ISSN: 2688-9323

Preparation and Adsorption Mechanism of Mercapto-Supported Magnetic Cobalt Ferrite /SBA15

Zetao Dai

North China Electric Power University, China

Abstract

A mesoporous adsorbent loaded with magnetic materials and grafted with sulfhydryl functional groups was prepared by hydrothermal synthesis and silane coupling methods. The structure of the adsorbent was characterized IR. The results showed that the mercapto group was successfully grafted onto the surface of the adsorbent. By analyzing the removal effect of the adsorbent on mercury ions in water, the kinetic adsorption mechanism and isothermal adsorption equation of the adsorbent were fitted respectively. The fitting results accord with pseudo first order kinetic adsorption equation and Langmuir adsorption equation. Results On the surface, under the given experimental conditions, the adsorbent can basically complete the removal of mercury ions in the solution within 1 hour, the removal efficiency is more than 85%.

Keywords

Mecury Removal; Magnetic Mesoporous Adsorbents; Sulfhydryl Functional Group.

1. Introduction

The existence of trace element mercury in water is one of the most difficult problems in environmental governance [1]. Mercury pollution caused by human activities mainly comes from waste water discharged from industries such as chlorine and alkali, plastics, batteries and electronics, as well as waste medical instruments. For instance, 1,000t of mercury is used to extract gold from 1,500 mines in 40 developing countries each year, leaving many areas exposed to mercury pollution. Mercury itself is toxic, and the presence of anaerobes leads to the formation of methyl mercury [2], which is the main cause of the Minamata Bay incident in Japan.

At present, the main treatment methods of wastewater containing mercury include: sulfide precipitation method, ion exchange method, electrolysis method, adsorption method and so on[3]. It is difficult to treat a large amount of solid waste residue containing mercury produced by sulfide precipitation method. The treatment cost of ion exchange method is high and the system maintenance is complex, and the electrolysis method needs to consume a large amount of electric energy. These methods cannot be used in most scenes due to their inherent defects. In contrast, adsorption method stands out among many methods for its advantages of high efficiency, energy saving and simple operation. [4-26].

Common adsorbent materials include activated carbon, coke, chitosan, graphene oxide, etc. In recent years, the application of mesoporous materials in the adsorption field of heavy metal ions in wastewater has attracted much attention due to their advantages of large specific surface area, regular pore channels and good stability. However, in practical application, mesoporous materials are often limited by the lack of active functional groups on their surface and the adsorption effect is not ideal, so it is necessary to modify the materials to meet the actual needs.

In this work, cobalt ferrite was loaded on the SBA15 skeleton to improve the magnetism of the adsorbent to achieve the purpose of rapid recovery, and mercapto group was grafted to provide

ISSN: 2688-9323

the adsorption of mercury ions in water. The purpose of this study is to prepare adsorbents with appropriate methods and study their adsorption efficiency for mercury ions under specific conditions including pH, temperature and concentration of mercury ions. At the same time, the removal mechanism of mercury ions was analyzed and the structure of the adsorbent was characterized by (Infrared spectra analysis) IR.

2. Experimental Apparatus and Methods

2.1. Reagents

All the chemical reagents are analytical pure, including ferric nitrate, cobalt nitrate, Polyethylene-polypropylene glycol, tetraethyl orthosilicate, anhydrous methanol, glycerol, sodium hydroxide, nitric acid and hydrochloric acid, (3-mercaptopropyl) trimethoxysilane.

2.2. Synthesis of the Adsorbent

Measure 60mL egg white in a 250mL beaker, place it in a blender and stir it mechanically for 30min until it becomes creamy. 8.0800g of iron nitrate and 2.9103g of cobalt nitrate were weighed and dissolved by adding deionized water. The solution was transferred to egg white solution, stirred for 2h, and then put into a water bath. The red-brown gelatinous substance was obtained by heating and evaporating at 80℃ for 26h.

Meanwhile, Weighed 2.9g P123 into a PTFE beaker and added 105mL of hydrochloric acid solution with a concentration of 2mol/L and 102mL of deionized water. Add 7.40ml tetraethyl orthosilicate and continue stirring for 1~2h until the solution is milky-white colloidal.

Further, The cobalt red ferrite gel was added to milky-white colloidal SBA15, stirred evenly and put into constant temperature magnetic stirring, stirred at 40℃ for 36h, until the yellow sol-form substance appeared, and transferred into the hydrothermal synthesis reaction kettle. Crystallization at 100℃ in Muffle furnace for 24h, and the filter residue obtained from product filtration was transferred into Muffle furnace. After calcination at 550℃ for 6h, the template was removed and cobalt ferrite/SBA15 was obtained.

Finally, in order to graft sulfhydryl groups, 0.5g cobalt ferrate /SBA15 was weighted into a beamer, 75mL deionized water was added for ultrasonic dispersion for 10min, then 37.5mL anhydrous methanol was added for ultrasonic dispersion for 30min, and 37.5mL glycerin was added for ultrasonic dispersion for 10min, to generate hydroxyl groups on the surface of SBA15. The solution was transferred to a three-mouth flask continuously filled with nitrogen. 25mL anhydrous methanol and 0.3ml MPTMS were evenly mixed and transferred to a three-mouth beaker. 1mL concentrated ammonia was added as catalyst for reaction under nitrogen protection at 80℃ for 2h, and then the flask was sealed to isolate oxygen for reaction for 5h. The solution was centrifugally washed with methanol and deionized water for several times to obtain the solid product, which was vacuum dried at 60℃ for 24h to obtain cobalt ferrite /SBA15-SH.

2.3. Experiment of Mercury Removal

The experiment can be divided into three steps: the preparation of mercury ion solution, the adsorption process under the addition of adsorbent, and the removal efficiency is calculated by comparing the concentration of mercury ions in the original solution and the adsorbed solution.

$$\eta = (1 - C_{ab}/C_{ori}) \times 100\%$$

where, η is the removal efficiency of mecurcy, %; C_{ab} and C_{ori} are the concentration of mecury ion at the absorbed and original solution respectively, mg/m^3.

ISSN: 2688-9323

The concentration of mercury ions was measured by atomic fluorescence method: reduction of bivalent mercury ions with stannous chloride solution as the mercury atoms, through nitrogen blow off into the fluorescence spectrometer, after mercury lamp of resonance radiation absorption return to ground state after a certain energy transition and emit resonance fluorescence converted to electrical signals were determined, when atomic vapor concentration is low, the measured fluorescence intensity is proportional to the concentration of mercury atomic vapor, which can be used for the determination of mercury. In this experiment, dilution to low mercury concentration was used for determination.

3. Results and Discussion

3.1. Analysis of IR

Through the infrared spectrum analysis of cobalt ferrite, SBA15, cobalt ferrite /SbA15 and cobalt ferrite /SbA15-SH, it can be seen that: The vibration peaks at 3420cm-1, 1630cm-1, and 1080cm-1 of the adsorbent grafted with thiol after introducing cobalt ferrite onto SBA15 are the same as those of the original sample, which correspond to the -OH stretching vibration and Si-O-Si stretching vibration of water molecules on the surface of the material, respectively. A new vibration peak appears at 2880-2900cm-1, which is caused by the extension vibration of methylene in the alkyl chain, i.e. the vibration of methylene C-H in -CH2-CH2-CH2-SH introduced during the sulfhydryl group grafting by organosilane coupling agent method, indicating the successful introduction of sulfhydryl functional group.

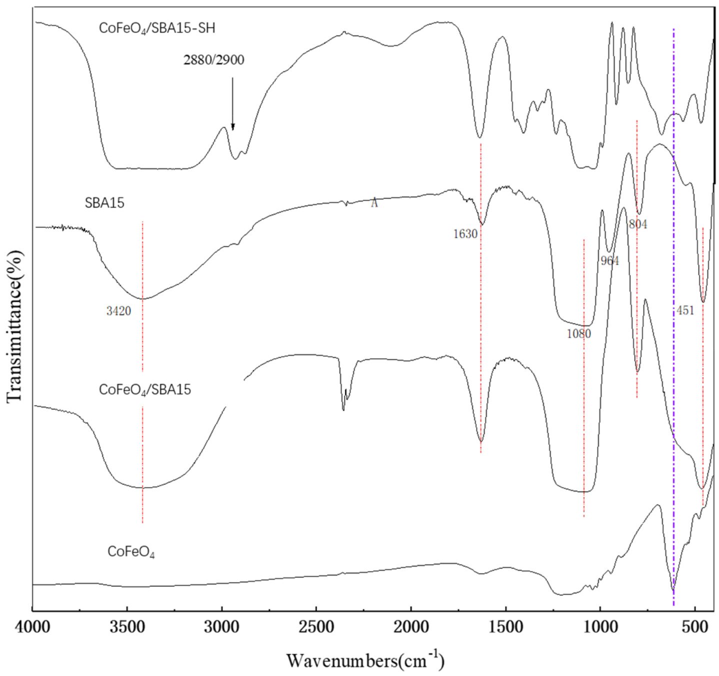
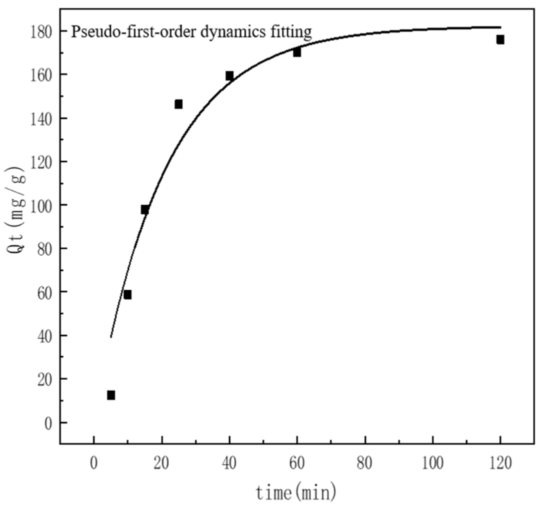


Fig 1. Image of Infrared spectrum characterization pattern

3.2. Adsorption Mechanism

3.2.1. Adsorption Kinetics

With potassium dichromate acidified by nitric acid as the fixed solution, a 100mL mercury solution with a concentration of 70mg/L was prepared as the adsorbent. Adjust pH =5, oscillate adsorption at the temperature T=308K, adsorb in the solution to be adsorbed for 5min, 15min, 25min, 30min, 40min, 60min and 120min respectively, take 0.1 mL solution and dilute it 1000 times, then use mercury meter to measure the concentration. The adsorption kinetics curves were drawn and shown in the Fig 2.and Fig 3.



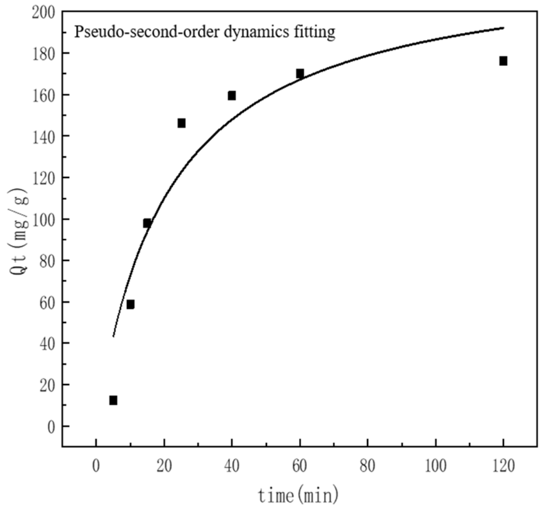


Fig 2. Pseudo-first-order dynamics fitting **Fig 3.** Pseudo-second-order dynamics fitting

Time plays an important role in the adsorption process. As can be seen in Fig 2. and Fig 3., when the time is 0-60min, the adsorption rate is very fast. Beginning of this may be due to that large surface of the adsorbent adsorption activity sites are remained. As time increases, the adsorption quantity increases unceasingly, adsorbent tends to saturation with the adsorption rate dropping. The adsorption of mercury ion also prevent further adsorption, at the same time. The surface of the adsorbent and the solution of the mercury ion concentration gradient has reduced, resulting in a loss of the adsorption rate leading into the final equilibrium.

Table 1. Results of kinetic fitting

Pseudo-first-order			Pseudo-second-order		
$Q = Q_e(1 - e^{-K_1 t})$			$Q = Q_e{}^2 K_2 t/(1 + Q_e K_2 t)$		
Q_e(mg/g)	K_1(min^{-1})	R^2	Q_e(mg/g)	K_2(g/mg/min)	R^2
182.22	0.04845	0.9372	225.57	2.11×10^{-4}	0.8924

Fig 2. is the pseudo-first-order fitting and Fig 3. is the pseudo-second-order fitting of dynamics respectively, and the fitting equation is obtained and the fitting degree is determined by calculating the correlation coefficient R2. Results can be seen in the Table 1. The fitting degree of the pseudo-first-order model is 0.9372, which is higher than that of the pseudo-second-order model. It shows that the adsorption process is more suitable to be described by the pseudo-first-order model, and the theoretical equilibrium adsorption capacity is 182.22mg/g.

3.2.2. Isothermal Adsorption Equation

Mercury solutions with concentrations of 20mg/L, 30mg/L, 50mg/L, 70mg/L and 100mg/L were prepared with nitrate acidified potassium dichromate as the fixed solution. Adjust pH =5, the addition amount of adsorbent cobalt ferrite /SbA15-SH was 0.02g, and the adsorption temperature was T=308K, and the adsorption time was 3h. After the reaction, the concentration of the adsorbed solution was measured with atomic fluorescence mercury-measured spectrometer, and the isotherm adsorption curve was drawn and fitted.

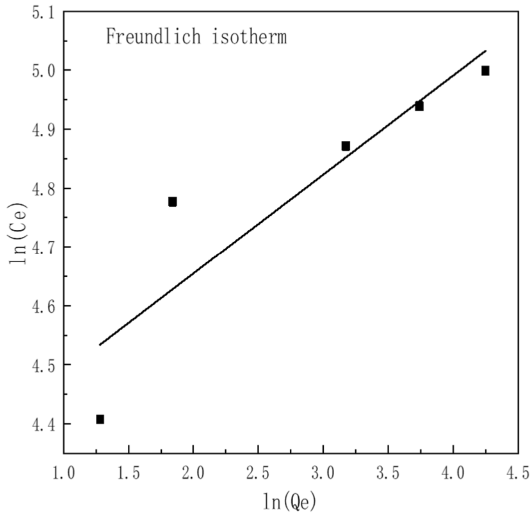


Fig 4. Frenudlich equation

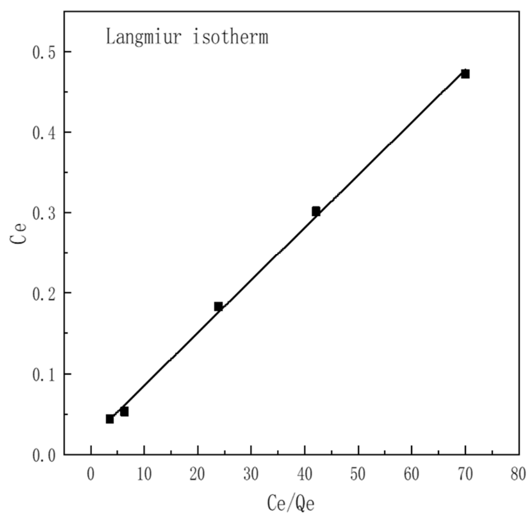


Fig 5. Langmuir equation

Fig 4. represents the Freundlich adsorption fitting model and Fig 5. represents the Langmuir adsorption fitting model. The parameters of the fitting equation are shown in Table 2, in which the phase relation value of Langmiur isothermal adsorption fitting R2 is 0.9985, which is significantly higher than the R2 obtained by Freundlich isothermal adsorption fitting (0.8182). This indicates that the Langmuir model is more suitable to describe the adsorption process of Hg ions by cobalt ferrite /SbA15-SH. According to Langmiur fitting, under the conditions of pH =5, temperature =308K and adsorbent dosage of 0.02g, the maximum adsorption capacity Qm of this adsorbent for mercury ions was 152.9mg/g.

Table 2. Results of isothermal adsorption equation fitting

Freundlich isotherm			Langmuir isotherm		
1/n	K_F	R^2	Q_m	K_L	R^2
0.168	75.1	0.8182	152.9	0.327	0.9985

4. Conclusion

In this research, Cobalt ferrite /SBA15-SH was prepared by hydrothermal synthesis and grafted with sulfhydryl groups by silane coupling method. In the study, the adsorbent showed a good adsorption rate and saturation of mercury ions. The adsorption of the mercury ion solution can be completed within one hour, the adsorption efficiency can reach more than 85%, and the unit saturation adsorption capacity can reach 150mg/L.

According to IR image, the sulfhydryl group was grafted successfully. The kinetic equation and isothermal adsorption equation were studied, and it was shown that the adsorbent prepared in this study was more consistent with the first-order kinetic equation and Langmuir equation in the adsorption process.

References

[1] Zhu He. Study on adsorption and mechanism of mercury in water by magnetic nanocomposites based on CoFe_2O_4/SiO_2 [D]. Suzhou University of Science and Technology,2017.

[2] MIAO L J. Agricultural Engineering,2013(3):83.

ISSN: 2688-9323

[3] Liu Yangzhi, Liu Peng. Research and progress of removal of heavy metal ions from wastewater [J]. Huadian Technology, 2019, 41(12):31-36.

[4] GILLIS A A, MILER D R.Some local environment effects on mercury emission and absorption at a soil surface [J].Science of the Total Environment, 2000, 260(1/2/3): 191-200.

[5] Zhao Yi, Ma Xiaoying, et al. Elemental mercury removal from flue gas by CoFe2O4 catalyzed peroxymonosulfate, Journal of Hazardous Materials, 2017, 341：228-237.

[6] Zhu He. Study on adsorption and mechanism of mercury in water by magnetic nanocomposites based on CoFe_2O_4/SiO_2 [D]. Suzhou University of Science and Technology,2017.

[7] Singh S,Barick K C,Bahadur D. Journal of Hazardous Materials,2011,192(3):1539.

[8] Yang W,Qi Y,Li Y, Wu J,Ma X,Yu C,Ji L. Journal of Hazardous Materials,2013,260(6):9.

[9] Sun Yue, Zhou Xiaoxin, Lou Zimo, Liu Yu, Fu Ruiqi, Xu Xinhua. Chemical Engineering Journal, 2016, 28 (08):1156-1169.

[10] Zhang Qingmei, Xiang Renjun, Cheng Yingxiang. Research of Environmental Sciences, 2010, 23 (07): 888-891.

[11] Kawamura M, Kawamura M, Kawamura M, et al. Synthesis and characterization of a novel mesoporous material [J]. Shandong University,2009.

[12] Kruk. M, Jaroniec. M, Ko C.H. Characterization of the Porous Structure of SBA-15[J]. Chem.Mater. 2000,12:1961-1968.

[13] Firouzi A, Atef F, Oerti Aqetal. Alkaline lyotropie silicate surfactant liquid crystals [J].J. Chem Soc, 1997, 119:3596-3610.

[14] LI Zong-hong. Preparation of modified cellulose and its adsorption capacity for Hg (Ⅱ) in water [D]. North China Electric Power University,2019.

[15] Hong fan. Preparation and removal of heavy metals from core-shell magnetic silica materials modified with sulfhydryl groups [D]. Huazhong University of Science and Technology,2008.

[16] Jr William S. Hummers, Offeman Richard E. Preparation of graphitic oxide [J]. Jourmal of the American Chemical Society, 1958, 80(6): 1339-1339.

[17] Dai Hongjie. Carbon nanotubes. Opportunities and challenges [J] Surface Science, 2002,500(1-3): 218-241.

[18] Hubicki Zbigniew, Koodynsk Dorota. Selective removal of heavy metal ions from waters and waste waters using ion exchange methods [M]. 2012, 91-106.

[19] Kuan Yu Chung, Lee I Hsien, Chem Jia Ming Heavy metal extraction from pcb wastetwater treatment sludge by sulfuric acid [J]. Journal of Hazardous Maternals, 2010, 177(1-3). 881-886.

[20] Chen Wenjuan, Fang Fengman, Yu Jian, et al. Journal of Anhui Normal University, 2009, 32(2):168-172.

[21] Firouzi A, Atef F, Oerti Aqetal. Alkaline lyotropie silicate surfactant liquid crystals [J]. J. Chem Soc, 1997, 119:3596-3610.

[22] Huo Q S, Megarlosel. Organization of organic molecules with inorganic Molecular species into nanocomposite dirphase array [J] Chem. Maet,1994, 6(8): 1176 -1191.

[23] Haiyan Chu, Wei Wang, Duanping Xu, Yeling Gao, Caixia Wen. Journal of Safety and Environment, 201, 21(01):383-389.

[24] Chunhua Xiong, Xiaomin Cai, Yinrong Xu, Minliang Zhu, Shuyi Wu, Mingfei Rao, Yanbo Wang. Preparation and adsorption of mercury ions in water by 3-AT-R resin based on response surface optimization [J]. Journal of Chemical Engineering of Chinese Universities, 2018, 32 (05): 1054 -1062.

[25] Huang S Z, Research on the removal mechanism of divalent mercury ions from water by sulfur-modified biochar [D]. South China University of Technology,2019.

[26] Liu F T. Study on functionalized MOF-based adsorption materials [D]. Jilin University,2019.