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Simultaneous removal of sulfur dioxide and nitrogen oxide from flue gas by phosphorus sludge: The performance and absorption mechanism



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ABSTRACT

Developing low-cost and green simultaneous desulfurization and denitrification technologies is of great significance for sulfur dioxide (SO₂) and nitrogen oxide (NO_x) emission control at low temperatures, especially for small and medium-sized coal-fired boilers and furnaces. Herein, phosphorus sludge, an industrial waste from the production process of yellow phosphorus, has been developed to simultaneously eliminate SO₂ and NO_x from coal-fired flue gas. The key factors affecting the experimental results indicate that desulfurization and denitrification efficiency of over 95% can be achieved at a low temperature of 55 °C. Further, the absorption mechanism was investigated by characterizing the solid and liquid phases of the phosphorus sludge during the absorption process. The efficient removal of SO₂ is attributed to the abundance of iron (Fe³⁺) and manganese (Mn²⁺) in the absorbent. SO₂ can be rapidly catalyzed and converted to SO₄^{2−} by them. The key to NO_x removal is the oxidation of NO toward water-soluble high-valent nitrogen oxides by oxidizing reactive substances induced via yellow phosphorus, which are then absorbed by water and converted to NO₃[−]. Meanwhile, yellow phosphorus is oxidized to phosphoric acid (H₃PO₄). The spent absorption slurry can be reused through wet process phosphoric acid production, as it contains sulfuric acid (H₂SO₄), nitric acid (HNO₃), and H₃PO₄. Accordingly, this is a technology with broad application prospects.

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1. Introduction

In recent decades, fossil energy such as coal, has injected inexhaustible impetus into China's industrial development, but sulfur dioxide (SO₂) and nitrogen oxides (NO_x) have inevitably discharged into the atmosphere, which poses a great threat to the ecosystem and human health [1,2]. Since the implementation of ultra-low emissions of flue gas in China, SO₂ and NO_x emissions have decreased significantly [3,4]. Nevertheless, the efficient and low-cost removal of these pollutants from the flue gas of small- and medium-sized coal-fired boilers is still a difficulty.

At present, there are hundreds of control technologies for SO₂ and NO_x removal. For SO₂ control, wet flue gas desulfurization techniques still dominate the market, among which calcium-based

processes are the most widely used. However, the calcium method will solve the problem of waste gypsum and acid waste water. It would not only take up a lot of ground but also pollute the environment and groundwater resources [5–7]. In terms of denitrification, catalytic reduction of NO_x was the most widely used denitrification method. The selective catalytic reduction (SCR) purification method uses ammonia (NH₃) as a reducing agent to reduce NO_x to nitrogen (N₂), which is very popular in thermal power plants [8,9]. Unfortunately, this technology is difficult to adapt to the flue gas of small and medium-sized coal-fired boilers because the low-temperature SCR catalysts are expensive [10–12]. Additionally, the traditional flue gas desulphurization and denitrification technology is difficult to widely introduce in medium- and small-sized enterprises due to the high investment costs and operating expenses. Based on the above, the simultaneous desulfurization and denitrification technology has received a lot of attention in recent years, owing to its characteristics of high

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efficiency and low cost. Until now, more than 70 kinds of simultaneous desulfurization and denitrification technologies have been studied, such as the ozone (O_3) oxidization method [13,14], the hydrogen peroxide (H_2O_2) oxidization method [15,16], the chlorine dioxide/sodium chlorite ($ClO_2/NaClO_2$) oxidization method [17,18], the potassium permanganate ($KMnO_4$) oxidization method [19], the plasma method [20,21], etc. Due to factors such as high operating costs and by-product treatment, only the ozone oxidation method is widely used. However, the cost of an ozone generator and the secondary pollution of ozone have also attracted widespread attention. Considering this, Okubo *et al.* [22–24] developed a plasma–chemical hybrid process that can significantly reduce the cost and avoid ozone emissions. Recently, resource recycling has become a trend. Industrial raw materials or waste materials are used as desulfurization and denitrification absorbents, including pyrolusite slurry [25], copper slag [26], phosphate rock slurry [27], water-quenched manganese slag slurry [28], red mud [29], and steel slag slurry [30]. Sun *et al.* [25] employed pyrolusite slurry to remove SO_2 and NO_x from flue gas. The SO_2 and NO_x were converted into sulfuric acid (H_2SO_4) and nitric acid (HNO_3), respectively, to decompose pyrolusite, and the deactivated pyrolusite slurry was further processed and utilized. Nie *et al.* [27,31] have built a desulfurization unit with phosphate rock slurry as an absorbent in the phosphorus chemical enterprise, realizing the recycling of SO_2 and phosphorus rock resources. In recognition of this, we developed phosphorus sludge, a kind of dangerous solid waste formed in the process of yellow phosphorus (P_4) production, as an absorbent to remove SO_2 and NO_x from the tail gas of coal-fired boilers. Phosphorus sludge is composed of P_4 , dust, and water. Among them, the mass content of P_4 is as high as 5%–30%. The P_4 reacts with dioxygen (O_2) to form trioxxygen (O_3), which can oxidize NO toward high-valence nitrogen oxides. These high-valence nitrogen oxides and SO_2 are dissolved in water to form nitric acid and sulfuric acid. Meanwhile, P_4 is oxidized to phosphoric acid (H_3PO_4). The deactivated slurry can be used for decomposing phosphate rock, realizing the purpose of recycling phosphorus, sulfur, and nitrogen resources.

In this work, phosphorus sludge is employed as an absorbent to remove SO_2 and NO_x in a bubbling reactor. The influencing factors of SO_2 and NO_x removal efficiency were investigated by controlling the operating conditions. Subsequently, the absorption mechanism

was discussed based on the analysis of absorbent composition during the reaction process.

2. Experimental

2.1. Materials

The phosphorus sludge used in the experiments is obtained from Yunnan Phosphate Technology Co., Ltd., China, and the P_4 mass content in phosphorus sludge was determined to be 7.95%. The higher the P_4 concentration, the better the denitrification effect, which was proved in our previous experimental research [31]. Therefore, in order to explore the influence of process conditions on the desulfurization and denitrification effects, we diluted 5 g of phosphorus sludge in 250 ml of deionized water as an absorbent. The phosphate rock (particle size <38 μm) was provided by Sinochem Yunlong Co., Ltd. of Yunnan, China. It is mainly composed of 9.2% (mass) magnesium carbonate calcium ($CaMg(CO_3)_2$), 79.37% (mass) fluorapatite ($Ca_5(PO_4)_3F$), and 4.74% (mass) silica [32]. The N_2 ($\geq 99.99\%$ (vol)), SO_2/N_2 (3% (vol) SO_2 , 97% (vol) N_2), O_2 ($\geq 99.50\%$ (vol)), and NO/N_2 (0.3% (vol) NO, 99.7% (vol) N_2) were purchased from Kunming Guangruida Industrial Trade Co., Ltd., China. Anhydrous calcium chloride (AR) was purchased from Tianjin Fengchuan Chemical Reagent Technology Co., Ltd., China.

2.2. Experimental apparatus

The schematic of the experimental setup is exhibited in Fig. 1. The simulated flue gas used in the experiment consists of four gases, including NO, SO_2 , O_2 , and N_2 . Each gas was metered by the flowmeter and then conveyed to the buffer bottle for mixing in order to obtain simulated flue gas with a certain SO_2 and NO_x concentration and flow. Subsequently, the simulated flue gas enters the bubbling reactor. The SO_2 and NO_x from the flue gas are absorbed by the phosphorus sludge absorbent. The temperature and mixing strength of the absorbent are controlled by a magnetic stirring reactor. The flue gas discharged from the outlet of the bubbling reactor is dried by anhydrous calcium chloride and then enters the multifunctional flue gas analyzer. Herein, the SO_2 , NO_x , and O_2 concentrations in the simulated flue gas are controlled at $2500\text{ mg}\cdot\text{m}^{-3}$, $780\text{ mg}\cdot\text{m}^{-3}$, and 10% (vol), respectively. The

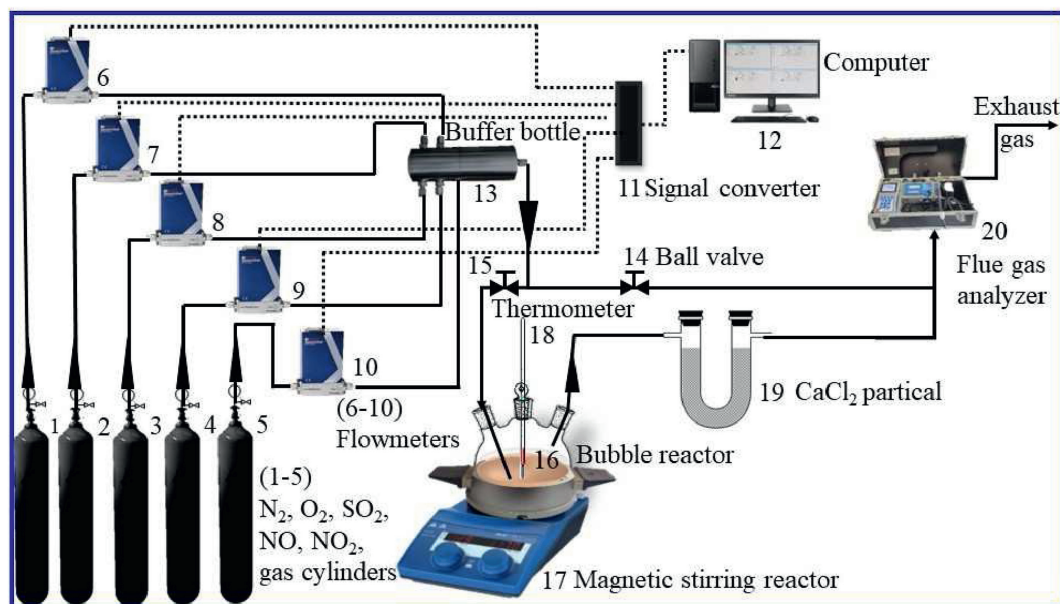


Fig. 1. Framework of the experimental apparatus.

NO_x consist of 97% (mass) NO and 3% (mass) NO_2 , to simulate coal-fired boiler flue gas. The SO_2 and NO_x removal efficiency was investigated under the following experimental conditions: phosphorus sludge of 5 g (excluding water); deionized water of 250 ml; reaction temperature of 65 °C; flue gas flow of 500 $\text{ml} \cdot \text{min}^{-1}$; stirring speed of 1000 $\text{r} \cdot \text{min}^{-1}$. It should be pointed out that when the influence of a single factor on the desulfurization and denitrification efficiency is examined, other experimental conditions except for variable factors are consistent with the experimental values specified above.

2.3. Analysis methods

During this experiment, the pH value of the phosphorus sludge absorbent was monitored by a pH meter (PHS-3C, Shanghai Leici Sensor Technology Co., Ltd., China). The liquid phase compositions of the absorbent were monitored by ion chromatography (IC, Model 883, Swiss Aptar, Switzerland) and inductively coupled plasma spectrometry (ICP, Avio 200, PE, America), and the solid phase material compositions were characterized by X-ray diffraction (XRD, Empyrean, PANalytical, Netherlands), Fourier-transform infrared spectroscopy (FTIR, Tensor Type 27, Bruker, Germany), and scanning electron microscopy (SEM, S-4800, Hitachi, Japan). The Rietveld method [33] was used to analyze the content of solid-phase material compositions. The O_3 generated in the reactor is monitored by the ozone detector (964, BMT, Germany). The flow rate and concentration of SO_2 , NO_x , and O_2 from the simulated flue gas at the inlet and outlet of the bubbling reactor were measured by the mass flow meter (CS200, Beijing Seven Star Huachuang Meter, China) and multifunctional flue gas analyzer (Ecom-J2KN, RBR, Germany), respectively, and the removal efficiency of SO_2 and NO_x is calculated by the following equation:

$$\text{SO}_2 \text{ removal efficiency} = ([\text{SO}_2]_{\text{inlet}} - [\text{SO}_2]_{\text{outlet}}) / [\text{SO}_2]_{\text{inlet}} \times 100\%$$

$$\text{NO}_x \text{ removal efficiency} = ([\text{NO}_x]_{\text{inlet}} - [\text{NO}_x]_{\text{outlet}}) / [\text{NO}_x]_{\text{inlet}} \times 100\%$$

3. Results and Discussion

3.1. Phosphorus sludge characterization

By means of XRD, ICP, and IC, the specific composition of the phosphorus sludge was analyzed in detail, and the experimental results are displayed in Fig. 2. It can be seen from Fig. 2(a) and (b) that the solid phase of phosphorus sludge is mainly composed of silica (SiO_2 , 39.53% (mass)), potassium aluminum silicate (KAlSiO_3 , 15.03% (mass)), calcium silicate (CaSiO_3 , 8.28% (mass)) and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, 7.13% (mass)). In addition, it also contains gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), zinc sulfide (ZnS), plumbojarosite ($\text{PbFe}_6(\text{SO}_4)_4(\text{OH})_{12}$), lead sulfide (PbS), phosphorus pentoxide (P_2O_5), iron oxide (Fe_2O_3), etc. Through the analysis of the liquid phase of phosphorus sludge in Fig. 2(c) and (d), it was found that the phosphorus sludge liquid phase contains Fe^{3+} , Mn^{2+} , magnesium ion (Mg^{2+}), aluminum cation (Al^{3+}), calcium ion (Ca^{2+}), PO_4^{3-} , and SO_4^{2-} . Among them, the contents of Fe^{3+} and Mn^{2+} are as high as 696.4 and 30.6 $\text{mg} \cdot \text{L}^{-1}$, respectively, which are of positive significance for efficient SO_2 removal [34–36].

3.2. Effects of process conditions on SO_2 and NO_x removal

3.2.1. Effects of temperature on SO_2 and NO_x removal

The effect of temperature on SO_2 and NO_x efficiency was investigated with phosphorus sludge as an absorbent, and the

results are shown in Fig. 3. From Fig. 3(a), it is seen that the desulfurization efficiency increases gradually with the ascent of the reaction temperature when the temperature is lower than 55 °C. The SO_2 removal efficiency is maintained above 95% within 3 h at a reaction temperature of 55 °C. As the temperature continues to rise, the desulfurization efficiency gradually decreases. From Fig. 3(b), it is found that the denitrification efficiency is kept above 90% for 3 h, when the reaction temperature is lower than 55 °C. The peak of NO_x absorption efficiency was introduced at 55 °C. Obviously, the denitrification efficiency drops significantly when the temperature exceeds 65 °C. When the reaction temperature drops below 55 °C, the removal efficiencies of SO_2 and NO_x show a similar increasing trend as the temperature increases. As the reaction temperature increases from 35 to 55 °C, the amount of active substance (O , O_3 , $\text{HO} \cdot$, etc.) generated by the reaction between P_4 and O_2 gradually increases. These active substances oxidize NO into water-soluble high-valent nitrogen oxides (NO_2 , NO_3 , etc.), which are then absorbed by phosphorus sludge and converted into HNO_3 [37]. At the same time, a portion of SO_2 is oxidized to SO_3 by the active substance. The desulfurization efficiency is improved because SO_3 is more easily absorbed by water and converted into H_2SO_4 [38]. The sharp decline in NO_x removal efficiency is mainly due to the rapid reaction of P_4 with O_2 to generate P_2O_5 at a higher temperature, which leads to a significant reduction in the duration of P_4 and only a small amount of active substance generated [37,39]. Meanwhile, the P_2O_5 is dissolved in water to form a large amount of PO_4^{3-} , which also has a negative impact on the absorption of SO_2 [40].

3.2.2. Effects of oxygen content on SO_2 and NO_x removal

The amount of O_2 is a crucial factor affecting the reaction between P_4 and O_2 . Since the O_2 content varies in the flue gas emitted by different types of coal-fired boilers and under different operating parameters, the influence of O_2 content on desulfurization and denitrification efficiency was investigated. From Fig. 4(a), SO_2 removal efficiency increases with the increase in O_2 content. When the O_2 content rises from 4% to 10% at 2 h after reaction, the desulfurization efficiency improves from 64% to 100%. As the O_2 content continues to increase, the magnitude of the rise in desulfurization efficiency decreases. Increasing the O_2 content is conducive to the conversion of SO_2 to H_2SO_4 , so the desulfurization effect is better under higher oxygen content conditions. It is observed from Fig. 4(b) that the O_2 content has almost no effect on the NO_x removal within 2 h before the reaction. After that, as the reaction time prolongs, the higher the O_2 content, the more significant the increase in denitrification efficiency. About 20% of the denitrification efficiency is enhanced when the O_2 content boosts from 4% to 14% at 3 h after reaction. The reaction between P_4 and O_2 is promoted when the O_2 concentration increases, which leads to rapid oxidation and absorption of NO_x [38].

3.2.3. Effects of stirring intensity on SO_2 and NO_x removal

Increasing the stirring speed can strengthen the dispersion of phosphorus sludge in the liquid phase. The P_4 in the colloidal center of phosphorus sludge can fully contact O_2 under the drive of mechanical action to generate more O , O_3 , and $\text{HO} \cdot$, which promotes NO oxidation. Fig. 5(a) and (b) demonstrated the effect of stirring intensity on SO_2 and NO_x removal efficiency. The time for efficient desulfurization and denitrification efficiency shortened with the rotating speed ranging from 600 to 1400 $\text{r} \cdot \text{min}^{-1}$. The time for desulfurization efficiency of over 90% is 3 h as long as the stirring speed is less than 800 $\text{r} \cdot \text{min}^{-1}$. When the stirring speed reaches 1400 $\text{r} \cdot \text{min}^{-1}$, the time is shortened to 1.5 h. For NO_x removal, the time for the removal efficiency of over 90% is shortened from 4 to 1 h when the stirring speed is improved from 200 to 1400 $\text{r} \cdot \text{min}^{-1}$.

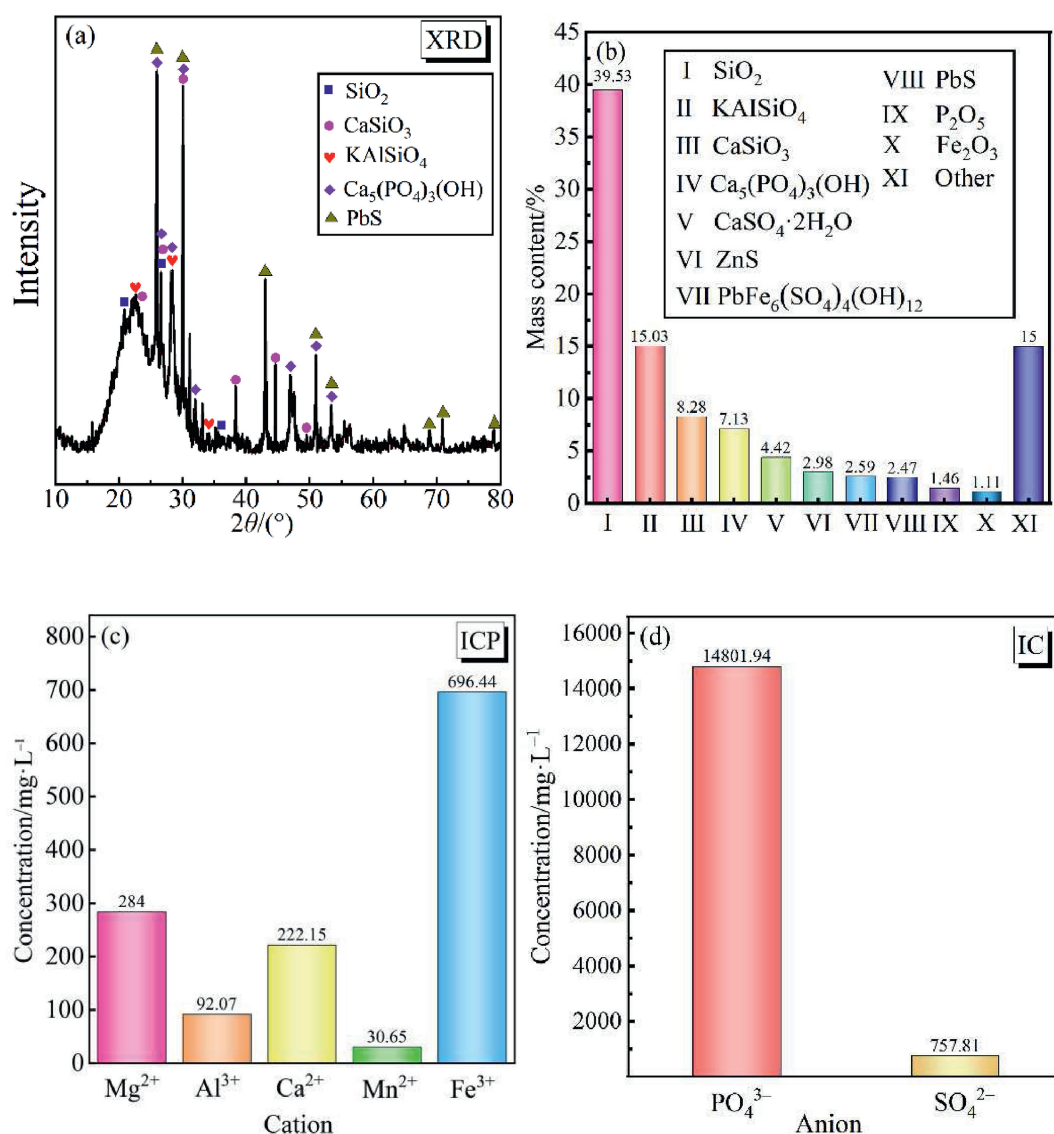


Fig. 2. Analysis of the solid phase and liquid phase composition of phosphorus sludge: (a, b) XRD results of the solid phase of phosphorus sludge; (c) ICP results of the liquid phase of phosphorus sludge; (d) IC results of the liquid phase of phosphorus sludge.

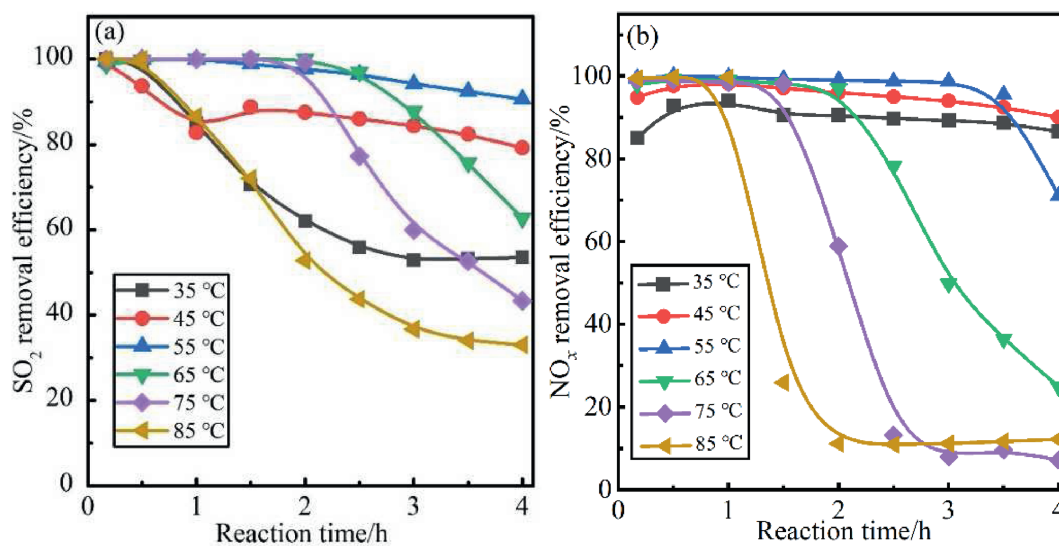


Fig. 3. Effects of reaction temperature on simultaneous (a) desulfurization and (b) denitrification efficiency.

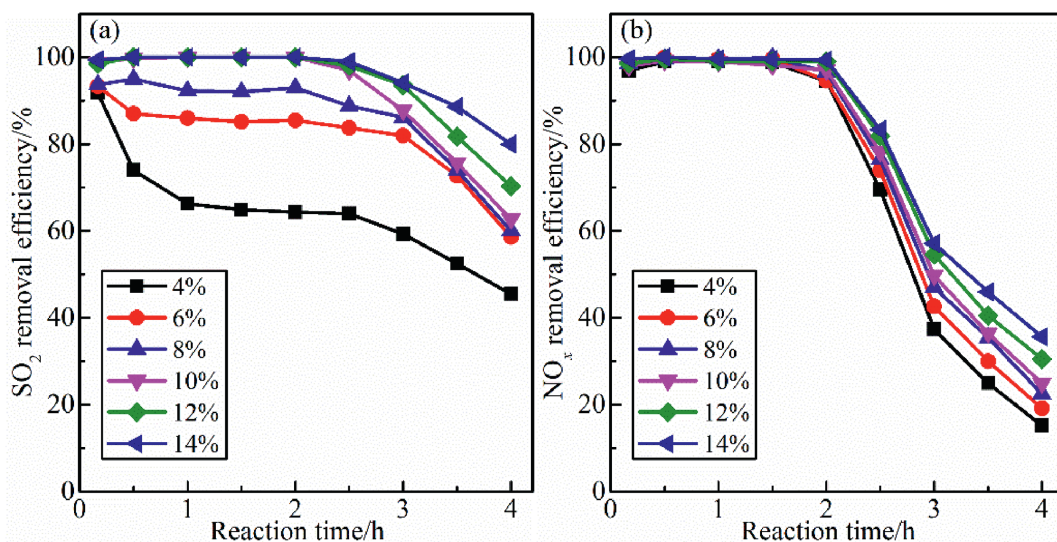


Fig. 4. Effects of oxygen volume content on simultaneous (a) desulfurization and (b) denitrification efficiency.

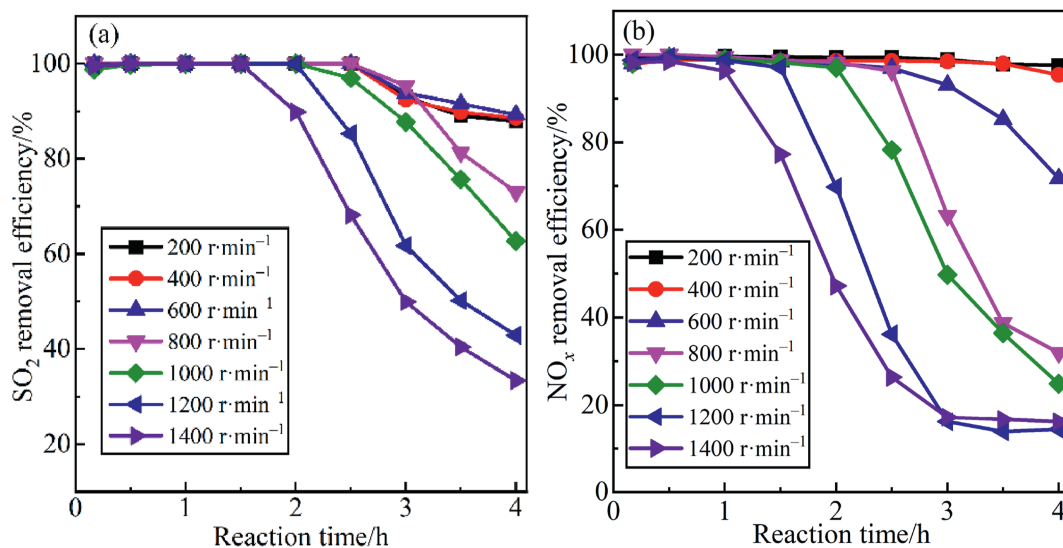


Fig. 5. Effects of stirring speed on simultaneous (a) desulfurization and (b) denitrification efficiency.

Clearly, increasing the stirring intensity will shorten the time for efficient desulfurization and denitrification. The reason is that the high stirring intensity promotes the consumption of P_4 , and the P_4 reacts quickly with O_2 to generate P_4O_{10} [37,39]. The P_4O_{10} dissolves in water and forms a large amount of PO_4^{3-} , which inhibits the absorption of SO_2 [32]. Hence, a stirring speed below $600 \text{ r} \cdot \text{min}^{-1}$ is preferred in order to maintain a stable and lasting desulfurization and denitrification efficiency and ease P_4 consumption.

3.2.4. Effects of gas flow on SO_2 and NO_x removal

The effect of gas flow on the absorption reaction can be mainly attributed to the difference in residence time. The results of desulfurization and denitrification efficiency under different gas flows are displayed in Fig. 6(a) and (b). In the first 2 h of continuous reaction, the gas flow has little effect on the SO_2 and NO_x removal efficiency due to the sufficient amount of absorbent and oxidation. After that, with the increase in gas flow rate, the removal efficiency decreased sharply. On the one hand, increasing the gas flow rate leads to an increase in the O_2 content per unit time, which accelerates the consumption of P_4 . On the other hand, the increase in gas

flow will reduce the retention time of SO_2 and NO_x in the reactor, so they will be discharged before they can be oxidized and absorbed. As a consequence, at the same time point, the total amount of unabsorbed SO_2 and NO_x and the consumption of P_4 increase with gas flow, which is an important reason for the rapid decline of the removal efficiency in the late reaction period.

3.2.5. Effects of phosphate rock additive on SO_2 and NO_x removal

The deactivated phosphorus sludge absorbent after desulfurization and denitrification can be further used to decompose phosphate rock in the wet process phosphoric acid production section, so phosphate rock is selected as an additive [27,31]. It can be seen from Fig. 7(a) that the SO_2 absorption efficiency has considerably enhanced with the addition of phosphate rock in the phosphorus sludge absorbent. When the concentration of phosphate rock reaches $12 \text{ g} \cdot \text{L}^{-1}$, the duration of 100% desulfurization efficiency is extended for 4 h compared with that of absorbent without phosphate rock. In our previous research [31,39], it has been established that magnesium calcium carbonate ($\text{CaMg}(\text{CO}_3)_2$), an effective component in phosphate rock, has excellent desulfurization

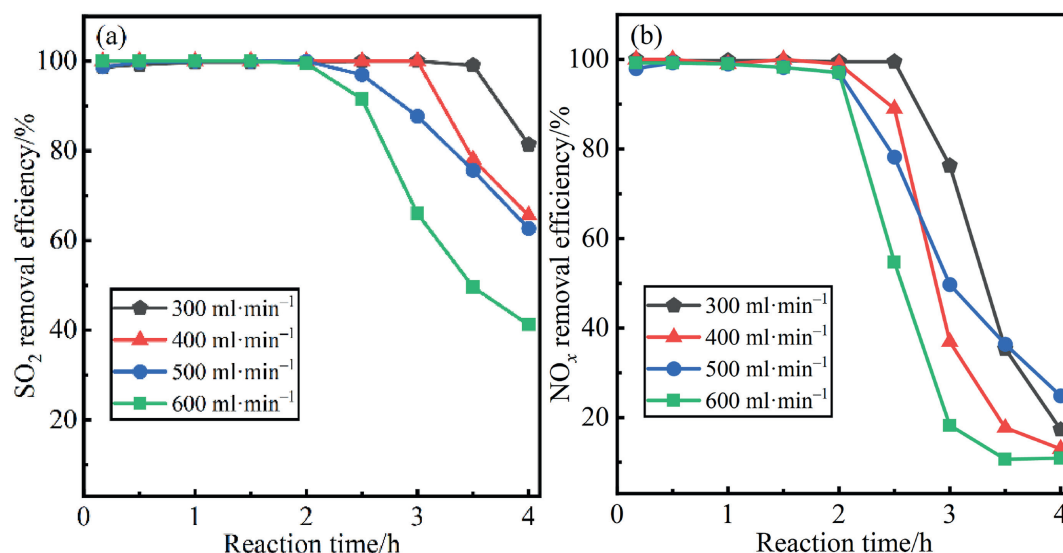


Fig. 6. Effects of gas flow on simultaneous (a) desulfurization and (b) denitrification efficiency.

performance. The elimination of NO_x is mainly affected by the amount of P_4 . Therefore, as shown in Fig. 7(b), the addition of phosphate rock does not greatly improve NO_x removal efficiency. Importantly, this result provides a basis for adding phosphate rock to phosphorus sludge absorbents to boost SO_2 absorption.

3.3. Analysis of phosphorus sludge absorbent in the reaction process

To investigate the mechanism of desulfurization and denitrification of phosphorus sludge absorbent, an experiment lasting for 8 h was conducted at a temperature of 55 °C, and the results are presented in Fig. 8. As can be seen in Fig. 8(a), the desulfurization and denitrification efficiency decreased from 97% and 96% to 89% and 93%, respectively, when the pH was dropped from 3.11 to 1.82. Subsequently, the absorption efficiency of SO_2 and NO_x descends dramatically. It can be inferred that the decrease in pH is an important reason for the attenuation in absorption efficiency [27]. To further elucidate the absorption mechanism, the solid and liquid phase compositions of the phosphorus sludge absorbent during the process of desulfurization and denitrification were further analyzed by IC, XRD, FTIR, and

SEM. Fig. 8(b) shows the changes of anion in the liquid phase of the absorbent at different reaction times. As the reaction time goes on, the IC peaks of SO_4^{2-} and NO_3^- in the liquid phase gradually strengthen, indicating that SO_2 and NO_x are absorbed and transformed into SO_4^{2-} and NO_3^- . Besides, the increase in PO_4^{3-} concentration is mainly due to the continuous oxidation of P_4 . Further, from Fig. 8(c), by comparing the XRD characteristic peaks of the samples, it can be found that the diffraction lines of $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ weakened in the spent samples after 4 h of reaction. This result is in agreement with the IC analysis, demonstrating that a part of PO_4^{3-} in the liquid phase comes from the decomposition of $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. In the reaction process, the diffraction peaks of SiO_2 , CaSiO_3 , kalsilite (KAlSiO_4), and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ have hardly changed, indicating that they do not participate in the absorption reaction. Furthermore, it can be clearly seen from Fig. 8(d) that four bands at 1097, 954, 798, and 467 cm^{-1} assigned to silicon species (SiO_2 , CaSiO_3 , and KAlSiO_4) appear in the spectra of the fresh and spent phosphorus sludge [40]. The bands observed at around 3436, 1630, and 1153 cm^{-1} are denoted as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The peaks at around 1450, 604, and 568 cm^{-1} are assigned to $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ [27]. There is no new infrared

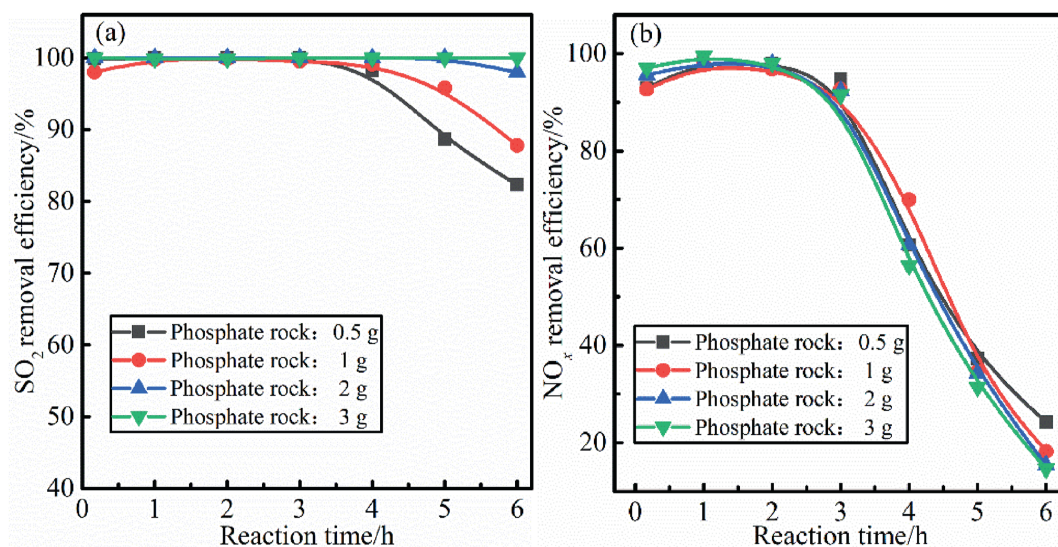


Fig. 7. Effects of phosphate rock on simultaneous (a) desulfurization and (b) denitrification efficiency.

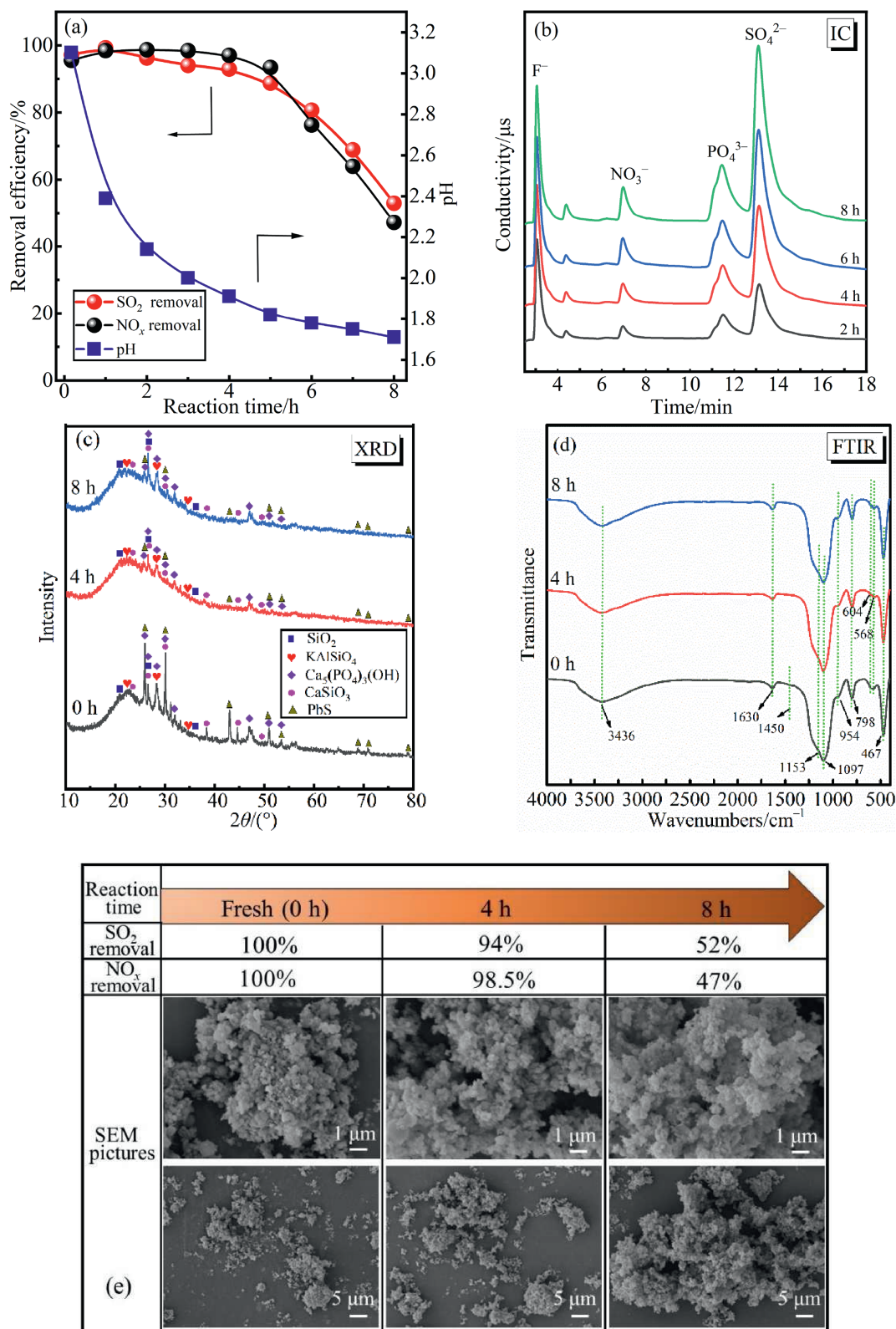


Fig. 8. (a) Variations in desulfurization efficiency, denitrification efficiency, and pH value with time using phosphorus sludge as an absorbent. (b) IC results of the liquid phase of the absorbent at different reaction times. (c–e) XRD, FTIR, and SEM results of the solid phase of the absorbent at different reaction time.

characteristic peak found in the reacted samples, which is consistent with XRD analyses. In addition, from Fig. 8(e), it is observed that the solid phase of phosphorus sludge is irregular and granular, and there is no obvious change as the desulfurization and denitrification

efficiency decrease. Consequently, based on the above analysis, it can be inferred that SO₂ and NO_x are mainly present in the liquid phase in the form of SO₄²⁻ and NO₃⁻ after being absorbed into the phosphorus sludge.

3.4. Absorption mechanism for SO₂ and NO_x

From the above analysis, it can be inferred that the desulfurization and denitrification reaction process, using phosphorus sludge as an absorbent, mainly involves the gas and liquid phases. When SO₂ dissolves from the gas phase to the liquid phase, it quickly reacts with H₂O to generate HSO₃⁻ and SO₄²⁻, according to reaction Eqs. (1)–(4) [41]. Subsequently, under the catalytic action of Fe³⁺ and Mn²⁺ metal ions, the HSO₃⁻ and SO₃²⁻ react with O₂ and rapidly convert to SO₄²⁻, based on Eqs. (5)–(7) [36]. As a result, the SO₂ is effectively converted into SO₄²⁻. As shown in Fig. 9(a), by comparing the effect of phosphorus sludge as well as its solid and liquid phases on SO₂ removal, it can be found that 100% desulfurization efficiency can be achieved for up to 8 h by using only the liquid phase of phosphorus sludge as an absorbent. This is because the liquid phase of phosphorus sludge contains a large amount of Fe³⁺ and Mn²⁺ (Fig. 2(c)), which can accelerate the conversion of HSO₃⁻ toward SO₄²⁻ [36]. However, due to the presence of P₄ in the phosphorus sludge and its solid phase, PO₄³⁻ gradually accumulates through the oxidation reaction of P₄ during the reaction process, which has an inhibitory effect on the conversion of SO₄²⁻ [32,42]. Hence, compared with the liquid phase of phosphorus sludge, the desulfurization performance is weaker. Yet it is worth noting that the P₄ plays a crucial role in the removal of NO_x. From Fig. 9(b), owing to the low water solubility of NO, the liquid phase of phosphorus sludge presents poor denitrification performance. When P₄ is present, a large amount of O, O₃, and HO· radicals are formed through the reaction between P₄ and O₂ (Eqs. (8)–(10)). The NO is oxidized by O and O₃ to water-soluble NO₂ and NO₃ by Eqs. (11)–(15), which react with H₂O to form NO₃⁻ (Eqs. (16)–(24)). In addition, from Eqs. (25) and (26), the NO can be directly oxidized to NO₂⁻ and NO₃⁻ through HO· radicals (Eqs. (25) and (26)) [37].

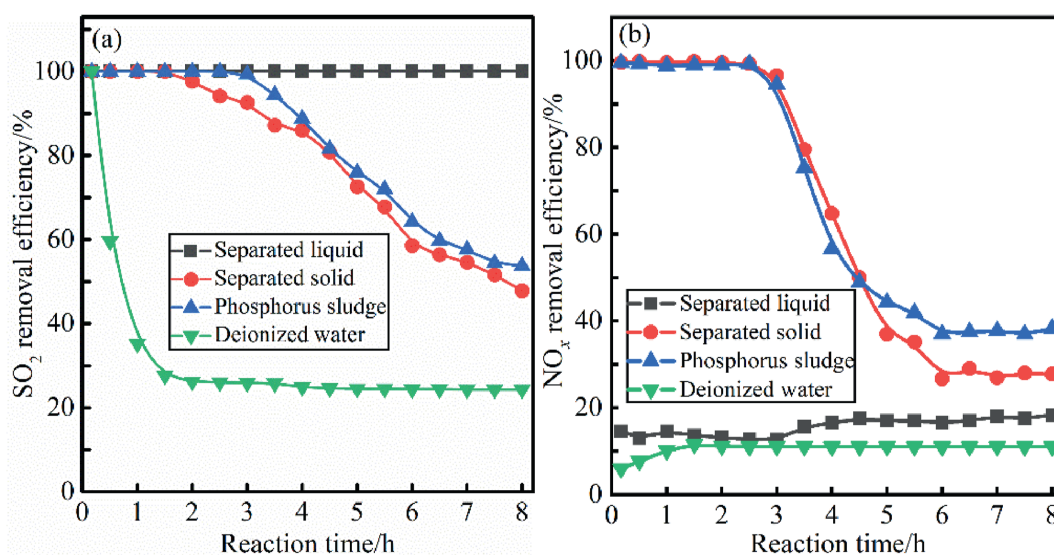
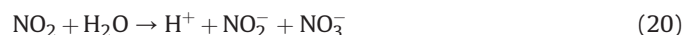
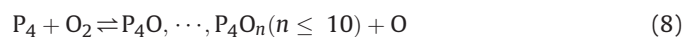
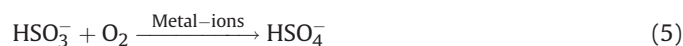


Fig. 9. Effects of liquid and solid components separated phosphorus sludge on simultaneous (a) desulfurization and (b) denitrification efficiency, respectively.



4. Conclusions

In this study, a novel method for simultaneous removal of SO_2 and NO_x using phosphorus sludge as an absorbent was studied. The key factors influencing SO_2 and NO_x absorption are studied, including reaction temperature, stirring intensity, gas flow, and phosphate rock additive. The reaction temperature should be controlled at 55 °C to achieve optimal desulfurization and denitrification effects. Because the P_4 from phosphorus sludge is easily oxidized to P_2O_5 , the stirring speed and gas flow rate should be controlled within an appropriate range. Adding phosphate rock to the phosphorus sludge absorbent can prolong the time for efficient SO_2 removal, but it has almost no promoting effect on NO_x removal. Furthermore, the absorption mechanism of SO_2 and NO_x has been proposed by conducting a series of online characterizations of the absorbent during the reaction process. The reason for the efficient absorption of SO_2 is that the Fe^{3+} and Mn^{2+} ions from the phosphorus sludge can rapidly catalyze the conversion of HSO_3^- and SO_3^{2-} towards SO_4^{2-} . The P_4 can induce O , O_3 , and $\text{HO} \cdot$ radicals by reacting with O_2 , which oxidizes NO into high-valent nitrogen oxides that are easily soluble in water. Ultimately, it exists in the liquid phase as NO_3^- . This technology shows good application prospects due to its low cost and high desulfurization and denitrification performance.

Declaration of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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