

Original Paper

Preparation of Material for Adsorption Ag(I) in the Solution

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Abstract

The application of silver in electronics, jewelry, catalytic and other industries often produces a large amount of silver-containing wastewater, which causes serious impact to the surrounding environment and human health, while silver has a certain economic value attached to it. Therefore, how to effectively treat and recover Ag(I) from the silver-containing wastewater is a hot topic of concern at present. In order to seek an efficient and environmentally friendly adsorbent, this paper compared the adsorption efficiency of purified, thermally modified, acid modified and thermally-acid modified Bentonite on silver, selected an economical and reasonable purified clay as a carrier, and then completed the preparation of modified Bentonite as well as the optimization of conditions with sodium silicate as a surfactant and 3-mercaptopropyltrimethoxysilane as a modifier. The experiments showed that under the conditions of sodium silicate dosage of 15% of Bentonite, Bentonite and modifier dosage of 1:1, solution pH of 9, temperature of 45 °C and modification time of 5 h, the synthesized sulfhydryl modified Bentonite has good adsorption performance on Ag(I), and its adsorption capacity can reach 293.7 mg g⁻¹.

Keywords

sulfhydryl modified Bentonite, silver, optimization, adsorption

1. Introduction

Silver is a common precious metal in daily life, and is widely used in electronic appliances, jewelry decoration, and catalysis due to its superior electrical and thermal conductivity, as well as its good malleability, ductility, and photosensitivity (Akgul, Karabakan, Acar, & Yurum, 2006; Tolaymat, El Badawy, Genaidy, Scheckel, Luxton, & Suidan, 2010). On the one hand, the increasing consumption of silver in industrial production is accompanied by a large amount of industrial wastewater containing Ag(I), which is biologically active and rapidly interacts with a variety of receptors on cell membranes of

mammalian and eukaryotic cells (Holt & Bard, 2005; Bianchini & Wood, 2003; Lansdown, 2006). If these wastewaters are discharged directly into the environment without treatment, they can cause serious harm to the natural environment, flora and fauna, and human health. On the other hand, as a precious metal with very low abundance, the demand for silver is far greater than the demand for silver from surveys (Fromm, 2011). It can be seen that the demand for silver is far greater than the supply, and the gap between the two cannot be ignored from the perspective of economic development. Therefore, the removal or recovery of precious metal silver from silver wastewater is of great research significance, both from the environmental protection and human health as well as economic perspectives.

At present, the main methods to remove or extract silver from silver-containing wastewater include: replacement method (Zheng, Wang, Shi, Dong, Meng, He, & Cai, 2020; Cao, Wang, Ge, & Zhou, 2015), precipitation method (Rivera, Juarez, Patino, Reyes, Roca, & Reyes, 2012), ion exchange method (Niu, Yan, Du, Hao, Wang, Wang, & Guan, 2020) electrolysis (Frioui, Oumeddour, & Lacour, 2017) and adsorption method (Phothitontimongkol, Sanuwong, Siebers, Sukpirom, & Unob, 2013; Ding, Shao, Luo, Yin, Yu, Fang, Yang, L., Yang, J., & Luo, 2020), etc. Most of these methods have the defects of high investment cost, complicated operation and secondary pollution. In contrast, adsorption is an efficient, simple, economical and environmentally friendly wastewater treatment method, so the search for an efficient and environmentally friendly adsorbent is the key to the wide application of this technology.

Bentonite is a lamellar clay mineral with large specific surface area and strong ion exchange capacity (Su, Wang, Ma, Han, Wang, Wang, & Liu, 2020). It is a natural adsorbent with abundant reserves, low cost and great potential. However, natural Bentonite cannot be used effectively due to some inherent disadvantages such as low adsorption capacity, so some modification of Bentonite is needed to improve its economic value and usability. Some recent studies have shown that the adsorption of Cu, Pb, Cd, Zn and other metals by sulfhydryl modified Bentonite has shown unique superiority (Song, Li, Z., Li, W., An, Li, M., Qin, & Liu, 2022; Pang, Yang, Huang, Lei, Zeng, & Li, 2018). Considering that Ag and Cu, Pb, Cd, Zn, etc. belong to the same sulphur-friendly elements, and according to Pearson's soft and hard acid-base theory (HSAB) (Pearson, 1963), It is known that Ag(I) as a soft acid ion, sulfhydryl as a typical soft base, the two can form a stable complex, so the sulfhydryl modified Bentonite should have good adsorption of Ag(I). However, In Guimar ã et al. (2009) a related study, the adsorption capacity of sulfhydryl modified Bentonite for Ag(I) was about 108 mg g⁻¹, and its adsorption effect was somewhat lower than the expected target. In addition, the material was made by reflux method under N₂ with toluene as solvent, and the synthesis method is not only complicated and costly, but also the large amount of toluene is easy to cause harm to the environment, plants and animals as well as human health. The addition of a small amount of surfactant can significantly enhance the adsorption effect of sulfhydryl modified Bentonite on metal ions (Dong, Zhu, & Cui, 2020). Therefore, in this study, by comparing the effects of purification, thermal modification, acid modification and thermal-acid modification on the adsorption of silver by Bentonite, an economical and reasonable carrier was selected, and 3-mercaptopropyltrimethoxysilane was grafted on the surface of Bentonite by a simple

and easy stirring method using sodium silicate as surfactant, and a material with high efficiency in the adsorption of Ag(I) was prepared by the optimization of relevant conditions. The above research work can provide relevant theoretical basis and technical support for the removal or recovery of Ag(I) from wastewater.

2 Experiment Section

2.1 Materials and Reagents

The materials and reagents used in this study were Bentonite (purchased from Lingshou, Hebei, China), 3-mercaptopropyltrimethoxysilane (purchased from Aladdin), sodium pyrophosphate, sodium silicate, anhydrous ethanol, sodium hydroxide, nitric acid (purchased from Chengdu Kolon Chemicals Co., Ltd.), silver flakes (purchased from Jomal Electronic Materials Business Department, Yushan Town, Kunshan, China), silver stock solution ($1.4657 \text{ mg mL}^{-1}$) was prepared by weighing 1.4657 g of silver flakes was dissolved in nitric acid and fixed in a 1000 mL volumetric flask with 5% dilute nitric acid (other concentrations were diluted as needed for the experiment), in which all materials used were analytically pure except silver flakes which were high purity.

2.2 Preparation of Adsorbent

2.2.1 Purification of Bentonite

0~5.0 g of sodium pyrophosphate dissolved in 1 L of ultrapure water, stirred for 30 min at 25 °C, then slowly added 100 g of raw Bentonite, continued to stir for 1 h and then left to settle, centrifuged the upper suspension and washed it repeatedly to neutral, dried it at 80 °C, ground it and passed it through 200 mesh sieve, bagged it and reserved it.

2.2.2 Thermal Modification of Bentonite

The Bentonite with better adsorption effect after purification was held at 160~560 °C for 2 h respectively to produce thermally modified Bentonite.

2.2.3 Acid Modification of Bentonite

2.0 g of purified and thermally modified Bentonite with good adsorption effect were added to 20 mL of nitric acid at concentrations of 2.0~10.0 mol L⁻¹ and shaken at 50 °C for 3h. After the solution cooled, the bottom product was washed by centrifugation, dried at 80 °C, ground and sieved through 200 mesh and bagged.

2.2.4 Preparation of Sulfhydryl Modified Bentonite

1.0 g of purified, thermally modified, acid modified and thermally-acid modified clays with the best adsorption effect were dispersed in 20 mL of ethanol solution at a concentration of 10%, respectively, then added in different amounts of sodium silicate (0~0.25 g) and different volumes of 3-mercaptopropyltrimethoxysilane (0~1.5 mL) and grafted at different acidity (pH=5~12) and temperature (15~55 °C) for different times (2~8 h). Finally, the modified product (sulfhydryl modified Bentonite) was washed repeatedly with ultrapure water to neutral, dried at 60 °C, ground through 200 mesh sieve, and sealed for storage.

2.3 Adsorption Test

50 mg adsorbent was added to 20 mL of Ag(I) solution of certain concentration at pH 6 and adsorbed at 25°C for 3 h. The equilibrium concentration of Ag(I) was determined by flame atomic absorption spectrometer (Zhejiang Fuli Analytical Instruments Co., Ltd.), and the adsorption rate η (%) and adsorption capacity Q_e (mg g^{-1}) were calculated by equations (1) and (2).

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

In the above equation, C_0 , C_e are the initial and equilibrium concentrations of Ag(I) in the adsorbent solution (mg mL^{-1}), respectively, V is the volume of the adsorbent solution (mL), and m is the mass of the adsorbent (g).

3 Results and Discussion

3.1 Effect of Purification, Thermal Modification, Acid Modification, and Thermal-acid Modification on the Adsorption of Ag(I) by Bentonite

The adsorption of Ag(I) was performed with purified, thermally modified, acid modified, and thermally-acid modified Bentonite, respectively, and the results are shown in Figure 1.

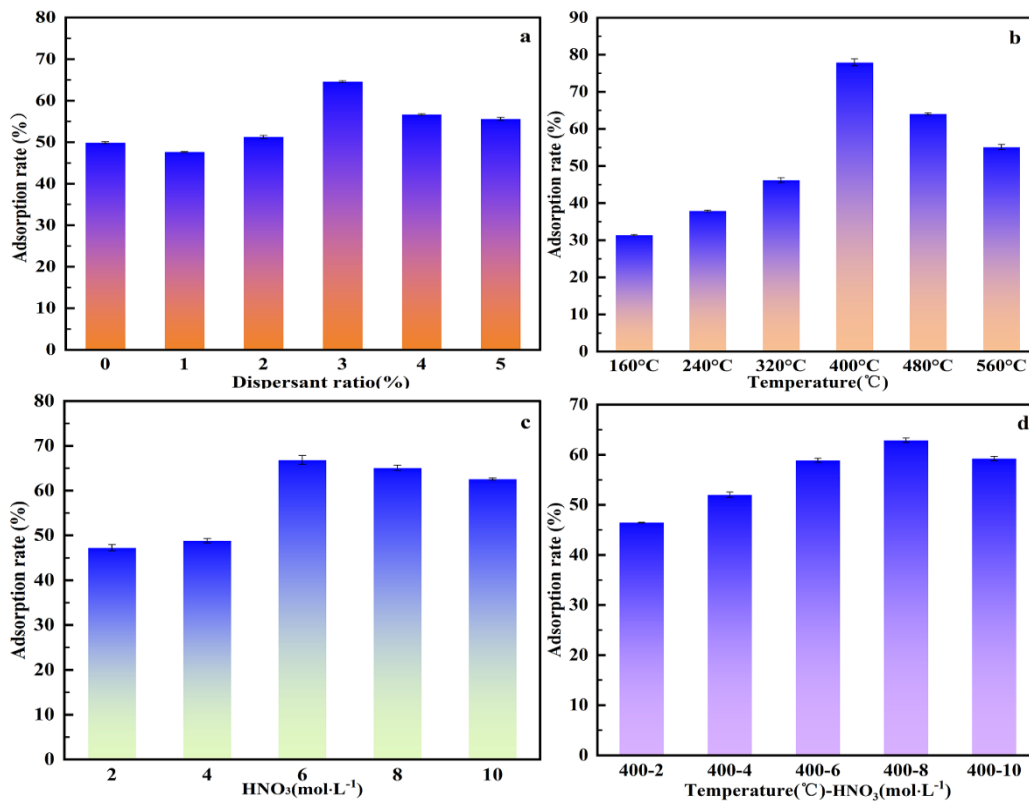


Figure 1. Effect of Different Treatments on the Adsorption of Ag(I) by Bentonite.

a. Dispersant Ratio. b. Temperature. c. HNO₃. d. Temperature-HNO₃.

As known from Figure 1a, the adsorption effect of purified Bentonite on Ag(I) gradually increased with the increase of sodium pyrophosphate, and the adsorption rate reached the maximum when its dosage was 3%. This is because the appropriate amount of dispersant can unclog the pore channels of the clay as well as remove impurities, thus increasing the active adsorption sites (Xingshun, Li, & Xianjun, 2005). However, the adsorption effect gradually decreased when the dosage exceeded 3%, which is because the excess sodium pyrophosphate will stack in the lamellar structure of the Bentonite and occupy the effective active adsorption sites of the Bentonite, thus reducing the adsorption of Ag(I).

Figure 1b showed that the adsorption rate of thermally modified Bentonite for Ag(I) increased gradually with the increase of temperature, reaching the maximum at 400 °C, and decreased instead after exceeding 400 °C. This is because the adsorbed water and crystalline water in the Bentonite will gradually decrease with the increase of temperature, which makes the Bentonite have more adsorption sites to accommodate Ag(I), but the continued increase of temperature will lead to the collapse of the internal structure of the Bentonite (Fu, Sun, Chen, Ying, Wang, & Hu, 2019; Oenal, 2007), so the adsorption capacity of Bentonite decreased.

From Figures 1c and 1d, it can be seen that nitric acid concentration of 6 mol L⁻¹ and 8 mol L⁻¹ had the best effect on the acidification of purified clay and 400 °C heat activated clay, respectively. This is because the appropriate amount of nitric acid can wash out the metal cations such as Fe(III), Al(III), Mg(II) and carbonate impurities in the Bentonite (Kooli, Liu, Al-Faze, & Al Suhaimi, 2015), and increased the adsorption surface area of the Bentonite, so that the adsorption performance can be improved.

3.2 Effect of Preparation Conditions on the Adsorption of Ag(I) by Sulfhydryl Modified Bentonite

According to the results of 3.1, Bentonite with the best adsorption effect was selected from them and grafted onto sulfhydryl groups, respectively. A suitable carrier was selected and optimized for the preparation conditions. The preparation process and experimental results were shown in Figure 2 and Figure 3.

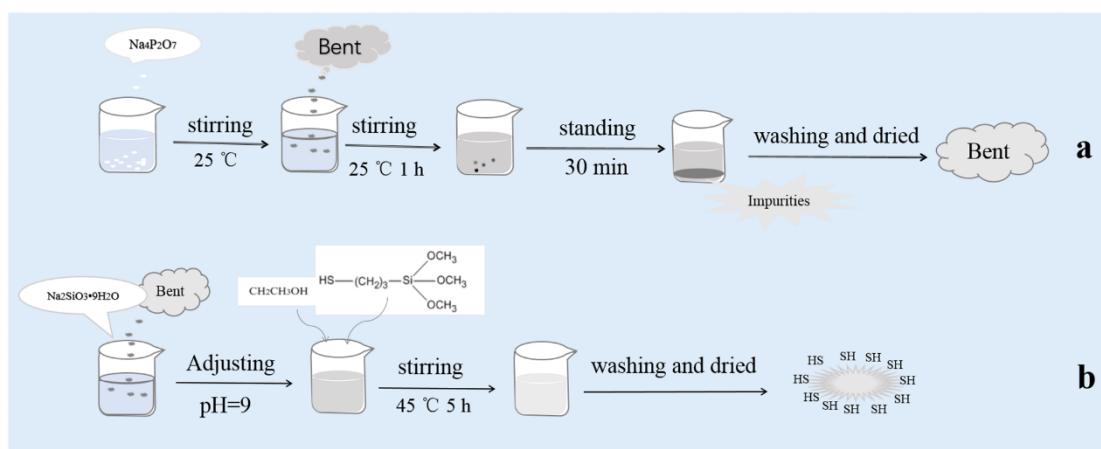


Figure 2. Preparation Process of Sulfhydryl Modified Bentonite.

a. Purified Bentonite. b. Sulfhydryl Modified Bentonite.

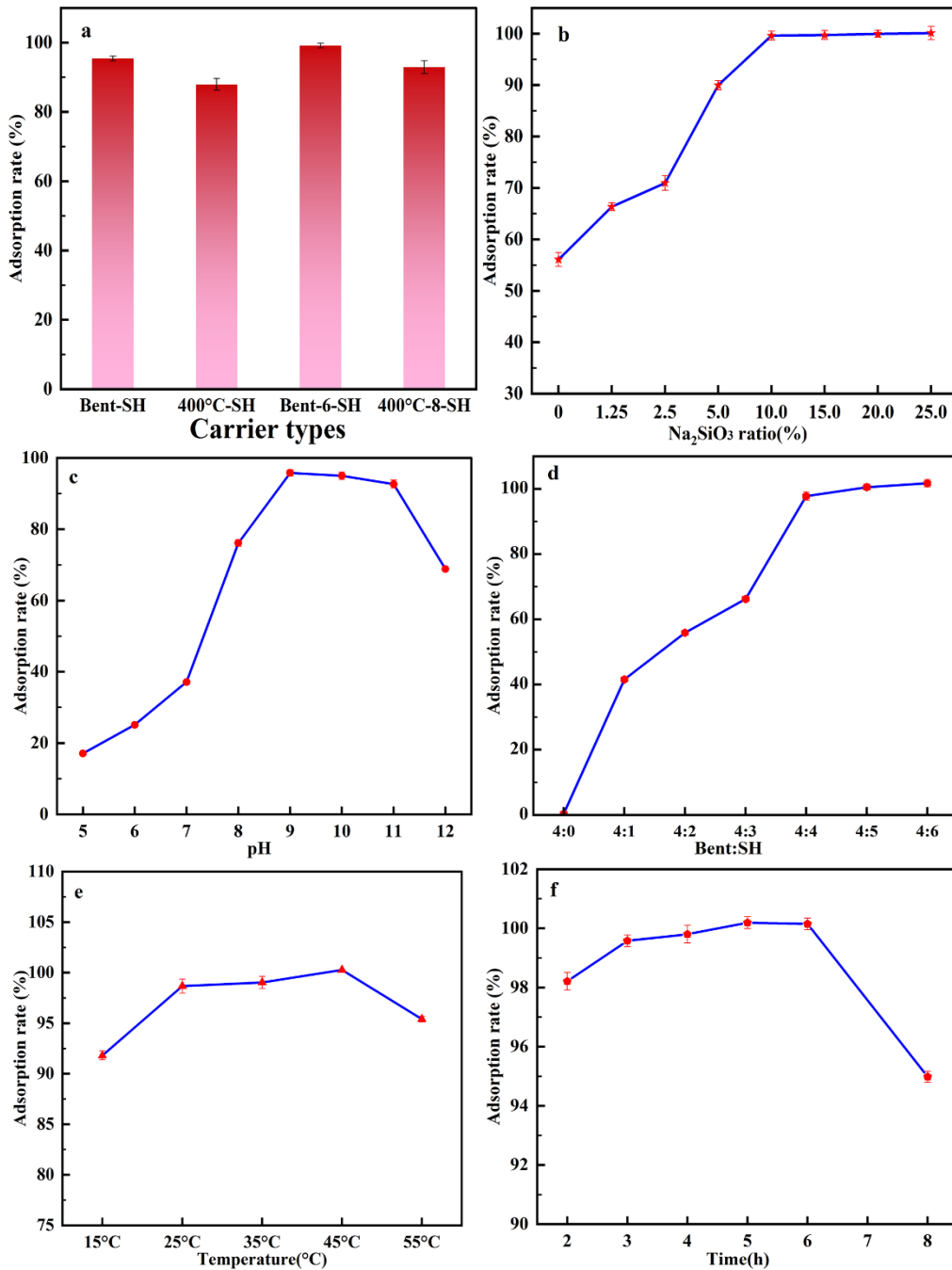


Figure 3. Optimization of the Preparation Conditions of Sulphydryl Modified Bentonite.

a. Type Carrier. b. NaSiO₃ Ratio. c. pH. d. Bent:SH. e. Temperature. f. Time.

From Figure 3a, it can be seen that the best adsorption effect of purified clay, acid modified clay and thermal-acid modified clay grafted with sulphydryl groups showed 95%, 99% and 93% adsorption of Ag(I), respectively. While the adsorption effect of thermal modified clay at 400 °C was relatively poor, which may be due to the high temperature causing the hydroxyl group inside the Bentonite to be taken off and reducing the grafting point of the sulphydryl group. To reduce the cost, purified clay was chosen as the carrier for sulphydryl grafting.

Figure 3b showed that the addition of sodium silicate can significantly improve the adsorption performance of sulfhydryl modified Bentonite on Ag(I). When the amount of sodium silicate was 10% of the Bentonite, the adsorption rate of modified Bentonite on Ag(I) could reach 99.59%, which was about twice as much as that of the single sulfhydryl modification. As its dosage continued to increase, the adsorption effect remained basically the same. This is because sodium silicate can not only enhance the adsorption force by reducing the positive charge at the end face of Bentonite, but also increase the dispersion of Bentonite as a surfactant, which makes the sulfhydryl group in full contact with Bentonite and makes silylation occur more easily (Dong, Zhu, & Cui, 2020).

The solution pH is an important factor affecting the sulfhydryl grafting. From Figure 3c, it can be found that the adsorption rates of modified Bentonite on Ag(I) were all below 40% when $\text{pH} < 7$, and increased significantly with the increasing pH of the solution. When $\text{pH} = 9$, its adsorption rate reached the maximum. When $\text{pH} > 11$, the adsorption rate dropped abruptly. This is because the modifier will hydrolyze with the increase of pH to produce more hydroxyl groups, which is beneficial to combine with the silica hydroxyl groups on the surface of Bentonite (Kang, Gao, Zhu, Lang, Jiang, & Wei, 2021). However, in the solution with high pH, the modifier itself will hydrolyze and polymerize, which will affect the grafting effect.

As can be seen from Figure 3d, the adsorption rate of Ag(I) by Bentonite without the addition of sulfhydryl groups was only 0.37%, but the adsorption rate of Ag(I) by modified Bentonite was also gradually increased when the amount of sulfhydryl groups was gradually increased, and when the solid-liquid ratio of Bentonite to sulfhydryl groups reached 1:1, the adsorption rate could reach 97.78%, and then the increase of the adsorption rate was relatively limited with the increase of sulfhydryl groups. This may be due to the fact that the hydroxyl group on the surface of Bentonite completed the grafting with the sulfhydryl group to the maximum extent at this time.

From Figure 3e, it was found that the adsorption rate of sulfhydryl modified Bentonite on Ag(I) increased with the increase of temperature. When the temperature reached 45 °C, the adsorption rate was close to 100%, but as the temperature continued to rise, the adsorption of Ag(I) by the modified material became worse instead. This is because, at too high temperature, the sulfhydryl reagent is unstable and easily oxidized, which affects the grafting effect.

From Figure 3f, it can be seen that extending the time can improve the density of sulfhydryl grafting, and the adsorption rate of modified Bentonite on Ag(I) was close to 100% when the modification duration was 5 h, but it decreased instead when the time continues to be extended. This is because too long time will cause the hydrolytic polymerization of 3-mercaptopropyltrimethoxysilane itself, which will affect the grafting density of sulfhydryl groups.

In a comprehensive study, the adsorption of Ag(I) by the sulfhydryl modified Bentonite prepared with 3% sodium pyrophosphate purified clay as carrier at a solution pH of 9, sodium silicate mass of 15% of the Bentonite, Bentonite to sulfhydryl dosage ratio of 1:1, temperature of 45 °C, and grafting time of 5 h, could reach 293.7 mg g^{-1} .

4. Conclusion

In this paper, by comparing the effects of purified, thermally modified, acid modified and thermally-acid modified Bentonite on the adsorption efficiency of Ag(I), chose an economical and reasonable purified clay as a carrier, sodium silicate as surfactant, the sulfhydryl successfully grafted on the Bentonite by simple and easy mixing and stirring method, and the optimization of the preparation conditions, the optimal preparation conditions were selected comprehensively. Namely, when the mass of sodium silicate was 15% of the Bentonite, the solid-liquid ratio of Bentonite to modifier was 1:1, the solution pH was 9, the temperature was 45 °C and the modification time was 5 h, the adsorption capacity of the prepared sulfhydryl modified Bentonite on Ag(I) could reach 293.7 mg g⁻¹.

In summary, suitable sulfhydryl modified Bentonite has superior application potential for the treatment of silver-containing wastewater, which has implications for improving clay utilization as well as environmental health.

References

- Akgul, M., Karabakan, A., Acar, O., & Yurum, Y. (2006). Removal of silver (I) from aqueous solutions with clinoptilolite. *Microporous and Mesoporous Materials*, 94(1-3), 99-104. <https://doi.org/10.1016/j.micromeso.2006.02.023>
- Bianchini, A., & Wood, C. M. (2003). Mechanism of acute silver toxicity in *Daphnia magna*. *Environmental Toxicology and Chemistry*, 22(6), 1361-1367. <https://doi.org/10.1002/etc.5620220624>
- Cao, M., Wang, Q., Ge, M., & Zhou, Q. (2015). Recovery of Silver from Silver Chloride Packed with Aluminum Sheet by Replacement Method. *Environmental Protection of Chemical Industry*, 35(3), 305-307.
- Ding, L., Shao, P., Luo, Y., Yin, X., Yu, S., Fang, L., Yang, L., Yang, J., & Luo, X. (2020). Functionalization of UiO-66-NH₂ with rhodanine via amidation: Towards a robust adsorbent with dual coordination sites for selective capture of Ag(I) from wastewater. *Chemical Engineering Journal*, 382. <https://doi.org/10.1016/j.cej.2019.123009>
- Dong, X., Zhu, X., & Cui, T. (2020). Preparation and Properties of Mercapto Bentonite. *Chinese Journal of Applied Chemistry*, 37(10), 1156-1163.
- Ferreira Guimaraes, A. d. M., Ciminelli, V. S. T., & Vasconcelos, W. L. (2009). Smectite organofunctionalized with thiol groups for adsorption of heavy metal ions. *Applied Clay Science*, 42(3-4), 410-414. <https://doi.org/10.1016/j.clay.2008.04.006>
- Frioui, S., Oumeddour, R., & Lacour, S. (2017). Highly selective extraction of metal ions from dilute solutions by hybrid electro dialysis technology. *Separation and Purification Technology*, 174, 264-274. <https://doi.org/10.1016/j.seppur.2016.10.028>
- Fromm, K. M. (2011). Give silver a shine. *Nature Chemistry*, 3(2), 178-178. <https://doi.org/10.1038/nchem.970>

- Fu, Y., Sun, Y., Chen, Z., Ying, S., Wang, J., & Hu, J. (2019). Functionalized magnetic mesoporous silica/poly(m-aminothiophenol) nanocomposite for Hg(II) rapid uptake and high catalytic activity of spent Hg(II) adsorbent. *Science of the Total Environment*, 691, 664-674. <https://doi.org/10.1016/j.scitotenv.2019.07.153>
- Holt, K. B., & Bard, A. J. (2005). Interaction of silver(I) ions with the respiratory chain of Escherichia coli: An electrochemical and scanning electrochemical microscopy study of the antimicrobial mechanism of micromolar Ag. *Biochemistry*, 44(39), 13214-13223. <https://doi.org/10.1021/bi0508542>
- Kang, C., Gao, L., Zhu, H., Lang, C., Jiang, J., & Wei, J. (2021). Adsorption of Hg(II) in solution by mercaptofunctionalized palygorskite. *Environmental Science and Pollution Research*, 28(46), 66287-66302. <https://doi.org/10.1007/s11356-021-15637-0>
- Kooli, F., Liu, Y., Al-Faze, R., & Al Suhaimi, A. (2015). Effect of acid activation of Saudi local clay mineral on removal properties of basic blue 41 from an aqueous solution. *Applied Clay Science*, 116, 23-30. <https://doi.org/10.1016/j.clay.2015.07.044>
- Lansdown, A. B. G. (2006). Silver in health care: antimicrobial effects and safety in use. *Current problems in dermatology*, 33, 17-34. <https://doi.org/10.1159/000093928>
- Niu, J., Yan, W., Du, J., Hao, X., Wang, F., Wang, Z., & Guan, G. (2020). An electrically switched ion exchange film with molecular coupling synergistically-driven ability for recovery of Ag⁺ ions from wastewater. *Chemical Engineering Journal*, 389. <https://doi.org/10.1016/j.cej.2020.124498>
- Oenal, M. (2007). Swelling and cation exchange capacity relationship for the samples obtained from a bentonite by acid activations and heat treatments. *Applied Clay Science*, 37(1-2), 74-80. <https://doi.org/10.1016/j.clay.2006.12.004>
- Pang, T.-w., Yang, Z.-j., Huang, Y.-c., Lei, X.-y., Zeng, X., & Li, X.-x. (2018). Adsorption Properties of Thiol-Modified, Sodium-Modified and Acidified Bentonite for Cu²⁺, Pb²⁺ and Zn²⁺. *Spectroscopy and Spectral Analysis*, 38(4), 1203-1208.
- Pearson, R. G. (1963). Hard and soft acids and bases. *Journal of the American Chemical Society*, 85(22), 3533-3539. <https://doi.org/10.1021/ja00905a001>
- Phothitontimongkol, T., Sanuwong, K., Siebers, N., Sukpirom, N., & Unob, F. (2013). Functionalized hectorite clay mineral for Ag(I) ions extraction from wastewater and preparation of silver nanoparticles supported clay. *Applied Clay Science*, 80-81, 346-350. <https://doi.org/10.1016/j.clay.2013.06.002>
- Rivera, I., Juarez, G., Patino, F., Reyes, I. A., Roca, A., & Reyes, M. I. (2012). Silver Precipitation Using Sodium Dithionite in Cyanide Media. *Journal of the Mexican Chemical Society*, 56(2), 156-162. <https://doi.org/10.29356/jmcs.v56i2.315>
- Song, R., Li, Z., Li, W., An, Y., Li, M., Qin, H., & Liu, C. (2022). Improved adsorption and desorption behavior of Cd on thiol-modified bentonite grafted with cysteamine hydrochloride. *Research on Chemical Intermediates*, 48(6), 2721-2744. <https://doi.org/10.1007/s11164-022-04711-y>

- Su, J., Wang, Y., Ma, X., Han, X., Wang, T., Wang, K., & Liu, S. (2020). Bentonite modification and adsorption capacity for Cr(VI) in water. *Journal of South China Agricultural University*, 41(1), 100-107.
- Tolaymat, T. M., El Badawy, A. M., Genaidy, A., Scheckel, K. G., Luxton, T. P., & Suidan, M. (2010). An evidence-based environmental perspective of manufactured silver nanoparticle in syntheses and applications: A systematic review and critical appraisal of peer-reviewed scientific papers. *Science of the Total Environment*, 408(5), 999-1006. <https://doi.org/10.1016/j.scitotenv.2009.11.003>
- Xingshun, C., Li, W., & Xianjun, L. U. (2005). a study on the preparation of ultra-fine Na-Bentonite. *Acta Mineralogica Sinica*, 25(4), 389-392.
- Zheng, X., Wang, H., Shi, Z., Dong, W., Meng, Z., He, H., & Cai, X. (2020). Study on the Process of Purifying Silver Waste Liquid by Copper Sheet Replacement Method. *Materials China*, 39(10), 787-789.