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Study of the influence of hydrophobic polymers on the wettability of minerals: chalcopyrite, galena and pyrite

Abstract: This study investigates the impact of hydrophobic polymers on the wettability and flotation efficiency of key minerals, including chalcopyrite, galena, pyrite, and quartz. Copolymers based on [[2-(methacryloyloxy) ethyl] trimethylammonium chloride] and styrene were synthesized using radiation copolymerization in various ratios. The chemical structures of the copolymers were confirmed through IR spectroscopy, highlighting the key functional groups that contribute to their effectiveness in modifying mineral surfaces. Contact angle measurements were used to assess the changes in wettability of mineral surfaces treated with these hydrophobic polymers. Results showed that the application of the copolymers significantly reduced the contact angles of chalcopyrite, galena, and pyrite, indicating an increase in their surface hydrophobicity. The study also explored the combined use of the polymers with traditional flotation reagents, such as sodium butyl xanthate, demonstrating a synergistic effect that enhanced the flotation process by further reducing contact angles and improving selectivity. The findings suggest that hydrophobic polymers can optimize flotation efficiency by altering the surface properties of minerals, leading to higher recovery rates and improved separation of valuable minerals from waste materials. Additionally, the use of polymers has the potential to reduce the environmental impact of flotation processes by lowering the consumption of toxic reagents.
Keywords: hydrophobic polymers, mineral wettability, copolymers, chalcopyrite, galena, pyrite.

Introduction

The ore beneficiation process plays a key role in the mining industry, as it enables the separation of valuable minerals from waste rock, thus increasing the overall efficiency of resource extraction. Among the various techniques used in mineral processing, flotation remains one of the most widely applied and effective methods. It operates by exploiting differences in the surface properties of minerals, allowing for the selective separation of valuable components from gangue.

In recent years, considerable attention has been directed toward the use of hydrophobic polymers in flotation processes, due to their ability to modify the surface properties of minerals such as chalcopyrite ($CuFeS_2$), galena (PbS), pyrite (FeS_2), and quartz (SiO_2). These minerals are often found together in polymetallic ores, and their selective separation remains a critical challenge in mineral processing. The ability to enhance the separation of valuable minerals from waste through selective modifications of surface properties is of great importance for optimizing the flotation process (Song et al., 2000; 2001; Kenzhaliyev et al., 2018; Kenzhaliyev, 2019; Wang et al., 2021; Kvon et al., 2023).

One of the key factors influencing flotation efficiency is the wettability of mineral surfaces. The degree of hydrophobicity or hydrophilicity of these surfaces plays a decisive role in determining the attachment of air bubbles to mineral particles, which is essential for successful flotation. Researchers have identified the contact angle, measured on the surface of minerals, as the primary parameter used to quantify hydrophobicity. A larger contact angle typically indicates higher hydrophobicity, which improves the flotation performance of the mineral (HUANG et al., 2018).

This study focuses on the interaction between hydrophobic polymers and the minerals chalcopyrite, galena, pyrite, and quartz. Specifically, it examines how these polymers influence the wettability of the mineral surfaces and how this modification can improve flotation efficiency. The primary objective of this research is to identify opportunities for increasing the selectivity and recovery of valuable minerals by altering their surface characteristics with hydrophobic polymers. Understanding these interactions at the molecular level could lead to more effective separation techniques and overall process optimization in the mineral beneficiation industry.

Research methods

The research was conducted using a combination of advanced experimental techniques and analytical methods to investigate the influence of hydrophobic polymers on the wettability of mineral surfaces. The following methods were employed:

Synthesis of Copolymers

Copolymers based on [[2-(methacryloyloxy) ethyl] trimethylammonium chloride] and styrene in various molar ratios were synthesized through radiation copolymerization. The copolymerization was performed using γ-radiation to initiate the polymerization process, ensuring a controlled reaction environment. Different copolymer compositions (e.g., 90:10, 60:40) were prepared by adjusting the monomer feed ratios to examine the impact of varying polymer structures on mineral surface modification.

Infrared (IR) Spectroscopy

To confirm the chemical structure of the synthesized copolymers and ensure the success of polymerization, infrared (IR) spectroscopy was used. The IR spectra of both the original monomers and synthesized copolymers were recorded. This allowed for the identification of key functional groups in the polymer chains, including characteristic absorption bands for $–CH_2$, C=O, and C–O–C groups. The analysis also helped assess the influence of different monomer ratios on the structural features of the copolymers.

Contact Angle Measurements

The wettability of mineral surfaces (chalcopyrite, galena, pyrite, and quartz) was evaluated through contact angle measurements. A goniometer was used to measure the contact angle of distilled water droplets placed on the mineral surfaces. The contact angle is a key parameter that reflects the hydrophobicity or hydrophilicity of the mineral surface. Higher contact angles indicate increased hydrophobicity, which is favorable for flotation processes. Contact angles were measured both in the absence of polymers (as a baseline) and after treating the mineral surfaces with different concentrations of synthesized hydrophobic polymers (e.g., 4 ppm). Additional tests were conducted using combinations of copolymers with traditional flotation reagents such as sodium butyl xanthate (Bx Na) to observe the synergistic effects.

These research methods provided a comprehensive framework to study the influence of hydrophobic polymers on the flotation efficiency of minerals, focusing on their ability to modify surface properties and enhance the recovery of valuable components from ore. The combination of contact angle measurements, flotation tests, and structural analysis enabled a detailed understanding of the mechanisms behind polymer-mineral interactions.

Results and discussions

Copolymers based on [[2-(methacryloyloxy) ethyl] trimethylammonium chloride] and styrene in different ratios were synthesized via radiation copolymerization. The chemical structures of the original monomers and synthesized copolymers were confirmed by IR spectroscopy, as shown in Figure 1. In the IR spectrum of [[2-(methacryloyloxy) ethyl] trimethylammonium chloride], absorption bands appeared at 2922 cm^{-1} and 1206 cm^{-1}, corresponding to the stretching vibrations of aliphatic $–CH_2$ and C–O groups, respectively. A broad peak at 3356 cm^{-1} indicates intermolecular hydrogen bonding, while a weak absorption band at 1436 cm^{-1} corresponds to the amine group –CH-O–.

In the IR spectrum of styrene, strong absorption bands at 1428 cm^{-1} and 1654 cm^{-1} were attributed to the stretching vibrations of the methylene group $-HRC=CH_2-$. The spectra of the copolymers displayed prominent carbonyl stretching vibrations from [[2-(methacryloyloxy) ethyl] trimethylammonium chloride] at 1323 cm^{-1} and 1298 cm^{-1}. Furthermore, the hydroxyethyl ether group from [[2-(methacryloyloxy) ethyl] trimethylammonium chloride] was confirmed by the presence of double peaks in the C–O–C stretching vibrations at 1143 cm⁻¹ and 1088 cm⁻¹. The intensity and position of these peaks varied with the composition of the monomer mixture, showing that lower styrene content increased the relative intensity of the hydroxyethyl ether group's vibration peaks.

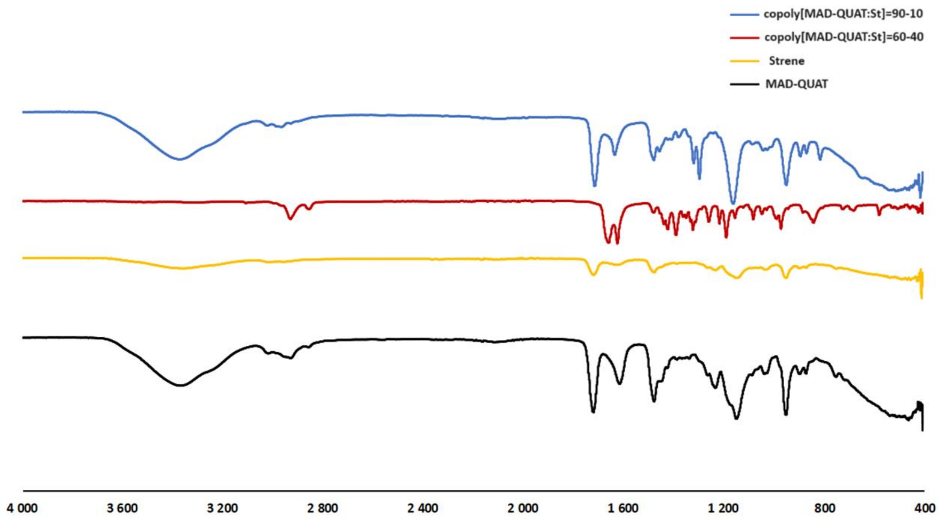

Figure 1. IR spectra of copolymers based on [MAD-QUAT-styrene]

Contact angle measurements were performed to evaluate the influence of hydrophobic polymers on the wettability of mineral surfaces in Figure 2. Without polymer treatment, the contact angle of chalcopyrite in distilled water averaged 80.25°, indicating moderate hydrophobicity. Upon adding a [MAD-QUAT]-[St] copolymer with a 90:10 ratio at 4 ppm concentration, the contact angle decreased to 74.99°, revealing enhanced hydrophobicity.

Galena, with an initial high contact angle of 101.03°, was highly hydrophobic in distilled water. Treatment with the same [MAD-QUAT]-[St] copolymer reduced the contact angle to 68.17°, demonstrating a significant change in wettability and an improved interaction with air bubbles. This result indicates a strong adsorption of the copolymer on the galena surface, likely due to its affinity for the sulfide groups present in the galena.

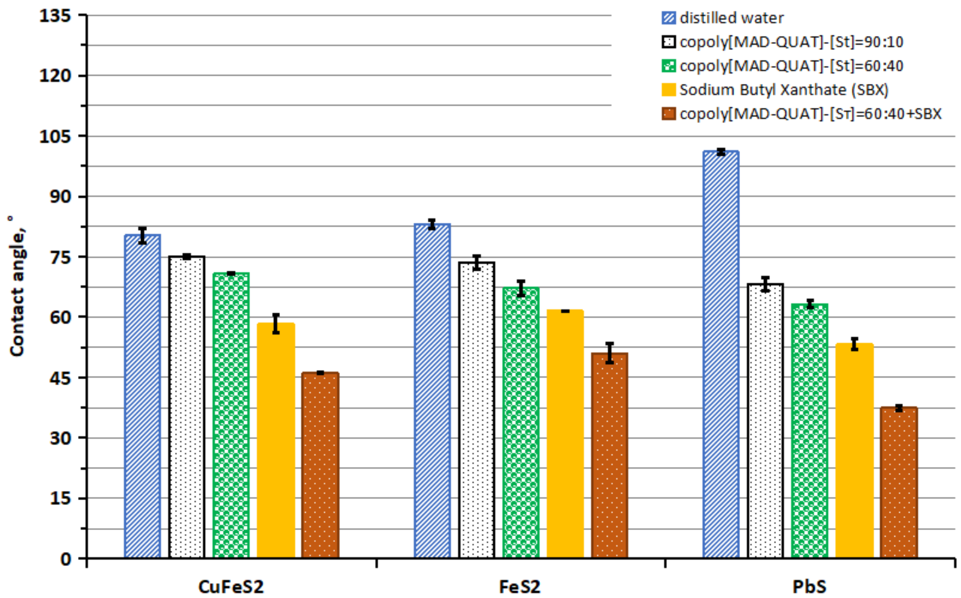

Figure 2. The influence of various reagents on the contact angles of a drop on the surface of minerals (Chalcopyrite, pyrite, galena)

Pyrite, another key mineral, had an initial contact angle of 83.00°, showing a natural hydrophobic character. After treatment with the [MAD-QUAT]-[St] copolymer, the contact angle dropped to 73.53°, further improving its hydrophobic properties, which suggests a potential enhancement in flotation performance.

A comparative analysis indicated that variations in the composition of copolymers affected their effectiveness. For example, when using the [MAD-QUAT]-[St] copolymer in a 60:40 ratio, the contact angle of chalcopyrite decreased to 70.78°, representing a less significant increase in hydrophobicity compared to the 90:10 ratio copolymer. A similar trend was observed in Galena, where the contact angle decreased to 63.15°.

The combination of copolymers with sodium butyl xanthate (Bx Na) produced the most significant reductions in contact angles. For instance, the contact angle of chalcopyrite treated with this combination averaged 46.12°, suggesting a high degree of hydrophobicity. Galena and pyrite exhibited similar behavior, with their contact angles decreasing to 37.41° and 51.06°, respectively, indicating the synergistic effect of combining polymers with traditional flotation reagents.

The mechanism of adsorption of hydrophobic polymers on mineral surfaces is largely governed by the physicochemical interactions between the functional groups of the polymers and the active sites on the mineral surfaces. For chalcopyrite and galena, the high contact angles can be attributed to the strong adsorption of the polymers, facilitated by the presence of sulfide groups that interact effectively with the hydrophobic portions of the polymer chains. This results in the formation of a hydrophobic film on the mineral surface, enhancing their flotation behavior through improved attachment to air bubbles (Scharnberg et al., 2023).

Despite the presence of sulfide groups, pyrite has a denser crystal structure, which can hinder the adsorption of polymers on its surface. However, the introduction of specific functional groups into the polymer structure may improve the polymer’s interaction with pyrite, thereby altering its wettability.

The use of hydrophobic polymers in conjunction with traditional flotation reagents offers a promising route for reducing reagent consumption and enhancing the efficiency of mineral beneficiation. This approach not only improves process efficiency but also reduces the volume of flotation waste, thereby mitigating the environmental impact. For example, reducing the use of conventional reagents like sodium butyl xanthate can decrease the toxicity of flotation tailings, making the process more environmentally friendly (Zhang et al., 2023).

The results of this study indicate that modifying the wettability of minerals using hydrophobic polymers presents new opportunities for optimizing flotation processes. Enhancing the hydrophobicity of valuable minerals such as chalcopyrite and galena through polymer treatment can lead to improved concentrate recovery and quality. Future research will focus on exploring the effects of various hydrophobic polymers and their combinations on a broader range of minerals, to develop more efficient and eco-friendly mineral beneficiation techniques (Li et al., 2024).

In conclusion, the use of hydrophobic polymers to modify the surface properties of minerals is a promising strategy for advancing flotation technology, which could significantly enhance the efficiency of mineral processing (Li et al., 2021).

Conclusions

The copolymers based on [[2-(methacryloyloxy) ethyl] trimethylammonium chloride] and styrene were successfully synthesized using radiation copolymerization, and their chemical structures were confirmed through IR spectroscopy. The composition of the copolymers played a crucial role in determining their effectiveness in modifying mineral surfaces. Specifically, a higher content of [[2-(methacryloyloxy) ethyl] trimethylammonium chloride] increased the hydrophobic properties of the polymers, making them more effective in enhancing mineral flotation performance.

The study demonstrated that hydrophobic polymers significantly influence the wettability of minerals, which is a critical factor in flotation. Contact angle measurements showed that the application of copolymers reduced the contact angles of chalcopyrite, galena, and pyrite, indicating an increase in surface hydrophobicity. The degree of hydrophobicity was dependent on both the polymer composition and concentration, with the 90:10 ratio of [MAD-QUAT]-[St] copolymer exhibiting the most pronounced effect.

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The combination of hydrophobic polymers with traditional flotation reagents, such as sodium butyl xanthate, produced a synergistic effect, further reducing the contact angles and enhancing the flotation efficiency of the minerals. This combination allowed for more selective separation of valuable minerals (e.g., chalcopyrite and galena) from waste materials (e.g., quartz and pyrite), resulting in higher recovery rates and improved concentrate quality. These findings suggest that hydrophobic polymers can be used to optimize flotation processes, reducing the need for higher amounts of conventional reagents.

The use of hydrophobic polymers offers a potential reduction in the consumption of traditional flotation reagents, such as xanthates, which are known for their environmental toxicity. By improving the selectivity and efficiency of the flotation process, the polymers contribute to reducing the volume of waste generated, leading to a lower environmental footprint in mineral processing operations. This opens the possibility for more environmentally sustainable beneficiation methods.

The study highlights the potential of using hydrophobic polymers to develop more efficient and eco-friendly flotation technologies. Future work could expand on this research by exploring other types of hydrophobic polymers and their interactions with a wider range of minerals. Moreover, investigating the long-term stability of the hydrophobic films formed on mineral surfaces and their behavior under varying flotation conditions will be crucial for further optimization.

In conclusion, the use of hydrophobic polymers represents a promising approach to improving the selectivity and efficiency of flotation processes in mineral beneficiation. The results of this study provide a foundation for future advancements in the development of innovative and environmentally friendly flotation techniques.

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References

Huang, X. Tao, Xiao, W., Zhao, H. Bo, Cao, P., Hu, Q. Xiu, Qin, W. Qing, Zhang, Y. Sheng, Qiu, G. Zhou, & Wang, J. (2018). Hydrophobic flocculation flotation of rutile fines in presence of styryl phosphonic acid. *Transactions of Nonferrous Metals Society of China (English Edition*), 28(7), 1424–1432. https://doi.org/10.1016/S1003-6326(18)64781-8

Kenzhaliyev, B. (2019). Innovative technologies providing enhancement of non-ferrous, precious, rare and rare earth metals extraction. *Kompleksnoe Ispolzovanie Mineralnogo Syra = Complex Use of Mineral Resources*, 310(3), 64–75. https://doi.org/10.31643/2019/6445.30

Kenzhaliyev, B., Kvyatkovsky, S., Kozhakhmetov, S., Sokolovskaya, L., & Semenova, A. (2018). Deparation of dump slags at the Balkhash copper smelting plant. *Kompleksnoe Ispolzovanie Mineralnogo Syra = Complex Use of Mineral Resources*, 306(3), 45–53. https://doi.org/10.31643/2018/6445.16

Kvon, S., Nesterova, V., Omarova, A., Kulikov, V., & Chsherbakova, Y. (2023). Study of the mineral composition of promising copper ores of the Republic of Kazakhstan. *Kompleksnoe Ispolzovanie Mineralnogo Syra = Complex Use of Mineral Resources*, 325(2), 87–93. https://doi.org/10.31643/2023/6445.22

Li, M., Xiang, Y., Chen, T., Gao, X., & Liu, Q. (2021). Separation of ultra-fine hematite and quartz particles using asynchronous flocculation flotation. *Minerals Engineering*, 164. https://doi.org/10.1016/j.mineng.2021.106817

Li, W., Cui, Y., Pan, Z., Jiao, F., Yang, C., Wang, X., Zhang, Z., & Qin, W. (2024). Hydrophobic agglomeration flotation of fine cassiterite induced by kerosene and sodium oleate. *Powder Technology*, 432. https://doi.org/10.1016/j.powtec.2023.119015

Scharnberg, A. R. A., Oliveira, H. A., Weschenfelder, S. E., Rubio, J., & Azevedo, A. C. (2023). Flocculation of emulsified oil-in-water with dodecylbenzene sulfonate and polyacrylamide and floc separation by dissolved air flotation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 669. https://doi.org/10.1016/j.colsurfa.2023.131496

Song, S., Lopez-Valdivieso, A., Luis Reyes-Bahena, J., & Israel Bermejo-Perez, H. (2001). Hydrophobic flocculation of sphalerite fines in aqueous suspensions induced by ethyl and amyl xanthates. *In Colloids and Surfaces A: Physicochemical and Engineering Aspects* (Vol. 181). www.elsevier.nl/locate/colsurfa

Song, S., Lopez-Valdivieso, A., Reyes-Bahena, J. L., Bermejo-Perez, H. I., & Trass, O. (2000). Hydrophobic flocculation of galena fines in aqueous suspensions. *Journal of Colloid and Interface Science*, 227(2), 272–281. https://doi.org/10.1006/jcis.2000.6857

Wang, Z., Liu, N., & Zou, D. (2021). Interface adsorption mechanism of the improved flotation of fine pyrite by hydrophobic flocculation. *Separation and Purification Technology*, 275. https://doi.org/10.1016/j.seppur.2021.119245

Zhang, H., Li, C., Li, L., Cheng, S., Wang, P., Sun, L., Huang, J., & Zhang, X. (2023). Uncovering the optimal structural characteristics of flocs for microalgae flotation using Python-OpenCV. *Journal of Cleaner Production*, 385. https://doi.org/10.1016/j.jclepro.2022.135748