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Effect of SO_3^{2-} and PO_4^{3-} on adsorption of S^{2-} performance by zeolite-loaded FeOOH@ZnO --Manuscript Draft--

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Cover Letter

Editor

KOREAN JOURNAL OF CHEMICAL ENGINEERING

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Dear Editor,

I would like to submit the paper “Effect of SO_3^{2-} and PO_4^{3-} on adsorption of S^{2-} performance by zeolite-loaded FeOOH@ZnO ” by Fen Li ,Youjing Li, Baocai Ge ,Jinguang Hu , Cailian Yu, Fanzhu Meng for possible publication in *KOREAN JOURNAL OF CHEMICAL ENGINEERING*. The work described has not been submitted elsewhere for publication, in whole or in part, and all the authors listed have approved the manuscript that is enclosed.

We deeply appreciate your consideration of our manuscript, and we look forward to receiving comments from the reviewers.

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Thank you very much for your time and consideration.

Yours sincerely,

Fen Li(Ph.D & Prof)

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Effect of SO_3^{2-} and PO_4^{3-} on adsorption of S^{2-} performance by zeolite-loaded FeOOH@ZnO

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Abstract

The present study prepares the zeolite-loaded FeOOH@ZnO by hydrothermal method, and discuss the influence of SO_3^{2-} and PO_4^{3-} on S^{2-} adsorption performance of the material. Results show that using HNO_3 modified zeolite to load FeOOH@Zn (FeOOH@ZnO/HZ) has the best adsorption effect on S^{2-} , with a removal rate of 94.2%, and it is mainly chemical adsorption. When SO_3^{2-} and PO_4^{3-} coexist with S^{2-} alone, the removal rate of S^{2-} can be reduced by about 12%, and the effect of SO_3^{2-} on S^{2-} adsorption is stronger than that of PO_4^{3-} . FeOOH@ZnO/HZ also has a certain adsorption effect on SO_3^{2-} and PO_4^{3-} , PO_4^{3-} is mainly chemical adsorption, and SO_3^{2-} is mainly physical adsorption. When the three ions of S^{2-} , SO_3^{2-} and PO_4^{3-} exist at the same time, the removal rate of S^{2-} is further reduced, but the removal rate of PO_4^{3-} and SO_3^{2-} itself also decreases slightly, and it is much lower than the removal rate of S^{2-} . Although coexisting ions affect the adsorption of S^{2-} , FeOOH@ZnO/HZ still has a competitive advantage for S^{2-} adsorption under competitive conditions.

Keywords: Adsorption S^{2-} ; Coexisting ions; Load; Zeolite; Hydrothermal

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1.Introduction

There is a wide range of sources of sulfide in the water, which can be produced during biological metabolic processes and fuel combustion. Industries such as oil refining,

1 petrochemicals, pharmaceuticals and leather making, which are closely related to life, will
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3 also generate a large amount of sulfur-containing wastewater. This kind of wastewater
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5 contains a high concentration of S^{2-} , and also exists pollutants such as SO_3^{2-} and PO_4^{3-} and the
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7 sulfur content and composition of wastewater discharged from different industries are quite
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9 different, which not only causes great pollution to the environment but also has a great impact
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11 on the normal operation of the wastewater treatment process, so it must be properly treated[1].
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14 The domestic and foreign treatment processes for wastewater mainly include precipitation,
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16 biological, oxidation and adsorption method, etc.[2]. Among them, the precipitation method,
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18 biological method and oxidation method are widely used in the treatment of sulfur-containing
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20 wastewater, but due to the lack of suitable adsorption materials, there are few reports on the
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22 adsorption technology in the treatment of sulfur-containing wastewater[3,4].
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31 Common adsorption materials in the field of water treatment include activated carbon,
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33 quartz sand and anthracite, etc. In recent years, iron-based materials have become a hotspot in
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35 the research of water pollutant adsorption due to their low cost and high reactivity[5]. FeOOH
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37 is a common iron-based material in soil, at natural pH, it is difficult to dissolve in water and
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39 has high thermodynamic stability and net surface charge, so it is an effective adsorbent for
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41 metal ions in water[6]. Jaiswal et al.[7] prepared α -FeOOH by chemical precipitation, and
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43 evaluated the adsorption performance of Cd(II) in different systems by changing the pH. The
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45 results showed that the removal rate of Cd(II) reached 87.50%. Chen and Li[8] prepared
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47 α -FeOOH and β -FeOOH nanomaterials by co-precipitation method, which has a high
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49 adsorption capacity for copper ions, the maximum adsorption capacity is 149.25 mg/g and
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51 84.46 mg/g, respectively. Jiang et al.[9] found that the adsorption behaviour of arsenate and
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chromium on α -FeOOH is affected by pH, ionic strength and cation concentration. The research by Astam et al.[10] showed that the Fe-OH surface group is the active site of Hg(II) adsorption. In order to improve the utilization of FeOOH, Yang et al.[11] developed biochar loaded FeOOH to adsorb Cr(VI) in water, Xiao et al.[12] prepared graphene-supported FeOOH for the oxidative removal of 2-chlorophenol and all achieved good adsorption and removal effects. When there are multiple ions in an adsorption system, competitive adsorption occurs between the ions, which affects the removal of the target ions by the material. Zhu[13] conducted a detailed study on this and found that the anions Cl^- , NO_3^- and CO_3^{2-} had no effect on the adsorption of heavy metals by FeOOH, SO_4^{2-} had less effect, H_2PO_4^- had the greatest effect. FeOOH adsorbed As(III) and Cr(VI), Cr(III) is easily affected by SO_4^{2-} and H_2PO_4^- and the maximum adsorption capacities for As(III), Cr(VI) and Cr(III) is 24.5 mg/g, 30.3 mg/g and 18.7 mg/g, respectively.

In summary, the existing iron-based materials currently focus on the adsorption and removal of heavy metal ions and organic pollutants[14-16]. Theoretical analysis shows that ferric iron in FeOOH is highly oxidizable and can undergo redox reactions with sulfur ions or generate sulfide precipitates, which will have a better adsorption effect, but there have been no research reports on the adsorption and removal of sulfur ions. In view of this, the FeOOH@ZnO was prepared in the early stage of this research group, which has a good adsorption effect on S^{2-} . However, during the research, it was found that FeOOH@ZnO powder was easily lost in water, and the presence of other ions in the actual wastewater would affect the adsorption of the main pollutants. Therefore, this article used the zeolite commonly used in water treatment as a carrier to support FeOOH@ZnO, While considering its

performance of adsorbing S^{2-} , it emphatically analyzed the influences of coexisting ions PO_4^{3-} and SO_3^{2-} on adsorption of S^{2-} performance of zeolite-loaded $FeOOH@ZnO$.

2. Materials and methods

2.1 Preparation of materials

The material preparation process is shown in Figure 1. The artificial zeolite ($Na_2O \cdot Al_2O_3 \cdot xSiO \cdot yH_2O$) used is spherical, and the particle size is 2-3mm, which was purchased and placed in Tianjin Fuchen Chemical Reagent Factory. HNO_3 solution was prepared, the zeolite was placed in HNO_3 solution of different concentrations (5%, 10%, 15%, 20%) according to the solid-liquid ratio 1:10, soaked for a certain time After time (2 h, 6 h, 12 h, 24 h, 48 h), then took out and washed to neutral, dried at $130^\circ C$ and set aside for use. HNO_3 modified zeolite was marked as HZ. KOH and $ZnCl_2$ modified zeolite process are the same as nitric acid-modified zeolite, and the concentration gradient of KOH and $ZnCl_2$ was the same as HNO_3 , in which KOH modified zeolite was marked as KZ, $ZnCl_2$ modified zeolite was marked as ZnZ.

Firstly, 6 mmol/L sodium dodecyl sulfate (SDS) and 0.02 mol/L $FeCl_3$ solution were configured, and ZnO particles with a grain size of about 10 nm were added according to the Fe/Zn molar ratio (4.0:1) to obtain $FeCl_3$ mixture liquid. Then 12 g of modified zeolite was weighed, and 20 mL of SDS solution (6 mmol/L) was measured and impregnated the zeolite while stirring for 1 h. Then $FeCl_3$ mixed was slowly dropped wised to the above SDS and zeolite mixed solution, after stirring for 15 min until fully mixed, slowly added 1.0 mol/L NaOH solution dropwise to pH 11 and stirred for 1 h, and set still for a period of time (2 h, 6 h, 12 h, 24 h, 36 h, 48 h), and finally transferred the solid-liquid to the reaction kettle, and placed the reaction kettle in an oven at $110^\circ C$ for 8 h. Finally, the precipitate in the reactor

1 was filtered after cooling, washed to neutrality, and dried at 60°C for 24 h to obtain the final
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3 material.
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5 6 *2.2 Characterization of materials* 7

8 In this experiment, the surface morphology of the material was analyzed by an
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10 Interactive Scanning Electron Microscope (SEM) manufactured by ZEISS, and the material
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12 was glued to a copper sheet with conductive adhesive. Before the test, a gold spray treatment
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14 was performed to improve the conductive performance, and then scan. The crystal form of the
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16 material was analyzed using the D8Advance X-ray diffractometer (XRD) produced by Bruker
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18 in Germany, Cu target, K_{α} radiation source, tube voltage was 40 kV, tube current was 40 mA,
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20 scanning range was 5-80°, scanning speed was 5°/min. The SP-3803AA atomic absorption
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22 spectrophotometer was used to analyze the iron content of the material, the Air-C₂H₂ flame,
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24 and the gas flow rate of 0.8-4.0 L/min.
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32 33 *2.3 Experiment method* 34

35 The water sample with S₂- concentration of 100.0 ± 0.5 mg/L was prepared, and 100 mL
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37 was placed in a conical flask. The material of 3.0 ± 0.0005 g was added to the conical flask
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39 containing sulfur water sample. A small amount of nitrogen was passed through the top of the
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41 liquid level for protection at the same time, and the bottle mouth was sealed with a sealing
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43 film to prevent air from entering and causing large errors. The conical flask was placed on the
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45 shaking bed, after slowly shaking for 10-60 min, it was static, and the supernatant was taken.
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49 The iodometric method (HJ/T60-2000) was used to determine the remaining sulfur ions in the
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51 water sample, the same sample was measured three times in parallel, and a blank control was
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57 performed. The removal rate of S₂- was shown in Equation 2-1:
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$$\eta = \frac{C_1V_1 - \left(C_2V_2 - \frac{C_3V_3}{2} \right)}{C_1V_1} \times 100\% \quad (2-1)$$

Each letter represents the meaning:

C_1 ---- S^{2-} original water sample concentration 3.125×10^{-3} mol/L;

V_1 ----Determine the volume of the water sample 100 mL;

C_2 ----Iodine standard solution concentration 5×10^{-3} mol/L;

V_2 ----The amount of iodine standard solution (mL);

C_3 ----The concentration of sodium thiosulfate standard solution is 5×10^{-3} mol/L.

The interference ions SO_3^{2-} and PO_4^{3-} were detected by the iodometric method (HG/T2967-2000) and molybdenum antimony spectrophotometric method (GB11893-89).

3. Results and discussion

3.1 Modified zeolite-loaded FeOOH@ZnO adsorbed S^{2-}

Artificial zeolite generally needs to be pre-treated before being used to improve the adsorption of pollutants. Because acid can remove impurities in zeolite and play a role of unclogging pores, alkali can desilicize with zeolite, reduce the silica-alumina ratio of zeolite and expand pores, and salt modification mainly uses ion exchange to dissolve Ca^{2+} , Mg^{2+} and other ions and increase the active site[17]. Therefore, this section used HNO_3 , KOH , and $ZnCl_2$ to modify the zeolite and load FeOOH@ZnO. And the S^{2-} adsorption performance was shown in Figure 2.

It can be seen from Figure 2 that FeOOH@ZnO/HZ has the best adsorption effect on S^{2-} , followed by FeOOH@ZnO/KZ, and FeOOH@ZnO/ZnZ has the worst effect. Combined with the SEM of Figure 3, it can be seen that the surface roughness of the zeolite decreases after modification with HNO_3 , but a large number of visible pores appear. Although the surface of

the KOH and ZnCl_2 modified zeolite has pores, the pores are relatively few. After loading FeOOH@ZnO , the roughness of the surface of the material has increased. Among them, FeOOH@ZnO/HZ also has a few holes, but the surface pores of FeOOH@ZnO/KZ and FeOOH@ZnO/ZnZ almost disappeared, indicating that nitric acid dissolves impurities in the pores of the zeolite and opens up holes to increase the specific surface area of the zeolite, and FeOOH@ZnO small particles are evenly distributed on the surface or pores of the modified zeolite, the utilization of FeOOH@ZnO is improved. After the KOH and ZnCl_2 modified zeolite are loaded FeOOH@ZnO , the surface of the zeolite has fewer pores, more FeOOH@ZnO particles accumulate on the surface of the zeolite, and FeOOH@ZnO utilization rate is reduced, which affects the adsorption performance of S^{2-} . Further analysis of the adsorption effect of FeOOH@ZnO/HZ finds that with the increase of the concentration of the modifier nitric acid, the performance of the material to adsorb S^{2-} show a rapid increase trend. When the concentration of the nitric acid solution is 15%, the adsorption effect is the best, and the S^{2-} removal rate is as high as 94.2%. The analysis shows that when the concentration of nitric acid is too low, the effect of clearing the pores is not obvious, which affects the adsorption. When the concentration is too large, the oxidizability of nitric acid will destroy the pore structure of the zeolite, reduce the specific surface area, and affect the load of FeOOH@ZnO . Therefore, the test uses 15% nitric acid to modify the zeolite. The prepared FeOOH@ZnO/HZ is determined by atomic absorption to have a loading capacity of 53.5 mg/g, and the adsorption capacity of S^{2-} can reach 94.2 mg/g.

Figure 4 is the X-ray diffraction (XRD) patterns of natural zeolite and FeOOH@ZnO/HZ . Compared with Figure 4a, it can be seen that after loading FeOOH@ZnO with

nitrate-modified zeolite (Figure 4b), the intensity of most diffraction peaks of the zeolite weakens or disappears. Figure 4b has diffraction peaks at 21.2°, 26.7°, 33.3°, 36.5°, and 53.1° of 2θ , compared with the standard spectrum, which are the diffraction peaks of (110), (310), (130), (101), and (221) crystal planes of α -FeOOH, the peak intensity is weak, indicating that the FeOOH@ZnO loading is less, and mostly exist in amorphous form. Combining the results of the adsorption test and the SEM photo analysis, it can be seen that the modification of zeolite with nitric acid not only removes impurities in the pores, but also destroys the crystal structure of the zeolite[18], and a large number of pores appear, and it provides enough space for the uniform distribution of FeOOH@ZnO on the surface and pores of the zeolite, increasing the utilization rate of FeOOH@ZnO, so the adsorption effect of FeOOH@ZnO/HZ on S^{2-} is significantly better than other materials.

3.2 Effect of coexisting ions on the adsorption of S^{2-} by FeOOH@ZnO/HZ

3.2.1 Effect of PO_4^{3-} on adsorption performance of S^{2-} by FeOOH@ZnO/HZ

Since temperature affects the migration speed of particles, high temperature is easy for particles to obtain energy, increase the diffusion speed in the system, and reduce the activation energy of the reaction, which is conducive to the progress of chemical adsorption reaction, but at the same time, high temperature will desorb the ions adsorbed on the surface of the material, inhibiting the process of physical adsorption. In order to obtain the effect of temperature on the adsorption effect of FeOOH@ZnO/HZ, this section explores the performance of FeOOH@ZnO/HZ for S^{2-} adsorption at different temperatures (Figure 5), and the effect of PO_4^{3-} coexistence on S^{2-} adsorption (Figure 5). It can be seen from Figure 5 that FeOOH@ZnO/HZ has the best S^{2-} adsorption effect at 35°C and the removal rate is 98.3%, the S^{2-} adsorption effect is poor at 30°C, the removal rate is 96.9%, and the S^{2-} adsorption effect is

1 the worst at 25°C, the removal rate is 95.1%. The higher the temperature, the better the
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3 adsorption effect, indicating that the adsorption of S^{2-} by FeOOH@ZnO/HZ between 25°C
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5 and 35°C is mainly chemical adsorption.
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9 It can be seen from Figure 6 that when PO_4^{3-} is present, the removal rate of S^{2-} at 25°C, 30°C
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11 and 35°C is 87.6%, 87.7% and 90.1%, respectively, which is 7%-8% lower than that of Figure
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13 5 at the same adsorption temperature, indicating that PO_4^{3-} occupies part of the active
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15 adsorption sites, and competitive adsorption between PO_4^{3-} and S^{2-} causes the adsorption
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17 performance of S^{2-} to decrease. The further comparison revealed that the adsorption rate of S^{2-}
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19 at 0-40 min in Figure 6 is lower than that of Figure 5, but the adsorption of PO_4^{3-} shows a
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21 rapid upward trend, indicating that the competitive adsorption process mainly occurs in the
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23 early stage of adsorption. During the 40-80 min adsorption time, the adsorption rate of PO_4^{3-}
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25 significantly decreases, while S^{2-} still maintains a faster adsorption rate, indicating that the
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27 adsorption of PO_4^{3-} is close to saturation in the mid-adsorption period. At 80-120 min, both
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29 ions reached adsorption equilibrium. The removal rates of PO_4^{3-} at 25°C, 30°C and 35°C are
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31 26.3%, 28.2% and 33.1%, respectively, FeOOH@ZnO/HZ's ability to remove S^{2-} is
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33 significantly better than PO_4^{3-} , and the removal of PO_4^{3-} does not occur desorption when the
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35 temperature increases. The analysis believes that the removal of PO_4^{3-} by FeOOH@ZnO/HZ
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37 is also mainly based on chemical adsorption, because the coordination of O on PO_4^{3-} with
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39 metal ions, especially with high-priced (+3) metal ions is stronger. It is precisely that Fe^{3+} in
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41 FeOOH participates in the reaction of PO_4^{3-} to generate $FePO_4$ precipitation, resulting in the
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43 removal of coexisting ions.
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58 The effect of different concentrations of PO_4^{3-} on the removal of S^{2-} properties by
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FeOOH@ZnO/HZ is shown in Figure 7.

It can be seen from Figure 7 that as the initial concentration of PO_4^{3-} increases, S^{2-} and PO_4^{3-} removal rates show an increasing trend. When the concentration of PO_4^{3-} is 100 mg/L, the removal rate of S^{2-} is the highest. When the minimum concentration of PO_4^{3-} is 10 mg/L, the removal rate of S^{2-} is the lowest (Figure 7a), indicating that there is not only a competitive relationship but also a mutual promotion effect between the two. According to the analysis, when the concentration of PO_4^{3-} is relatively low, the interaction force between S^{2-} and PO_4^{3-} anion groups will make the reaction mostly proceed on the surface of the material, and the product formed by the action of S^{2-} and iron covers the adsorption site and then blocks the pores to reduce S^{2-} removal rate. As the PO_4^{3-} concentration increases, the interaction force between the two ionic groups loses balance, allowing some of the ions to enter the pores to participate in the reaction and improve the utilization of the material. because the affinity of iron in FeOOH@ZnO/HZ for S^{2-} is higher than that of PO_4^{3-} [19], the adsorption sites are mostly occupied by S^{2-} so that the removal rate of S^{2-} is always higher than that of PO_4^{3-} .

3.2.2 Effect of SO_3^{2-} on adsorption of S^{2-} by FeOOH@ZnO/HZ

To explore the effect of SO_3^{2-} on the removal of S^{2-} from FeOOH@ZnO/HZ at different temperatures, experimental results are shown in Figure 8. It can be seen from Figure 8 that in the presence of SO_3^{2-} , the maximum removal rate of S^{2-} at 25°C, 30°C and 35°Cs 82.3%, 85.6% and 86.9%, respectively, which is 12%-13% lower than the data in Figure 5, and the decrease is relatively large, which also indicates that the adsorption between SO_3^{2-} and S^{2-} is competitive, and the effect of SO_3^{2-} on the adsorption is higher than that of PO_4^{3-} . Compared with the data in Figure 5, it is found that the reaction rate of sulfur ions at 0-60 min is lower

1 than that at the time of single adsorption, the reaction rate is flat at 60-80 min, and the
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3 adsorption equilibrium state can be reached in 80-120 min. The adsorption of SO_3^{2-} shows a
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5 trend of first increasing and then decreasing, the removal rate is the highest at 30 minutes, and
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7 the maximum adsorption rates at 25°C and 35°C are 29.2%, 31.0% and 32.2%, respectively. With
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9 the extension of the adsorption time, the adsorption performance of SO_3^{2-} decreased, and the
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11 adsorption equilibrium was reached at 120 min. At this time, the removal rates at different
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13 temperatures were 9.2%, 7.7%, and 5.7%, respectively, which is compared with the highest
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15 removal rate in the adsorption process, the decline is larger. This shows that the removal of
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17 SO_3^{2-} by FeOOH@ZnO/HZ is mainly physical adsorption, and the desorption of SO_3^{2-}
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19 occurred with the increase of adsorption time.
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28 In order to study the effect of different concentrations of SO_3^{2-} on FeOOH@ZnO/HZ
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30 adsorption of S^{2-} , the competitive adsorption of different concentrations of sulfite and sulfur
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32 ions was discussed. The test results were shown in Figure 9. It can be seen from Figure 9 that
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34 the removal rate of S^{2-} in different concentrations of SO_3^{2-} reaction system is 71.3%, 71.6%,
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36 81.2%, 82.1% and 82.3%, respectively, that is, as the concentration of SO_3^{2-} increases, the
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38 removal rate of S^{2-} also increases accordingly. It indicates that the SO_3^{2-} concentration is low
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40 to inhibit the adsorption of S^{2-} , and the reaction principle is similar to that of PO_4^{3-} and S^{2-}
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42 competitive adsorption. As the concentration of SO_3^{2-} increases, the removal rate decreases,
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44 and the adsorption amount increases, but the range is not large. The adsorption curves of
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46 SO_3^{2-} with different concentrations increase with the adsorption time, and the removal rate
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48 also shows the trend of first rising and then decreasing. It is further explained that SO_3^{2-} is
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50 mainly based on physical adsorption, and the adsorption sites exposed by desorption after 40
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min further promote S^{2-} adsorption.

3.2.3 Effect of coexistence of PO_4^{3-} and SO_3^{2-} on $FeOOH@ZnO/HZ$ adsorption of S^{2-}

To explore the competitive adsorption relationships of PO_4^{3-} , SO_3^{2-} and S^{2-} at three different temperatures of 25°C, 30°C and 35°C, and discussed the effect of temperature on the target pollutants during the adsorption process. The test results were shown in Figure 10.

It can be seen from Figure 10 that when PO_4^{3-} and SO_3^{2-} coexist, the removal rate of S^{2-} at 25°C, 30°C and 35°C is 79.2%, 82.8% and 83.8% respectively, which is lower than the adsorption effect when adsorption alone and two ions coexist separately, indicating that the coexistence of PO_4^{3-} and SO_3^{2-} has a greater effect on the adsorption of S^{2-} . PO_4^{3-} and S^{2-} have little effect on the adsorption capacity of SO_3^{2-} , and the adsorption temperature rises, SO_3^{2-} appears desorption phenomenon. At the same time, the influence of S^{2-} and SO_3^{2-} on PO_4^{3-} is also small, and the removal rate at adsorption equilibrium is between 20%-25%.

In order to study the effect of different concentrations of PO_4^{3-} and SO_3^{2-} on removal S^{2-} performance of $FeOOH@ZnO/HZ$, competitive adsorption tests for PO_4^{3-} and SO_3^{2-} and S^{2-} were designed. The results are shown in Figure 11.

It can be seen from Figure 11 that the equilibrium concentration of S^{2-} and the equilibrium adsorption amount increase with the increase of the concentration of PO_4^{3-} and SO_3^{2-} , and the equilibrium adsorption amount of SO_3^{2-} and PO_4^{3-} also increase with the increase of their own concentration, but when its concentration reaches 70-100 mg/L, the removal rate will not change too much. Observing the removal rate between the three, S^{2-} showed an increasing trend with the increase of the concentration of PO_4^{3-} and SO_3^{2-} , while the removal rate of PO_4^{3-} and SO_3^{2-} decreased to some extent with the increase of their own

concentration. This shows that under the three ion competition conditions, S^{2-} occupies a competitive advantage, and as the concentration of the other two competing ions increases, the adsorption sites of FeOOH@ZnO/HZ are also mainly occupied by S^{2-} .

4. Conclusion

1. The zeolite was modified with different concentrations of HNO_3 , KOH , and $ZnCl_2$, and loaded with FeOOH@ZnO to study its S^{2-} adsorption performance. The results showed that the crystal structure of zeolite treated with 15% HNO_3 was destroyed, a large number of visible pores appeared, and the small particles of FeOOH@ZnO appeared on the surface were evenly distributed, and the S^{2-} removal rate could reach 94.2%, which was the best effect.

2. When PO_4^{3-} and SO_3^{2-} coexisted with S^{2-} , respectively, it would affect FeOOH@ZnO/HZ adsorption of S^{2-} , and the influence of SO_3^{2-} was stronger than that of PO_4^{3-} . With the increased of adsorption temperature, the removal rate of S^{2-} and PO_4^{3-} showed an increasing trend, but the phenomenon of SO_3^{2-} first increased and then decreased, indicating that FeOOH@ZnO/HZ mainly chemically adsorbed PO_4^{3-} and S^{2-} , and the SO_3^{2-} was mainly physical adsorption.

3. When PO_4^{3-} , SO_3^{2-} and S^{2-} coexisted at the same time, the S^{2-} removal rate of FeOOH@ZnO/HZ was lower than the adsorption effect when single adsorption and two kinds of ions coexisted. As the concentration of PO_4^{3-} and SO_3^{2-} increased, the removal rate of S^{2-} also increased, but the removal rate of PO_4^{3-} and SO_3^{2-} itself decreased to a certain extent, which showed that although PO_4^{3-} and SO_3^{2-} affected S^{2-} adsorption, but under competitive conditions, S^{2-} still occupied a competitive advantage in adsorption.

Conflicts of interest

There are no conflicts to declare

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Data Availability Statement

Some or all data, models, or code that support the findings of this study are available from the corresponding author upon reasonable request.

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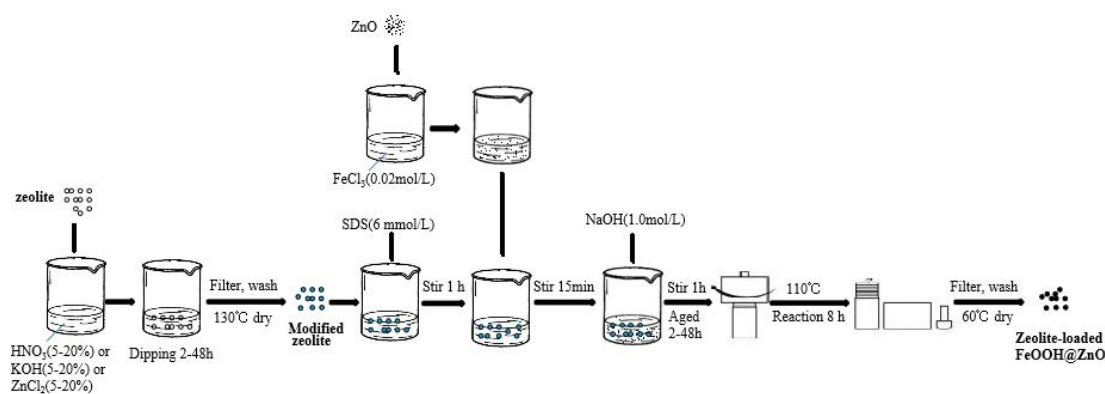


Fig. 1 Flow chart of material preparation

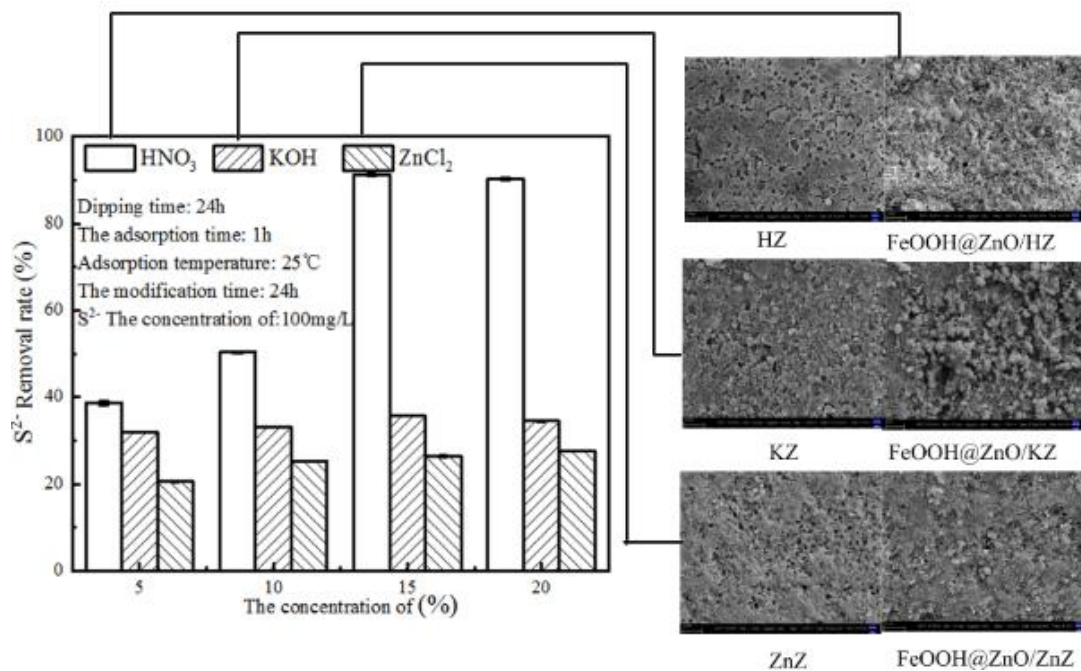


Fig. 2 Properties of acid - base salt modified

Fig. 3 SEM images

zeolite supported by FeOOH@ZnO adsorbed S^{2-}

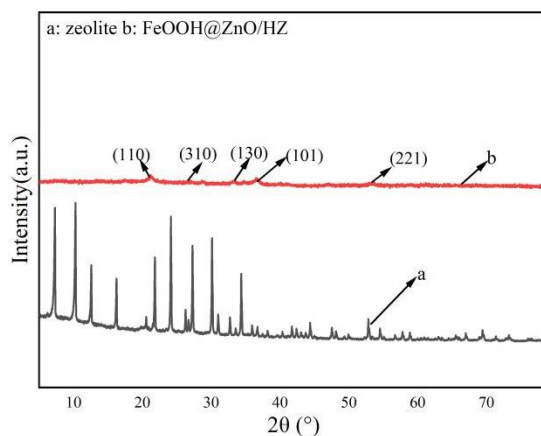


Fig. 4 XRD diffraction pattern

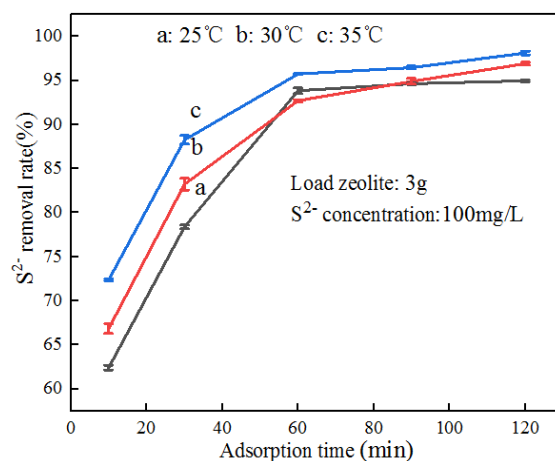


Fig. 5 Adsorption curves of S^{2-} at different temperatures

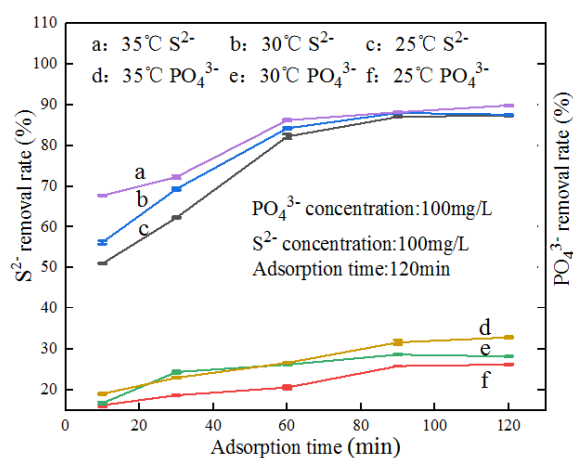


Fig. 6 Interference adsorption of PO_4^{3-} to S^{2-} at different temperatures

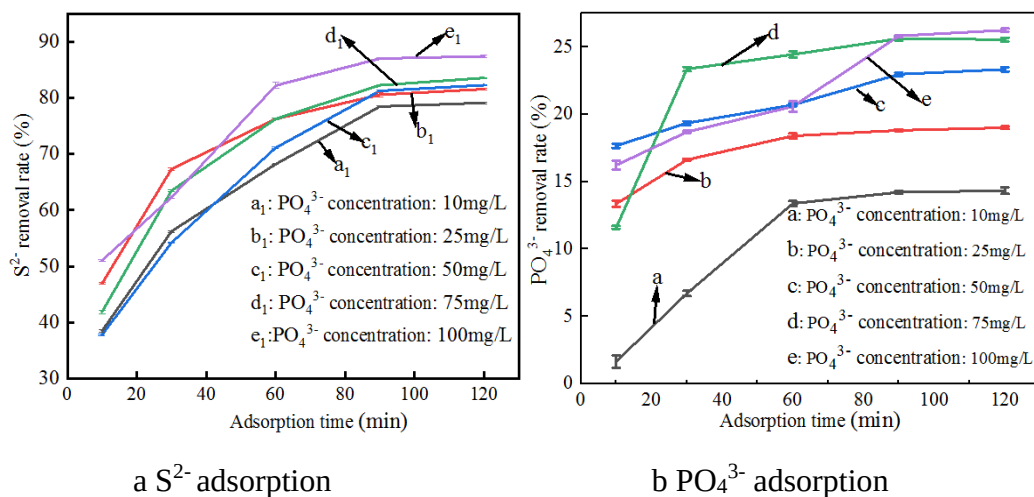


Fig. 7 Interference adsorption of PO_4^{3-} to S^{2-} at different concentrations

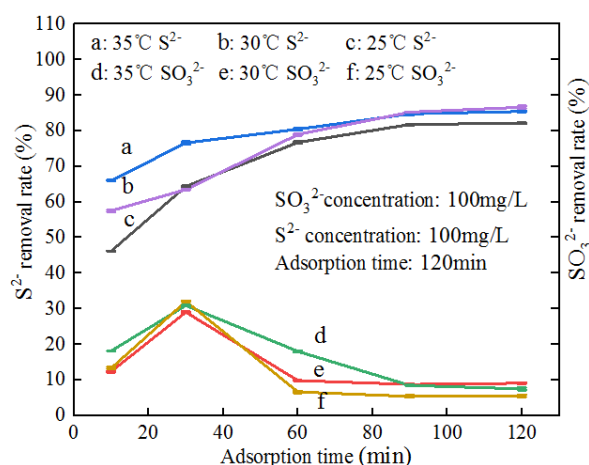
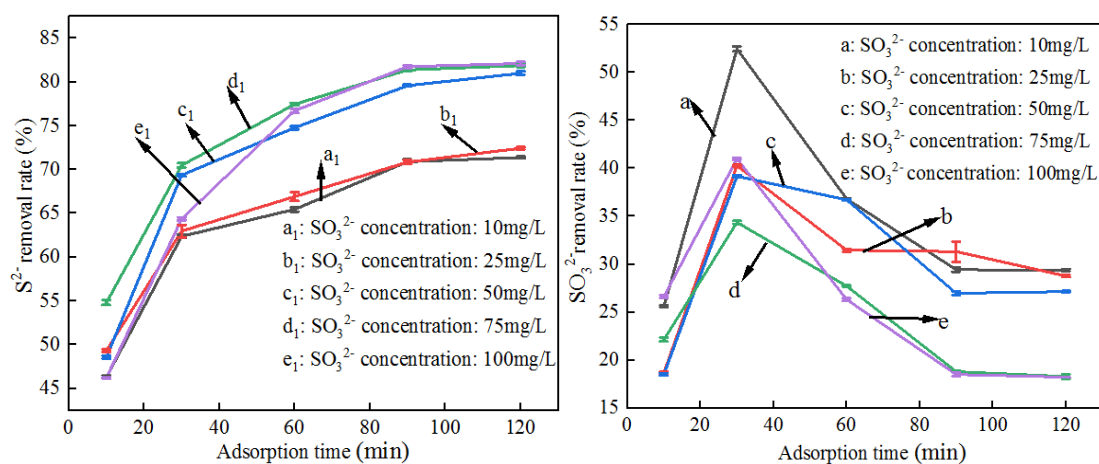


Fig. 8 Interference adsorption of SO_3^{2-} to S^{2-} at different temperatures



a S^{2-} adsorption

b SO_3^{2-} adsorption

Fig. 9 Interference adsorption of S^{2-} by SO_3^{2-} at different concentrations

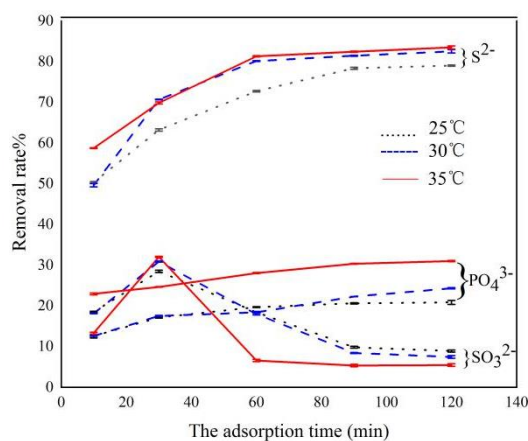


Fig. 10 Interference adsorption of PO_4^{3-} and SO_3^{2-} to S^{2-} at different temperatures

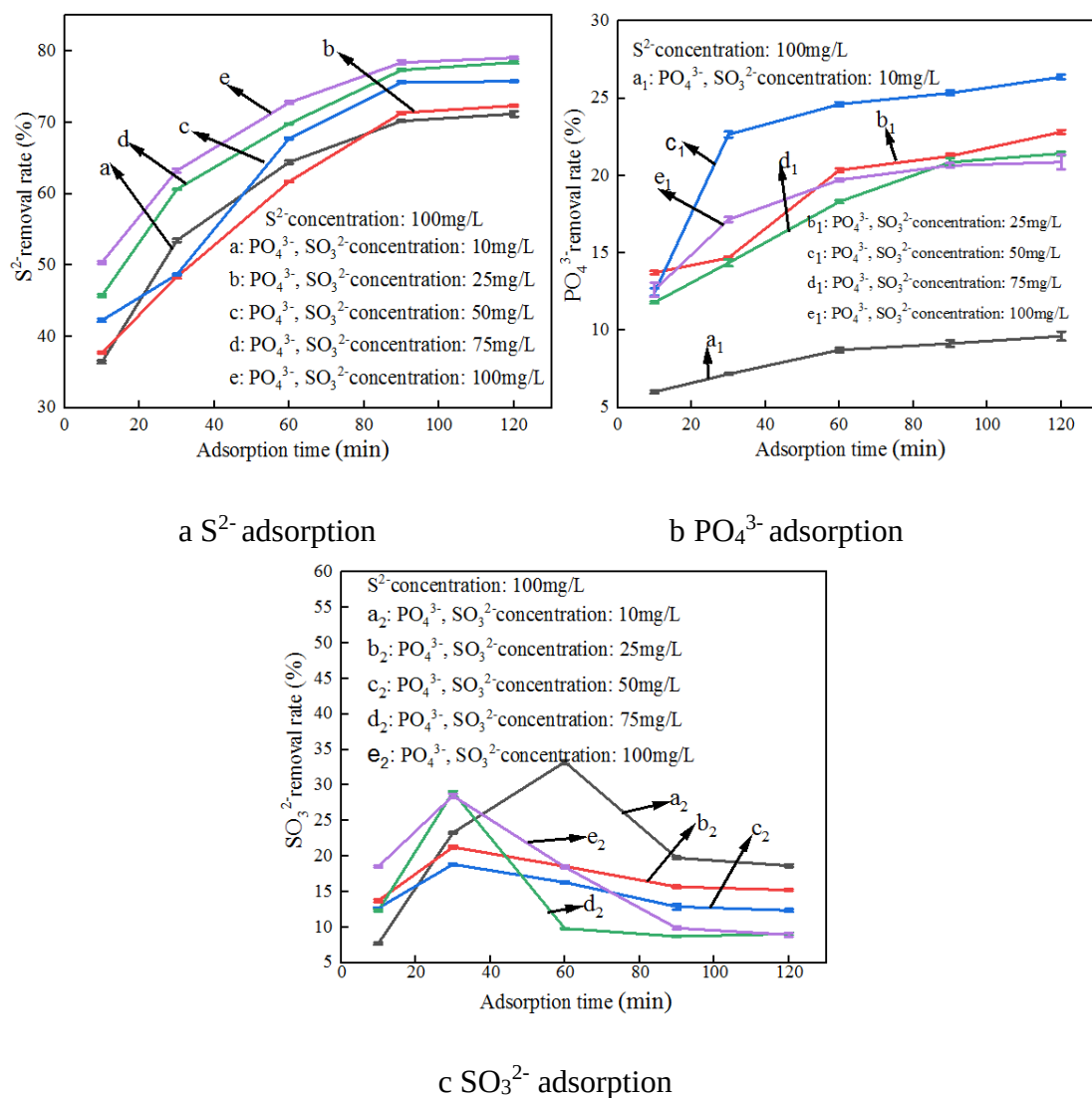


Fig. 11 Interference adsorption of S^{2-} by PO_4^{3-} and SO_3^{2-} at different concentrations

Figure 1 Flow chart of material preparation

Figure 2 Properties of acid - base salt modified zeolite supported by FeOOH@ZnO adsorbed S^{2-}

Figure 3 SEM images

Figure 4 XRD diffraction pattern

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Figure 11 Interference adsorption of S^{2-} by PO_4^{3-} and SO_3^{2-} at different concentrations