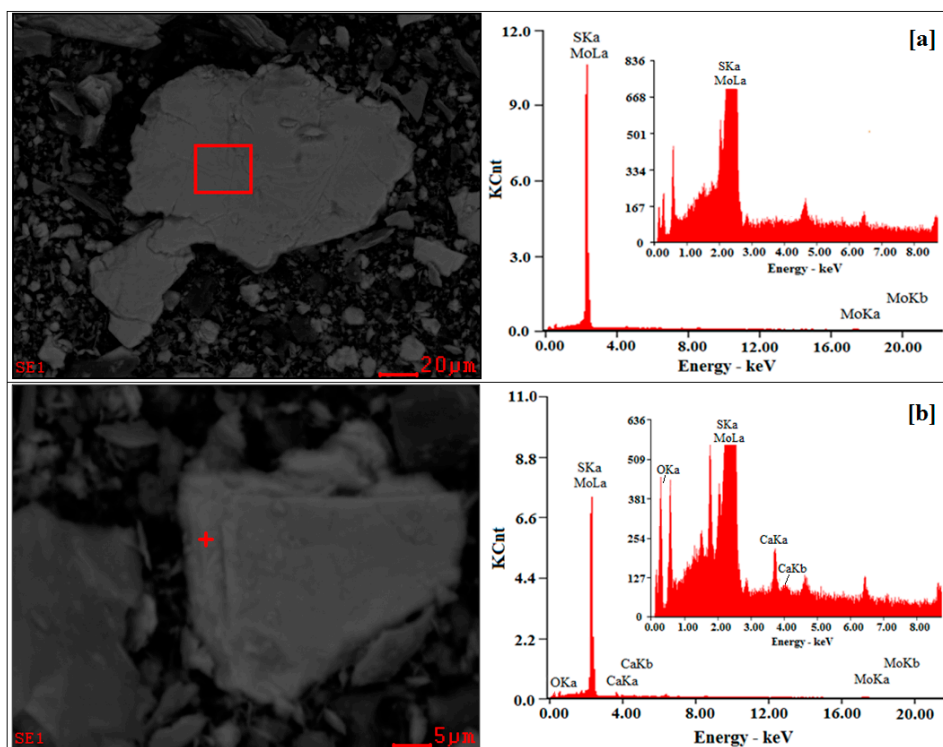


Figure 6. SEM images and EDS analysis of molybdenite faces and edges after treated with 20 mg/LDO in the presence of 800 mg/L Ca^{2+} at pH 7: (a) SEM images and EDS analysis of molybdenite faces; (b) SEM images and EDS analysis of molybdenite edges.

3.3. The Influence of Ca^{2+} Concentration on PAHs Adsorption on Molybdenite

Figure 7 shows PAHs adsorption on molybdenite after treated with 20 mg/L XLM as a function of Ca^{2+} concentration at pH 7. The maximum PAHs adsorption on molybdenite was 0.481, 0.730, 0.918 and 0.980 mg/g in the presence of 0, 100, 400 and 800 mg/L Ca^{2+} , respectively. PAHs adsorption increased with the Ca^{2+} concentration, and this increase slowed down at Ca^{2+} concentrations greater than 400 mg/L. In fact, the higher the Ca^{2+} concentration, the easier the reaction (8) to form calcium molybdate and CaMoO_4 precipitates, which promoted PAHs adsorption on molybdenite edges.

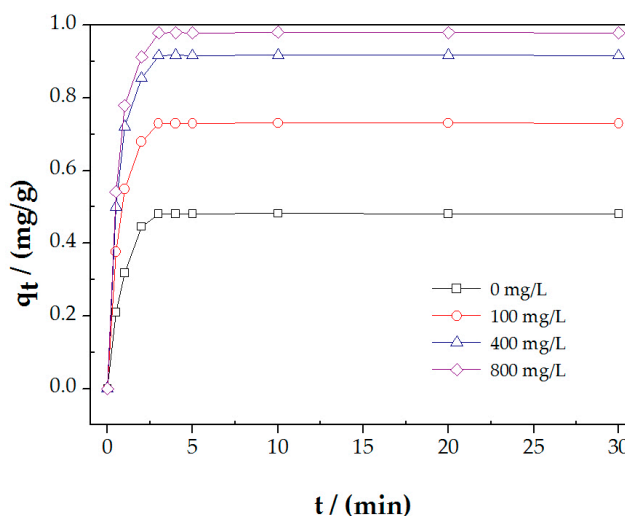


Figure 7. PAHs adsorption on molybdenite as a function of Ca^{2+} concentration at pH 7.

3.4. The Influence of pH on PAHs Adsorption on Molybdenite

Figure 8 shows PAHs adsorption on molybdenite after treated with 20 mg/L XLM as a function of pH in the presence of 800 mg/L Ca^{2+} . The maximum PAHs adsorption on molybdenite was 0.980, 0.961, 0.942 and 0.886 mg/g at pH 7, 8, 9 and 10, respectively. It can be seen that PAHs adsorption on molybdenite decreased with an increase in pH. At the pH greater than 8, this increase was slight.

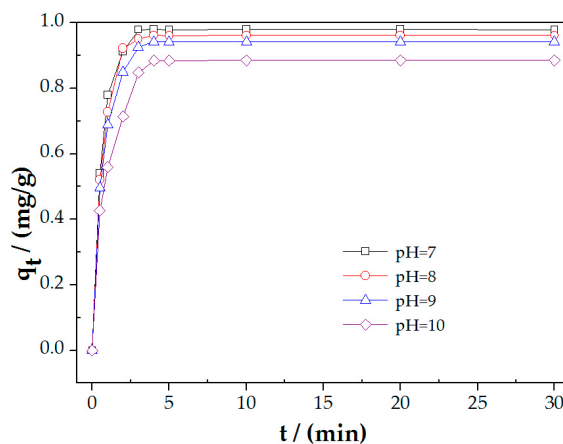


Figure 8. PAHs adsorption on molybdenite as a function of pH in the presence of 800 mg/L Ca^{2+} .

Figure 9 shows the distribution of calcium species as a function of pH at 800 mg/L total calcium. At pH below 6.2, the Ca^{2+} in the solution is relatively free to move around. However, at pH above 6.2, the free Ca^{2+} begins to react with hydroxyl ions, and hence, form a variety of hydroxyl compounds. Some of these hydroxyl compounds are $\text{Ca}(\text{OH})^+$, $\text{Ca}(\text{OH})_2(\text{aq})$ and $\text{Ca}(\text{OH})_2(\text{s})$. The concentration of these hydroxyl compounds increases with an increase in pH. The concentration of free Ca^{2+} reaches a maximum and then remains unchanged until pH 12. At pH above 12, the free Ca^{2+} concentration decreases substantially.

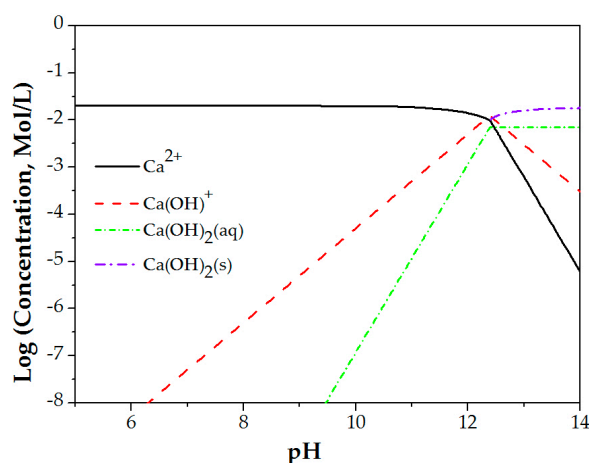


Figure 9. The distribution of calcium species as a function of pH at 800 mg/L total calcium.

Since PAHs adsorption on molybdenite decreased with an increase in pH or the concentration of hydroxyl compounds, hydroxyl compounds may inhibit PAHs adsorption. It seems that these hydroxyl compounds may compete with Ca^{2+} for molybdenite edges. It confirms that it was Ca^{2+} that react with MoO_4^{2-} to form CaMoO_4 precipitates that promote PAHs adsorption on molybdenite edges.

3.5. Zeta Potential Measurements

The zeta potential of molybdenite in the absence and presence 20 mg/L DO or XLM as a function of Ca^{2+} concentration was measured at pH 7, which would indicate the role PAHs as part of XLM played. The results are shown in Figure 10. The initial zeta potential of molybdenite was about -29 mV in all the three conditions without Ca^{2+} and increased with Ca^{2+} concentration. The zeta potential reversed to positive at 180 mg/L Ca^{2+} . Figure 10 also shows that the presence of DO only slightly lowered the zeta potential of molybdenite, but the presence of XLM significantly lowered the zeta potential of molybdenite due to the existence of PAHs. For example, at 2000 mg/L Ca^{2+} , the zeta potential of molybdenite was about 10 mV in the absence and presence of DO, but about 5 mV in the presence of XLM. Obviously, the 5 wt % PAHs in XLM contributed to the decrease of zeta potential probably due to the negatively charged π bonds. It has been reported that molybdate ions also have the π bonds [31,32]. It is likely that the cation- π interaction between PAHs and adsorbed Ca^{2+} and the π - π interaction between PAHs and MoO_4^{2-} take place on molybdenite edges supported by previous studies [33–39]. In fact, the cation- π interaction and the π - π interaction have been widely observed in biological systems [40].

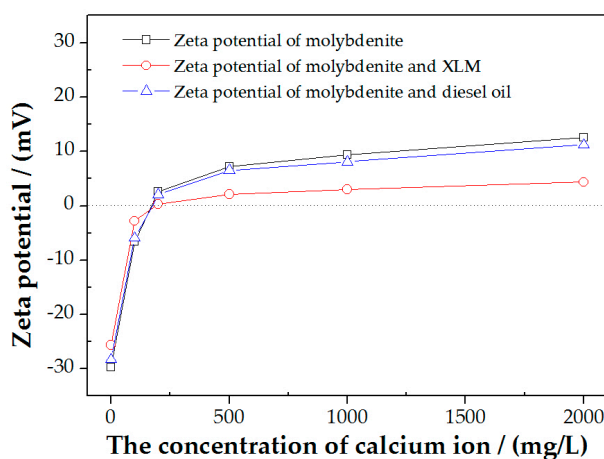
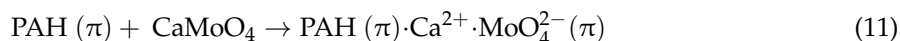
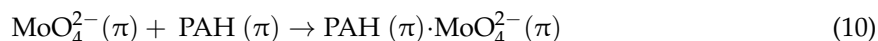
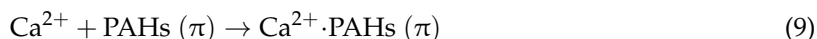


Figure 10. The zeta potential of molybdenite in the absence and presence of XLM and diesel oil as a function of Ca^{2+} concentration at pH 7.

This study indicates that the presence of CaMoO_4 precipitates on molybdenite edges is the main reason that PAHs could adsorb on molybdenite edges. Firstly, Ca^{2+} could react with MoO_4^{2-} , the oxidation product, on molybdenite edges to form CaMoO_4 precipitates. Secondly, PAHs could adsorb on molybdenite edges by the cation- π interaction between PAHs and adsorbed Ca^{2+} and the π - π interaction between PAHs and MoO_4^{2-} and the electrostatic interaction between PAHs and adsorbed Ca^{2+} . The reactions responsible for the adsorption of PAHs on molybdenite edges were proposed as follows:



4. Conclusions

PAHs, as part of the composite collector, XLM, could adsorb on molybdenite edges in the presence of Ca^{2+} . PAHs adsorption on molybdenite edges increased with Ca^{2+} concentration. It is possible that Ca^{2+} reacted with molybdenite edges to form CaMoO_4 precipitates, which promoted the adsorption of PAHs. The reaction of CaMoO_4 precipitates with PAHs may form $\text{PAHs-Ca}^{2+}\text{-MoO}_4^{2-}$ with a structure

of π -cation- π by (1) the cation- π interaction between PAHs and adsorbed Ca^{2+} , (2) the π - π interaction between PAHs and MoO_4^{2-} and (3) the electrostatic interaction between PAHs and adsorbed Ca^{2+} .

PAHs adsorption on molybdenite decreased with an increase in pH while the concentration of hydroxide compounds increased. It is possible that the hydroxide compounds competed with Ca^{2+} for molybdenite edges. The stronger the competitive adsorption, the less the CaMoO_4 precipitates on molybdenite edges to promote PAHs adsorption.

Fine molybdenite particles have more edges with more CaMoO_4 precipitates on molybdenite edges to reduce the hydrophobicity in the presence of a high amount of Ca^{2+} . The addition of PAHs in XLM may allow the adsorption of PAHs on molybdenite edges in the presence of Ca^{2+} , hence mitigating the deleterious effect of Ca^{2+} on fine molybdenite flotation.

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Author Contributions: He Wan, Wei Yang, Tingshu He and Yongjun Peng conceived and designed the experiments; He Wan performed the experiments and analyzed the data; Jianbo Yang and Lin Guo contributed to the preparation of reagents/materials.

Conflicts of Interest: The authors declare no conflict of interest.

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