Influencing mechanisms of sodium hexametaphosphate on molybdenite flotation using sea water

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Abstract: Flotation using sea water has been considered as a promising alternative to concentrate molybdenite (MoS_2) under alkaline conditions due to scarcity of fresh water and increasingly strict regulations on the quality of discharged water. However, the MoS_2 recovery with sea water during flotation has not been satisfactory, owing to the depressing effects from the hydrophilic metallic species onto MoS_2 surface. This study combines experimental and theoretical studies of MoS_2 flotation to investigate how the physicochemical properties of MoS_2 vary with the addition of a dispersant, sodium hexametaphosphate (SHMP), and in sea and fresh water. Our experimental results show that the addition of SHMP during flotation has increased the recovery of MoS_2, via reducing the adsorption of the hydrophilic metallic precipitation onto MoS_2 surface. The DLVO calculation confirms that the addition of SHMP increases the floatability of MoS_2 by dispersing the formed hydrophilic metallic precipitation ($Mg(OH)_2$ colloids) from the MoS_2 surface, via reversing attraction force to repulsion force, thereby improving MoS_2 flotation recovery.

Keywords: sodium hexametaphosphate, flotation, molybdenite, sea water, mechanism

1. Introduction

Molybdenite (MoS_2), the largest source of molybdenum (Mo) on the Earth, with approximately half of the Mo being beneficiated from the Cu-Mo ores via flotation process (Liu, 2012). Water, primarily fresh water, is essential to various steps of the flotation process and the water use could be quite high. Due to the increasing scarcity of fresh water and increasingly strict regulations on the quality of discharged water, more processing operations utilised sea water as an alternative water resource for mineral flotation (Wang and Peng, 2014), especially for those sited in the sea water-abundant area, *e.g.*, in Chile, Australia (Arias et al., 2017; Li et al., 2018).

However, many previous studies show that the use of sea water reduces MoS_2 floatability under high alkaline condition (Qiu et al., 2016; Ramos et al., 2013; Rebolledo et al., 2017; Suyantara et al., 2018). For instance, Ramos et al. (2013) reported that the decreased MoS_2 recovery was mainly due to the adsorption of hydrophilic Mg species formed on the MoS_2 surface. Qiu et al. (2016) found that both $Mg(OH)_2$ and $CaCO_3$ were formed on MoS_2 surface, reducing the hydrophobicity and floatability of MoS_2. In those studies, the precipitation on MoS_2 surface contributed to the hydrophobic surface.

Sodium hexametaphosphate (($NaPO_3)_6$, SHMP) is normally used as a dispersant in mineral flotation, with the hydrogen phosphates as its effective component in solution (Lu et al., 2019). Li et al. (2017) found that SHMP can change the surface charge of serpentine and ascharite, thereby preventing the inter-particle agglomeration between minerals and particles. Rebolledo et al. (2017) investigated the possibility of MoS_2 flotation in sea water in the presence of SHMP. Recently, Li et al. (2018) reported that the addition of SHMP can reduce the adsorption of precipitation on chalcopyrite surface. However, the mechanism has not been fully understood, especially in the sea water system.

The objective of the present study is to investigate how the physicochemical properties vary with and without SHMP in fresh and sea water. Both water type and the addition of SHMP can influence surface reactivity of MoS_2 and hence impact the flotation recovery. Flotation tests, as well as various measurements such as contact angle, zeta potential and XPS were thus carried out to better understand the influencing mechanisms of SHMP on MoS_2 flotation in sea water. In addition, DLVO theory was applied to calculate the forces between the formed species and MoS_2 surface.

2.   Material and methods

2.1. Samples and reagents

The MoS_2 samples were sourced from Guilin city, Guangxi province of China. After crushing and grinding, the MoS_2 powders were wet sieved, a particle size of 38~75µm was used for flotation tests while the -38µm powders were prepared for zeta potential measurements. All analytical reagents were purchased from China Sinopharm Chemical Reagent Co., Ltd, *e.g.* sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium chloride (NaCl), potassium chloride (KCl), calcium chloride ($CaCl_2$), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), sodium bicarbonate ($NaHCO_3$), magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$) and potassium bromide (KBr).

2.2. Flotation experiments

The flotation tests were carried out in a XFG-type flotation machine (same to the Fig. 1 shown in Li and Li (2019)) made by Wuhan Exploration Machinery Factory (Wuhan, China). 0.25g of MoS_2 particles was added into the flotation cell filled with 25 mL solution. The composition of sea water is same to that reported in Qiu et al. (2016) and Li and Li (2019), including 0.47 NaCl, 0.01 M KCl, 0.01 $CaCl_2$, 0.025 M $MgCl_2$, 0.0018 M $NaHCO_3$, 0.028 M $MgSO_4$ and 0.00087 M KBr. The flotation machine was operated at 1200 rpm and the pulp pH was controlled using NaOH or HCl at a desired value during the first 6 minutes. After introducing air (100 mL min^{-1}), the froth product was collected every 10 s. Both the floated concentrates and tailings were filtered and air dried, and then weighed for the calculation of cumulative recovery.

2.3. Contact angle measurements

The fresh MoS_2 surface was obtained by peeling of the chuck sample using adhesive tape and bathed in solution for 10 minutes. After that, the MoS_2 surface was washed three times using ultrapure water. After air drying, the MoS_2 surfaces treated under different conditions were placed into a contact-angle measuring device (JC2000C, Shanghai Zhongchen Digital Technology, China). The contact angles of several different areas on the treated MoS_2 surface were measured and the average values were reported.

2.4. Zeta potential measurements

The -38 µm MoS_2 particles were further ground to -5 µm in the Planetary Ball Mill Machine (DECO-PBD-V-0.4L, Changsha, China). 0.05g of obtained MoS_2 powders was placed into 50 mL conditioned solution and stirred for 10 minutes. NaOH or HCl was subsequently applied to adjust the solution pH. Then the zeta potential of the prepared pulp was determined by a Nano-ZS90 zeta potential analyzer (Malvern Co., Ltd, Malvern, UK). The average zeta potentials of three times were reported herein.

2.5. XPS measurements

Thermo Fisher ESCALAB 250Xi spectrometer (Waltham, MA, USA) with an Al K_α X-ray source was applied to determine the MoS_2 surfaces treated under the conditions same to those for flotation. XPS Peak 4.1 software was used for analysis (Li and Li, 2019).

2.6. EDLVO calculation

The extended Derjaguin-Landau-Verwey-Overbeek (EDLVO) theory was used to explain the interaction between MoS_2 particles and other particles, where the total interaction energies (V_T) equals to the sum of the Van der Waals interaction (V_W), the electrostatic interaction (V_E), and steric hindrance

effects (V_{SR}), as shown in Eq. 1:

$$V_T = V_W + V_E + V_{SR} \tag{1}$$

where V_W can be calculated according to Eq. 2 while A can be calculation based on Eq. 3:

$$V_W = -\frac{A}{6H}\left(\frac{R_1 R_2}{R_1 + R_2}\right) \tag{2}$$

$$A = \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)\left(\sqrt{A_{22}} - \sqrt{A_{33}}\right) \tag{3}$$

where A_{11} and A_{33} are the Hamaker constants of MoS_2 (9.38×10^{-20}J) (Li et al., 2018) and water (3.7×10^{-20}J). A_{22} is the Hamaker constant of MgO as the alternative to $Mg(OH)_2$ due to its unavailability. V_E can be calculated by Eq.4:

$$V_E = \frac{\pi \varepsilon_0 \varepsilon_r R_1 R_2}{R_1 + R_2}\left(\psi_1^2 + \psi_2^2\right)\left\{\frac{2\psi_1\psi_2}{\psi_1^2 + \psi_2^2}\ln\left[\frac{1+\exp(-\kappa H)}{1-\exp(-\kappa H)}\right] + \ln[1-\exp(-2\kappa H)]\right\} \tag{4}$$

where ε_0 and ε_r are the vacuum dielectric constant and relative vacuum dielectric constant (6.95×10^{-10} C^2 · J^{-1} · m^{-1}). κ ($0.18\,nm^{-1}$) is the debye-huckl parameter. φ_1, φ_2 are the surface potentials of MoS_2 and $Mg(OH)_2$ particles. Usually, the surface potential of particles is represented by the zeta potential. The steric hindrance interaction energy V_{SR} can be described by Eq. 5:

$$V_{SR} = \frac{4\pi R^2\left(\delta - \frac{H}{2}\right)}{Z(R+\delta)}kT\ln\left(\frac{2\delta}{H}\right) \tag{5}$$

where R is the radius of particles. δ (5.45 nm) represents the thickness of adsorbed layer after addition of SHMP. Z (1.9×10^{-16} m²) refers to the covering area of the macromolecules on the particle surface. In addition, k (1.381×10^{-23} J/K) is the Boltzmann constant.

3.   Results and discussion

3.1. Flotation

Fig. 1 shows the recovery of MoS_2 in pure water and sea water at pH ranging from 4 to 12. MoS_2 recovery in sea water was greater than that in pure water when the solution pH was lower than 8, indicating that sea water was beneficial to MoS_2 floatability at pH < 8. However, the MoS_2 recovery in pure water was greater than that in sea water when the pH was over 8. This suggests that the flotation of MoS_2 in sea water was depressed significantly at strong alkaline condition, consistent with previous studies (Castro et al., 2016; Jeldres et al., 2017; Li et al., 2018; Qiu et al., 2016). For instance, Suyantara et al. (2018) reported that the apparently decreased MoS_2 recovery in sea water was attributed to the formation of Ca and Mg precipitation on mineral surface when pH was higher than 9. However, MoS_2 recovery was only slightly decreased with increased pH in pure water, indicating that pH played an insignificant role on the natural floatability of MoS_2. Most previous studies indicated that MoS_2 flotation was conducted under alkaline conditions, *e.g.* pH 10, at which some metallic ions can be precipitated due to the low solubility (Luis et al., 2015; Suyantara et al., 2018). The precipitated species might adsorb onto the mineral surface, thereby decreasing the flotation recovery (Li et al., 2018; Li et al., 2018; Wangqing et al., 2017). Further investigation of the beneficial conditions for MoS_2 flotation was conducted at a selected pH of 10, based on the rational that MoS_2 flotation was significantly decreased in sea water under alkaline conditions.

Fig. 2 shows the MoS_2 recovery in pure and sea water at pH 10, with and without SHMP (50 mg/L). It is obvious that the recovery of MoS_2 in pure water was not increased with the SHMP addition, indicating that SHMP had negligible effects on the natural floatability of MoS_2 in pure water. In contrast, the addition of SHMP significantly increased MoS_2 recovery in sea water, achieving a high recovery of 95%, compared to only approximately 60% without SHMP. Moreover, the flotation rate of MoS_2 in the first 5 min was faster than that in the latter 5 min. Therefore, SHMP can relieve the inhibition effects of sea water on MoS_2 flotation under alkaline conditions, resulting in faster kinetics and higher recovery.

3.2. Contact angle

A higher contact angle corresponds to a lower wettability of minerals (Lazghab et al., 2005), generally resulting in greater floatability (Xia, 2017). Fig. 3 shows the effects of pH on contact angle of MoS_2 surface treated under different conditions. The contact angle of MoS_2 was reduced slightlywith increased pulp
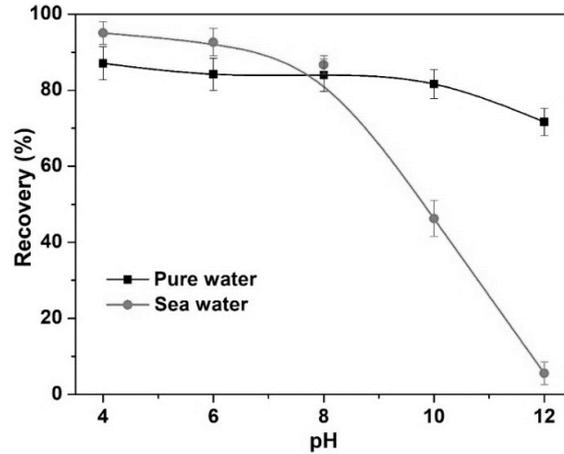
Fig. 1. MoS$_2$ recovery in pure water and sea water as a function of pH
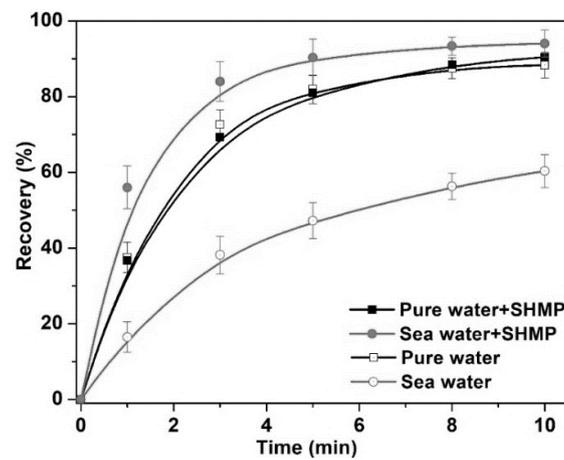

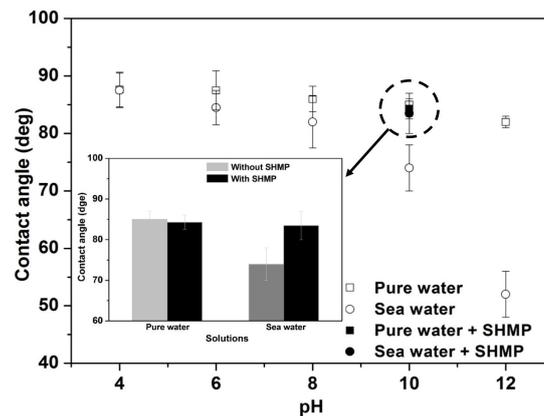Fig. 2. MoS$_2$ recovery in pure water and sea water with/without 50 mg/L SHMP

Fig. 3. Contact angle of MoS$_2$ treated in pure water and sea water

pH for pure water, suggesting that pH might play a negligible role on the hydrophobicity of MoS$_2$ surface. The presence of SHMP did not significantly change the contact angle of MoS$_2$ in pure water at pH 10, revealing that the addition of SHMP did not influence the natural wettability of MoS$_2$, similar to that found for CuFeS$_2$ (Li and Li, 2019). However, the contact angle of MoS$_2$ surface was decreasedin sea water with rising pH, showing that sea water adversely affected the hydrophobicity of MoS$_2$ surface. In addition, SHMP greatly increased the contact angle from 74° to 84° in sea water at pH 10, revealing that SHMP can relieve the decreased contact angle insea water.

3.3. Zeta potential

Fig. 4 shows the zeta potential of MoS_2 in pure water and sea water with and without SHMP within pH $4 \sim 12$. The zeta potential of MoS_2 in pure water was negative and gradually decreased with increased pH. Differently, the zeta potential of MoS_2 in sea water was higher than that in pure water and increased with increasing pH. Specially, when MoS_2 was treated in seawater, the zero electric point appeared at pH 9.2 where the zeta potential of MoS_2 was reversed from negative to positive. These indicate that the positively charged metallic precipitation (hydrophilic) is adsorbed on the negatively charged MoS_2 surface, thereby reducing MoS_2 hydrophobicity and flotation recovery (Li et al., 2018).
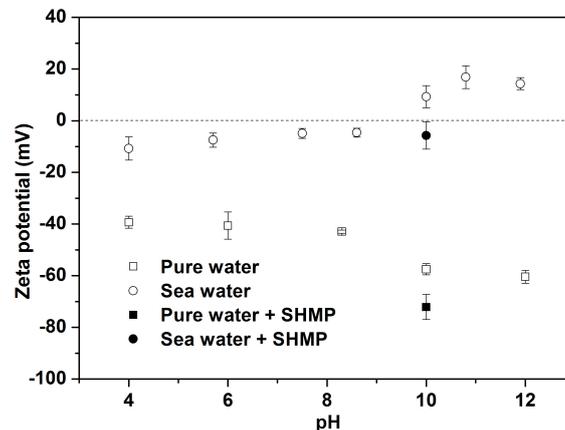

Fig. 4. Zeta potential of MoS_2 in pure water and sea water as a function of pH

In addition, when SHMP was added at pH 10, the zeta potentials of MoS_2 in both solutions were decreased and the zeta potential in sea water was even reversed from positive to negative again, indicating that the SHMP was capable of removing positively charged hydrophilic precipitation from MoS_2 surface, presenting a cleaner surface for greater flotation recovery.

3.4. XPS analysis

Fig. 5 shows the XPS measurements of MoS_2 surfaces treated under different conditions. Comparing to the untreated MoS_2 (Fig. 5a), the peak intensities of Ca 2p, O 1s and Mg 2s were significantly increased in sea water in the absence of SHMP (Fig. 5b). Qiu et al. (2016) reported that $CaMg(CO_3)_2$ may form in pH 7~10, while $Mg(OH)_2$ and $CaCO_3$ were formed at pH greater than 9.5 and 10, respectively. In addition, MoS_2 recovery in sea water was reduced with increased pH. Therefore, these precipitates mainly contributed to the depressed flotation recovery in sea water, consistent with many previous studies reporting that the depression of sea water on sulfide flotation was mainly due to the presence of hydrophilic $Mg(OH)_2$ on minerals surface, thereby inhibiting mineral floatability (Jeldres et al., 2016; Ramos et al., 2013; Rao et al., 2016; Suyantara et al., 2018).
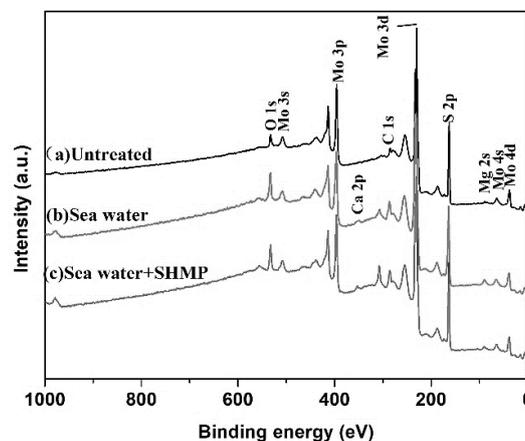

Fig. 5. XPS survey of MoS_2, (a) untreated, treated in (b) sea water and (c) sea water +SHMP at pH 10

Table 1 further shows that the concentrations of O 1s, Ca 2p and Mg 2s were increased from 7% to 11%, 0 to 1% and 1% to 4%, respectively, when sea water was applied as flotation medium, suggesting that both Mg and Ca species were adsorbed onto the MoS_2 surface. However, Mg and O concentrations were decreased from 4% to 2%, and 11% to 7%, respectively, in the addition of SHMP, suggesting that SHMP reduced the attachments of these species on MoS_2 surface in sea water. The surfacial species is likely $Mg(OH)_2$, which has been reported in previous studies (Qiu et al., 2016; Ramos et al., 2013; Rebolledo et al., 2017; Suyantara et al., 2018).

Table1 Elemental quantification (at. %) of MoS_2

Element	Binding Energy (eV)	Conditions		
		Untreated	Sea water	Sea water+SHMP
C 1s	284.8	6	15	15
S 2p	162.4	54	41	43
Mo 3d	230.0	32	28	32
O 1s	533.2	7	11	7
Ca 2p	351.0	0	1	1
Mg 2s	89.5	1	4	2

3.5. DLVO calculation

Fig. 6 shows the DLVO interaction energy between MoS_2 and $Mg(OH)_2$ colloids at pH 10 with and without SHMP. In the absence and presence of SHMP, the zeta potentials of $Mg(OH)_2$ at pH 10 was 11.6 mV and -23.2 mV, respectively, while the zeta potentials of MoS_2 was -57.5 mV and -71.9 mV, respectively. Without SHMP, the V_T between MoS_2 and $Mg(OH)_2$ particles was negative in the pH range examined, indicating that the attraction force was dominated between MoS_2 and $Mg(OH)_2$ colloids. In other words, $Mg(OH)_2$ can attach onto MoS_2 surfaces (Yu et al., 2018). After the addition of SHMP, the V_T was reversed from negative to positive values, suggesting that the repulsion force was dominated. This means that the precipitation of $Mg(OH)_2$ was hard to adsorb on the MoS_2 surface in the presence of SHMP. Therefore, the increased MoS_2 recovery in the presence of SHMP was mainly due to the prevention of hydrophilic $Mg(OH)_2$ precipitation attaching onto MoS_2 surface.
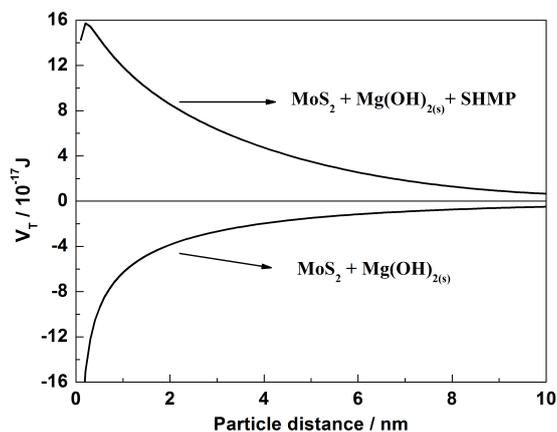
Fig. 6. Interaction energy between MoS_2 particles and $Mg(OH)_2$ colloids

4.   Conclusions

The flotation recovery of MoS_2 in sea water was significantly reduced under alkaline condition, primarily due to the attachment of formed hydrophilic metallic species onto MoS_2 surface. The addition of SHMP reduced the adsorption of such precipitation. DLVO theoretical calculation demonstrated that the dominant interaction force between MoS_2 and $Mg(OH)_2$ colloids was attraction force, which was reversed to repulsion force in the presence of SHMP, thereby improving MoS_2 flotation recovery by removing $Mg(OH)_2$ from MoS_2 surface.

5. Acknowledgements

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