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Original Paper

Preparation of Attapulgite Loaded Nano Zero Valent Iron Material and Its Adsorption of Silver

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Abstract

In the extensive industrial production process, a large amount of silver containing wastewater has been produced, and the veil of its potential harm has gradually been unveiled. The emission standards of various pollutants formulated and issued by the Ministry of Ecology and Environment of China have already strictly limited the emission limits of silver. In this paper, a simple, environment-friendly and inexpensive method was used to synthesize a composite material with reducing and adsorbing effects on silver by using purified attapulgite and ferrous salt ($FeSO_4\ 7H_2O$) as raw materials, potassium borohydride (KBH_4) as reducing agent, and chemical liquid phase reduction method. The experimental results showed that under the conditions of 1:1 ratio of iron to soil, 0.25 mol L^{-1} concentration of KBH_4, 25 ℃ temperature and 120 min time, the synthesized attapulgite loaded nano-zero-valent iron composite (nZVI/ATP) had good adsorption performance for Ag(I).

Keywords

Attapulgite, Nano zero valent iron, Silver, Restore, adsorbent

1. Introduction

The treatment of heavy metal polluted wastewater has become a serious global problem. In the process of some industrial production, a large amount of wastewater containing silver is produced. Water soluble silver compounds such as nitrates have local corrosion, which may lead to fatal poisoning if swallowed carelessly. Long term human exposure can lead to silver poisoning, which is a clinical symptom characterized by grayish blue skin and other body organs. Repeated exposure of animals to silver may lead to anemia, cardiac hypertrophy, growth retardation and liver degeneration. The harmfulness of silver and its compounds is gradually revealed. The Ministry of Ecology and

Environment of China has also made strict regulations on the emission limits of silver (Ministry of Ecology and Environment, 2008).

At present, the main methods for removing heavy metals are adsorption (Qu, Sun, Zhang, Chen, Wang, Ji, & Liu, 2010), coprecipitation (Gash et al., 1998) and ion exchange (Liu, Valsaraj, Devai, & DeLaune, 2008). However, these methods have some drawbacks, which will cause new pollutants to the ecological environment. In the method of removing silver containing wastewater, chemical reduction (Zhou, Zhang, Qiu, & Wang, 2013) uses the electrode potential between elements to reduce the high valence elements to low valence ones for removal. The reduction method has the advantages of low cost, simple operation and high efficiency, which can effectively remove heavy metals and other pollutants and stand out from them.

Nano-zero-valent iron (nZVI) has attracted much attention due to its attractive advantages such as strong reducibility, high removal rate, less intermediate products, and environmental friendliness (Zhang, Qian, Chen, Ouyang, Han, Shang, Li, Gu, & Chen, 2021). The particle size of nZVI is within 1-100nm, which is iron in essence, has a huge surface area and a large number of active sites. At present, studies have proved that nZVI is a core-shell structure, with the core of zero valent iron and the shell of iron oxide. The reaction first adsorbs heavy metals through the shell oxide, and finally is reduced by zero valent iron in the core (Yan, Herzing, Kiely, & Zhang, 2010). The ferric hydroxide and iron oxide generated in the reaction also have a certain flocculation and adsorption effect on heavy metal pollutants. However, due to the nature of nZVI, it is easy to agglomerate, which reduces the reaction activity and affects the adsorption effect (Zhang, Xuan, Xie, Jiang, Chen, & Oh, 2012).

Attapulgite (ATP), also known as attapulgite or palygorskite, is a layer chain clay mineral rich in magnesium aluminum silicate. The better adsorption capacity of attapulgite depends on its large specific surface area and a large number of micropores. Composite materials are prepared by fixing nZVI on clay minerals, which avoids nZVI agglomeration, has low cost and strong applicability, and has a very high research focus in the adsorption of pollutants.

In this study, purified ATP was used as a carrier to remove Ag(I) from wastewater by optimizing the preparation conditions of matrix and nZVI/ATP.

2. Experimental Section

2.1 Preparation of Main Chemical Reagents and Solutions

The used in this study attapulgite was obtained from Xuyi City, Jiangsu Province, PRC; Other reagents: high-purity silver was purchased from North Weiye Measurement Technology Research Institute, and ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), sodium pyrophosphate, sodium hydroxide, hydrochloric acid, nitric acid, phosphoric acid, anhydrous ethanol, potassium dichromate were purchased from Chengdu Kelong Chemical Co., Ltd.

Instrument: high-speed centrifuge, freeze dryer, oven, ultrasonic machine, PH meter.

Preparation of main solutions.

Ag (I) standard stock solution (1.400 mg mL^{-1}).

Accurately weigh 1.400 g of high-purity silver in a 250 mL beaker, add 15 mL of 65% mass fraction of HNO_3 and 70 mL of ultrapure water at 65 ℃ in a water bath to dissolve, and then cool and volume into a 1000 mL volumetric flask with ultrapure water.

2.2 Material Preparation

2.2.1 Purification of Attapulgite

Add 5 g of sodium pyrophosphate into 1000 mL of ultrapure water at 40 ℃, stir for 30 min, add 100 g of attapulgite original soil, stir for 1 h, stand for 40 min, centrifuge the upper suspension, wash the bottom product to near neutral with distilled water, dry it at 60 ℃ for 12 h, grind it through a 200 mesh sieve, seal and bag it for standby.

2.2.2 Thermal and Acid Modifications of Attapulgite

Weigh 2 g of purified attapulgite and keep it at 250, 300, 350, 400, 450, 500 and 550 ℃ for 2 h. Select 2 g of attapulgite with the best thermal activation effect, place it in 20 mL of three different kinds and concentrations of inorganic acids (nitric acid: 1, 2, 4, 6, 8, 10 mol L^{-1}; hydrochloric acid: 1, 2, 4, 6, 8, 10 mol L^{-1}; phosphoric acid: 1, 2, 4, 6, 8, 10 mol L^{-1}), shake it at 40 ℃ for 4 h, cool it, and centrifuge the solution, the following procedures are the same as Section 2.2.1.

2.3 Preparation of Composite Materials

The preparation principle of attapulgite loaded nano-zero-valent iron is shown in Figure 1.

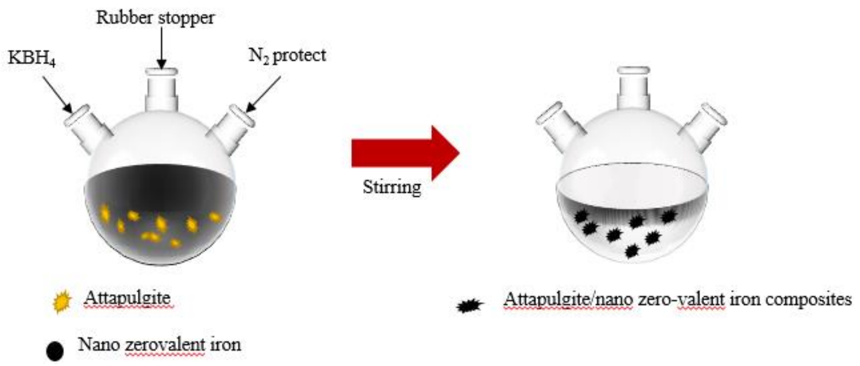

Figure 1. Preparation Principle

Take purified, thermally activated and thermally acid activated attapulgite as the loading material, KBH_4 as the reducing agent, add 100 mL of alcohol water mixture (alcohol water ratio is 1:4) into a 250 mL beaker, and then add $FeSO_4 \cdot 7H_2O$ and attapulgite quantitatively, stir at 25 ℃ for 30 min to make ferrous sulfate completely dissolved, and then move it into a 500 mL three necked flask by ultrasonic vibration for 30 min, fill it with nitrogen for 30 min, drop KBH_4 solution of a certain concentration into a constant pressure drop funnel at a rate of 1~2 d/s. Stir for 2 h after completion to make it completely react. Filter the mixed solution with a Buchner funnel, load the attapulgite obtained with nano-zero-valent iron composite, wash it to near neutral with ultrapure water, and then wash it three times with anhydrous ethanol, After freeze-drying for 24 h, grind it through a 200 mesh sieve and pack it in a sealed bag.

2.3.1 Different iron-soil Ratio

Calculate the masses of $FeSO_4 \cdot 7H_2O$ and attapulgite for iron-soil ratios of 1:3, 1:2, 1:1, 2:1, and 3:1, and add $FeSO_4 \cdot 7H_2O$ and attapulgite for sample preparation, respectively. other operation steps are the same as 2.3.

2.3.2 Different Concentrations of Potassium Borohydride

The samples were prepared using KBH_4 solutions at concentrations of 0.05, 0.15, 0.2, 0.25, 0.3, 0.35 and 0.45 mol $\cdot L^{-1}$, respectively, and other procedures were the same as 2.3.

2.3.3 Different Sample Preparation Temperatures

The sample preparation temperature was set to 15, 20, 25, 30, 35, 40 and 45 ℃ for sample preparation, and other operation steps were the same as 2.3.

2.3.4 Different Sample Making Time

The sample preparation time was set to 10, 30, 60, 120, 240, 360 and 480 min for sample preparation, and the other operation steps were the same as in 2.3.

2.4 Adsorption Experiments

Take 0.05 g of ATP in a 50 mL polypropylene centrifuge tube, add 20 mL of Ag(I) solution with appropriate concentration, adjust pH=6 with HNO_3 and NaOH solution, oscillate at 220 rpm for 2 h at the set temperature, centrifuge at 5000 rpm for 5 min after the adsorption is completed, and then dilute the supernatant to the appropriate concentration. The concentration of Ag(I) in the equilibrium solution was determined by using AAS-1700 flame atomic absorption spectrometer. The adsorption rate η (%) was calculated according to equation (1).

$$\eta=(C_0-C_e)/C_0\times100\% \qquad (1)$$

Where C_0 is the initial concentration of Ag(I) (mg $\cdot mL^{-1}$), Ce is the equilibrium concentration (mg $\cdot mL^{-1}$), m is the mass of the adsorbent (g), and V is the volume of Ag(I) solution (mL).

3. Results and Discussion

3.1 Optimization of Preparation Conditions of Modified Attapulgite

3.1.1 Effect of Purification on the Adsorption rate of Ag(I)

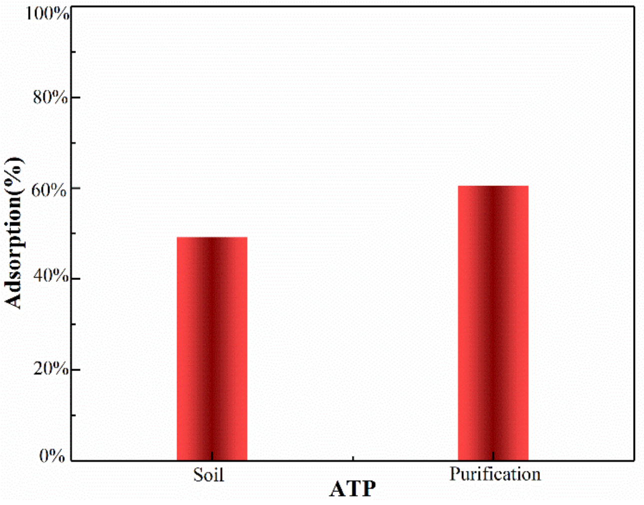

Figure 2. Effect of ATP on the Adsorption Rate of Ag(I) before and after Purification

The experimental results are shown in Figure 2 after purification, the adsorption rate of attapulgite for Ag(I) is increased from 49.18% to 60.59%, 11.41% higher than that before purification. This may be due to the purification and removal of some impurities in attapulgite, the increase of dispersion of attapulgite, the dredging of pores in attapulgite, and the increase of adsorption capacity of attapulgite for Ag(I).

Therefore, attapulgite used in subsequent experiments is used after purification.

3.1.2 Effect of Thermal Activation on the Adsorption Rate of Ag(I)

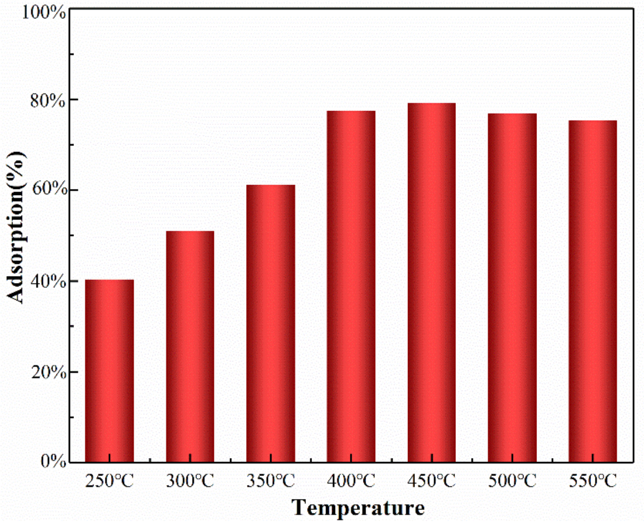

Figure 3. Effect of Different Thermally Activated ATP on the Adsorption Rate of Ag(I)

The experimental results are shown in Figure 3. With the increase of thermal activation temperature, the adsorption rate of attapulgite for Ag(I) also gradually increases, reaching the maximum value (79.18%) at 450 ℃; Subsequently, with the gradual increase of temperature, the adsorption rate of attapulgite on Ag(I) shows a downward trend, which may be caused by the fact that the thermal activation temperature of attapulgite generally does not exceed 500 °C (Lu, 2010). At higher temperatures, the volatilization of internal structural water or the stripping of surface hydroxyl groups of attapulgite results in the collapse of internal pores and the accumulation of fiber bundles, leading to the reduction of pore volume and specific surface area, and weakening the adsorption capacity of attapulgite (Fu, Sun, Chen, Ying, Wang, & Hu, 2019).

Therefore, attapulgite activated at 450 °C was selected for subsequent experiments.

3.1.3 Effect of Acid Modification on the Adsorption Rate of Ag(I)

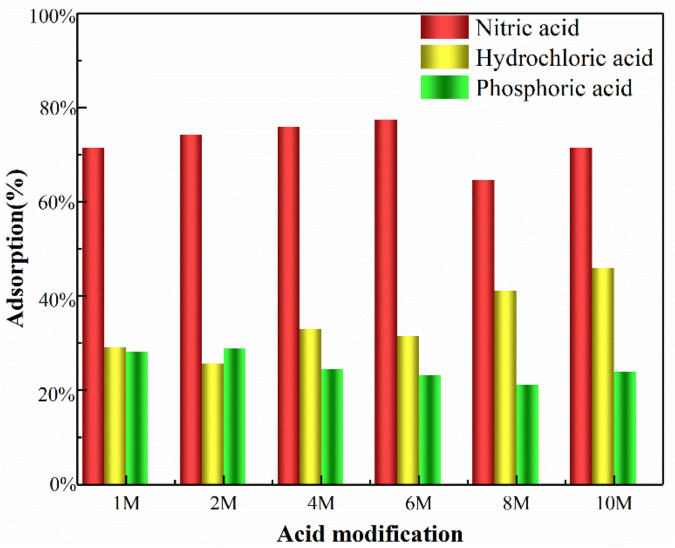

Figure 4. Effect of Different Acid-modified ATP on the Adsorption Rate of Ag(I)

It is observed from Figure 4 that for attapulgite after acidification with nitric acid, when the concentration of nitric acid is lower than 6 mol L^{-1}, the adsorption rate of attapulgite to Ag(I) increases with the increase of acid concentration, and reaches the maximum when the acidification concentration is 6 mol L^{-1}, when the concentration of nitric acid is higher than 6mol L^{-1}, the adsorption rate of attapulgite for Ag(I) decreases with the increase of acid concentration; When the concentration of hydrochloric acid is lower than 10 mol L^{-1}, the adsorption rate of attapulgite to Ag(I) increases with the increase of acid concentration, and reaches the maximum value at 10 mol L^{-1}. At this time, the concentration of hydrochloric acid has reached a high concentration, and subsequent increase of acid concentration will damage the structure of attapulgite; When the concentration of phosphoric acid is lower than 2 mol L^{-1}, the adsorption rate of attapulgite to Ag(I) increases with the increase of acid concentration. When the concentration of hydrochloric acid is higher than 6 mol L^{-1}, the concentration of nitric acid is higher than 6 mol L^{-1}, and the concentration of phosphoric acid is higher than 2 mol L^{-1}, the adsorption rate of attapulgite to Ag(I) after acid activation decreases with the increase of acid concentration.

The reason for this phenomenon may be that under low acidity, cations such as Al^{3+} and Fe^{3+} in attapulgite are replaced by H^+, which causes the depolymerization of attapulgite rod crystal fiber bundles, increases the pore volume and specific surface area, and improves the ion exchange capacity and adsorption capacity of attapulgite; At higher acidity, pore collapse occurred in the crystal structure of attapulgite, which led to the reduction of specific surface area and was not conducive to adsorption. Therefore, 6 mol $Ł^{-1}$ HNO_3, 10 mol $Ł^{-1}$ HCl, and 2 mol $Ł^{-1}$ H_3PO_4 acidified attapulgite were selected for subsequent experiments.

3.2 Preparation of Attapulgite Loaded Nan-ozero-valent Iron

With attapulgite (purified, thermally activated and acid activated) under the above optimal conditions as the carrier, the traditional chemical liquid phase reduction method is used to reduce ferrous salts into zero valent iron loaded on attapulgite. The results are shown in Figure 5.

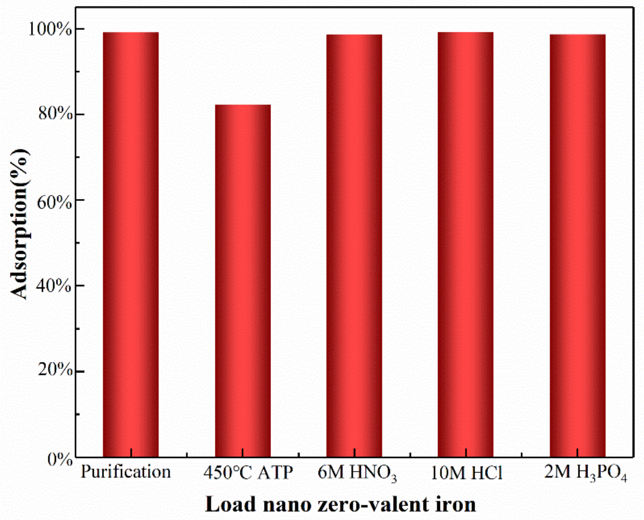

Figure 5. Effect of nZVI/ATP Preparation on Ag(I) Adsorption Rate under Different Modification Conditions

The adsorption capacity of the heat-activated attapulgite loaded with nano-zero-valent iron was found to be worse than several other modified attapulgite for Ag(I) by different pretreatment conditions. Overall, there was no significant difference in the adsorption capacity of purified, nitric acid-activated, hydrochloric acid-activated and phosphoric acid-activated attapulgite and for silver ions. Therefore, in the subsequent operation to save the experimental cost, the purified attapulgite was chosen as the carrier for the preparation of attapulgite loaded nano-zero-valent iron composites.

3.2.1 Effect of Iron-soil Ratio

The loading of nano zero valent iron is mainly affected by the ratio of iron to soil. In order to determine the best preparation conditions, we changed the ratio of iron to soil 1:3, 1:2, 1:1, 2:1 and 3:1 to prepare attapulgite loaded nano-zero-valent iron materials. The results are shown in Figure 6.

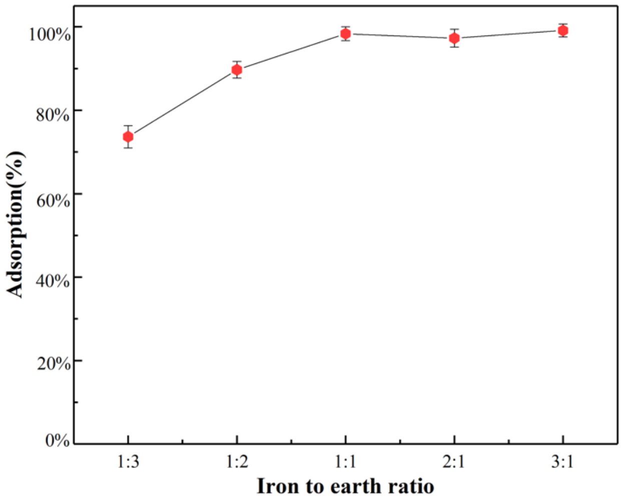

Figure 6. Effect of nZVI/ATP on the Adsorption Rate of Ag(I) at Different Iron to Soil Ratios

The adsorption rate of attapulgite Loaded nano-zero-valent iron on Ag (I) increases with the increase of the ratio of iron to soil, and reaches the maximum and tends to be stable when the ratio of iron to soil is 1:1. This is because with the increase of ferrous salt, the amount of reduced zero valent iron load to attapulgite increases, and the surface has reached the maximum load value at 1:1, so the amount of subsequent increase of iron soil ratio has no obvious change.

3.2.2 Effect of Potassium Borohydride Concentration

Change the concentration of KBH_4 to 0.05, 0.15, 0.2, 0.25, 0.3, 0.35 and 0.45 mol Ł$^{-1}$ to prepare attapulgite loaded nano-zero-valent iron material, respectively. The experimental results are shown in Figure 7.

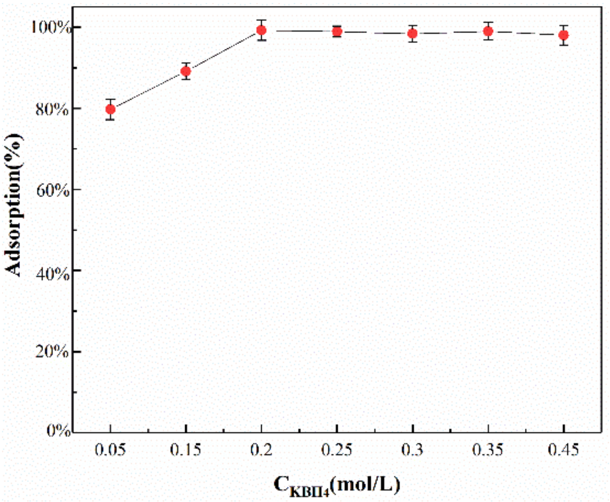

Figure 7. Effect of nZVI/ATP on the Adsorption Rate of Ag(I) at Different KBH_4 Concentrations

The adsorption rate of attapulgite loaded nano-zero-valent iron on Ag (I) showed a trend of rapid increase at first and then gradually stable with the increase of potassium borohydride concentration, and the maximum concentration of potassium borohydride was 0.25 mol Ł$^{-1}$. The reason may be that when potassium borohydride first appeared, Fe^{2+} in the solution was rapidly reduced to Fe^0, but the concentration of potassium borohydride in the range of 0.05~0.2 mol Ł$^{-1}$ was relatively low, and the ability to reduce Fe^{2+} was limited, resulting in that nZVI in the synthetic material was not enough to completely reduce Ag (I) in the solution; When the concentration of potassium borohydride is 0.25 mol Ł$^{-1}$, Fe^{2+} is completely reduced to Fe^0, and the adsorption rate of Ag(I) is the largest; Subsequent increase of concentration will only cause excessive BH_4^- content in the solution, resulting in waste.

3.2.3 The Effect of Sample Preparation Temperature

Change the sample preparation temperature to 15, 20, 25, 30, 35, 40 and 45 °C respectively to prepare attapulgite loaded nano-zero-valent iron material. The results are shown in Figure 8.

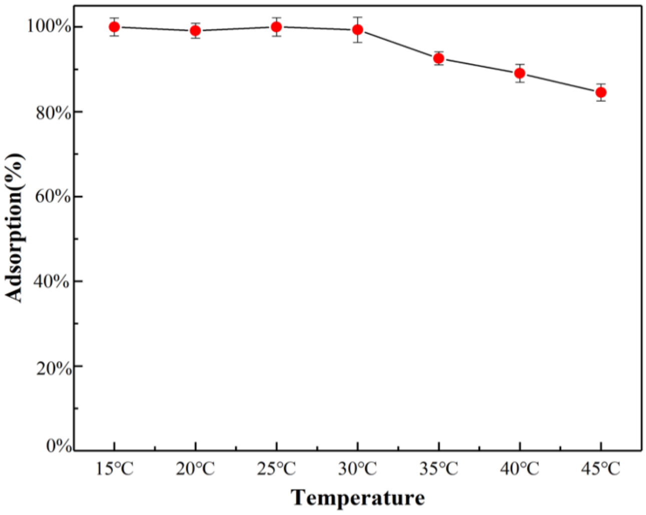

Figure 8. Effect of nZVI/ATP on the Adsorption Rate of Ag(I) at Different Sample Preparation Temperatures

With the increase of the preparation temperature of the material, the adsorption rate of attapulgite loaded nano-zero-valent iron on Ag(I) gradually decreases with the increase of the temperature. The possible reason is that the higher the synthesis temperature is, the easier the nZVI is to be oxidized, thus reducing the reduction effect of Ag(I).

3.2.4 The Effect of Sample Preparation Time

The reaction times were 10, 30, 60, 120, 240, 360, and 480 min for the preparation of the attapulgite loaded nano-zero-valent iron materials. The experimental results are shown in Figure 9.

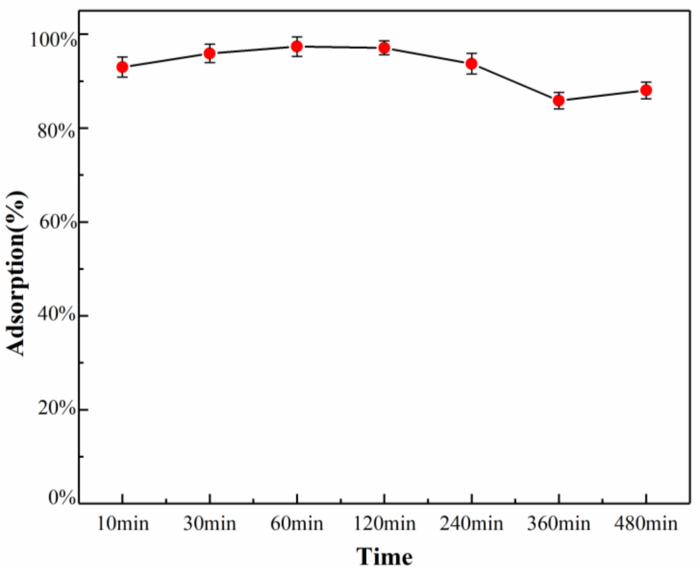

Figure 9. Effect of nZVI/ATP on the Adsorption Rate of Ag(I) at Different Sample Preparation Times

With the increase of sample preparation time, the adsorption rate of attapulgite loaded nano-zero-valent iron on Ag(I) reached the maximum at first and then decreased gradually. The adsorption rate of Ag(I) on attapulgite loaded with nano-zero-valent iron reached the maximum at 120 min, because too short stirring time would affect the loading of nZVI; When the synthesis time reaches 120 min, the nZVI in the solution can be fully loaded on attapulgite; The subsequent increase of time may lead to the oxidation of nZVI and affect its adsorption effect.

In summary, the optimal preparation conditions selected for this experiment were as follows: the iron soil ratio, KBH_4 concentration, synthesis temperature and time of 1:1, 0.25 mol·L^{-1}, 25 ℃ and 120 min, respectively.

4. Conclusion

The attapulgite loaded nano-zero-valent iron composites were prepared and used for the adsorption of Ag(I). The natural attapulgite from Xuyi, Jiangsu Province was used as raw material to load nano-zero-valent iron through purification, thermal modification and acid modification. After optimization of matrix selection and preparation conditions, the attapulgite loaded nano-zero-valent iron materials were produced. The purified attapulgite was determined to be the best loading carrier, under the conditions of 1:1 iron soil, 0.25 mol·L^{-1} reductant KBH_4 concentration, 25 °C sample preparation temperature and 120 min sample preparation time, the modified attapulgite loaded nano-zero-valent iron has a good adsorption of Ag(I). This is of positive significance for the development and utilization of attapulgite mineral resources and the treatment of silver pollution in the water environment.

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