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Enhanced SO$_2$ Absorption Capacity of Sodium Citrate Using Sodium Humate

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Abstract: A novel method of improving the SO$_2$ absorption performance of sodium citrate (Ci-Na) using sodium humate (HA–Na) as an additive was put forward. The influence of different Ci-Na concentration, inlet SO$_2$ concentration and gas flow rate on desulfurization performance were studied. The synergistic mechanism of SO$_2$ absorption by HA–Na and Ci-Na was also analyzed. The consequence shows that the efficiency of SO$_2$ absorption by Ci-Na is above 90% and the desulfurization time added with the Ci-Na concentration rising from 0.01 to 0.1 mol/L. Both the desulfurization efficiency and time may increase with the adding of HA–Na quality in Ci-Na solution. Due to adding HA–Na, the desulfurization efficiency of Ci-Na increased from 90% to 99% and the desulfurization time increased from 40 to 55 min. Under the optimum conditions, the desulfurization time of Ci-Na can exceed 70 min because of adding HA–Na, which is nearly doubled. The growth of inlet SO$_2$ concentration has little effect on the desulfurization efficiency. The SO$_2$ adsorption efficiency decreases with the increase of inlet flow gas. The presence of O$_2$ improves the SO$_2$ removal efficiency and prolongs the desulfurization time. Therefore, HA–Na plays a key role during SO$_2$ absorption and can dramatically enhance the SO$_2$ adsorption performance of Ci-Na solution.

Keywords: sodium citrate; sodium humate; SO$_2$; absorption

1. Introduction

It is well known that fossil fuels is mainly used to generate electrical energy in power plants and the combustion of fossil fuels generates SO$_2$, which is the major source of acid rain and a major air pollutant, which severely influences the atmosphere environment and human health if not controlled [1,2]. Controlling SO$_2$ is critical to improve air quality and has always caught people's eye in recent years due to the environmental issues [3–5]. Therefore, improving the desulfurization performance economically and effectively of existing desulfurization technology has become a research hotspot at home and abroad [6–8].

There are plenty of desulfurization processes developed on the laboratory scale, some of which are applied at industrial standards around the world [9]. In the traditional methods, limestone, sodium hydroxide solutions, calcium hydroxide and magnesium hydroxide and a number of organic solvents have been used as an adsorbent [10]. There are other desulfurization processes such as the citrate method. During the citrate process, SO$_2$ in the flue gas is absorbed by the sodium citrate (Ci-Na) solution [11,12]. According to the physical characteristics of Ci-Na [13], adopting the desulfurization technology of Ci-Na can meet the advantages of environmental protection, flexible operation, recyclable absorbents and recyclable SO$_2$ for resource utilization, also meeting the increasingly strict requirements of environmental protection, desulfurization, etc. [14–16].

Humic acid (HA) is a type of amorphous organic molecular compound, most of these extensively exist in nature. It can be obtained from lignite and peat [17,18]. Due to its "sponge-like" structure, HA produces a large surface area (330–340 m^2/g) and surface energy and has a strong adsorption capacity [19]. The adsorption capacity of HA is not

only related to its surface area and surface energy, but also the swelling property of HA to water [20]. Sodium humate (HA–Na) is a water-soluble sodium salt of HA and a cost-effective absorbent, which reacts with H^+ to produce HA precipitate thus promoting the dissolution of SO_2 in the water [21]. They have been studied more broadly for biological breeding and pollution control due to their characteristics of adsorption, chelation and ion exchange [22]. HA–Na has higher swelling property than HA itself [23]. With the enhancement of the swelling property of HA, the active groups of HA can be more fully exposed in the aqueous solution and the probability of contact between HA and adsorbed ions is increased and then it improves the adsorption effect [24–26]. However, there have been few reports with regard to the addition of HA–Na to modify the Ci-Na solution to improve the adsorption capacity [27].

Sun et al. [28] investigated the desulfurization activity of the HA–Na/α-Al$_2$O$_3$ composite adsorbent on the fixed-bed quartz reactor. A series of characterization showed that coating α-Al$_2$O$_3$ fibers after being immersed in HA–Na solution can enhance the flue gas desulfurization performance of the α-Al$_2$O$_3$ carrier. The reason is that the HA–Na adsorbent has a stronger adsorption capacity for NH$_4$OH. The longer the conversion rate of SO$_2$ is maintained, the more NH$_4$OH will be adsorbed in the HA–Na/α-Al$_2$O$_3$ adsorbent. According to the previous study, it revealed that the HA–Na solution has good SO$_2$ absorption characteristics. The desulfurization products can be made into the HA compound fertilizer, which provides an economical and effective way to reduce SO$_2$ from flue gas [29].

This paper studies the absorption performance of HA–Na/Ci-Na and the desulfurization mechanism, which will lay the foundation for further research and popularization in the future.

2. The Enhancement Mechanism

HA–Na may bring an enhancement effect on SO$_2$ capture by the Ci-Na method. Table 1 shows the relevant reactions and the enhancement mechanism was put forward as follows: (1) The SO$_2$ absorption by Ci-Na mainly depend on the buffering properties of its absorbing solution. (2) After adding HA–Na, the carboxyl (COO–) and hydroxyl (OH–) of HA–Na reacts with H^+ rapidly and HA–Na is transferred to the HA sediment (Equation (8)). Due to these reactions, the reaction equilibrium of Equations (1)–(7) moves to the right and the amount of SO$_2$ dissolved into solution is increased. (3) HA–Na may reduce the rate of pH decline of Ci-Na solution since the HA–Na solution is also a kind of acidic buffer solution, which also may enhance SO$_2$ absorption.

Table 1. The reaction equation of CO$_2$ capture.

Reaction Equation	Number
$SO_2(g) \leftrightarrow SO_2(aq)$	(1)
$SO_2(aq) + H_2O \leftrightarrow 2H^+(aq) + SO_3^{2-}(aq)$	(2)
$C_i^{3-}(aq) + H^+(aq) \leftrightarrow HC_i^{2-}(aq)$	(3)
$HC_i^{2-}(aq) + H^+(aq) \leftrightarrow H_2C_i^-(aq)$	(4)
$H_2C_i^-(aq) + H^+(aq) \leftrightarrow H_3C_i(aq)$	(5)
$H_2O \leftrightarrow H^+(aq) + OH^-(aq)$	(6)
$R - (COONa)_n(aq) \leftrightarrow R - (COO^-)_n(aq) + nNa^+(aq)$	(7)
$R - (COO^-)_n + nH^+(aq) \leftrightarrow R - (COOH)_n(s)$	(8)

R–(COONa)$_n$ is the structural formula of HA–Na and R–(COOH)$_n$ is the structural formula of HA.

3. Results and Discussion

3.1. Desulfurization Performance of Only Ci-Na

The influence of different concentrations of Ci-Na on the removal rate of SO$_2$ was analyzed as can be seen in Figure 1. It shows the relationship of Ci-Na concentration and SO$_2$ desulfurization efficiency [30]. The SO$_2$ absorption by different concentrations of

Ci-Na all shows higher efficiency and the SO_2 absorption efficiency had no obvious change and basically maintained above 90% with the increase of Ci-Na concentration. The duration of high efficiency desulfurization also added with the increasing of Ci-Na concentration. When the concentration of Ci-Na added from 0.01 to 0.1 mol/L, the desulfurization time was extended from 20 to 80 min, which was increased by 4 times.
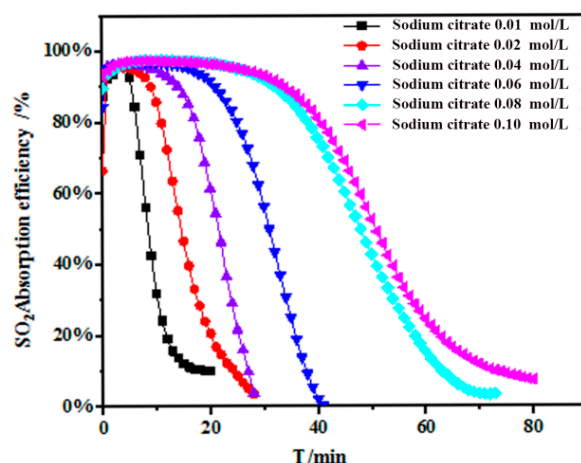

Figure 1. Effect of Ci-Na concentration on desulfurization efficiency. SO_2 = 2300 ppm, gas flow = 1.68 L/min and absorption solution = 60 mL and 25 °C.

Figure 2 shows the relationship between desulfurization time and Ci-Na concentration. The desulfurization time experienced two rapid growth phases with the growth of Ci-Na concentration and it tended to be flat after 0.08 mol/L. The Ci-Na solution is weakly alkaline and the citrate ion has good buffering capacity. In this experiment, the concentration of 0.06 mol/L Ci-Na was selected as the optimum condition and the SO_2 absorption efficiency was 96.4% and the duration was 40 min.
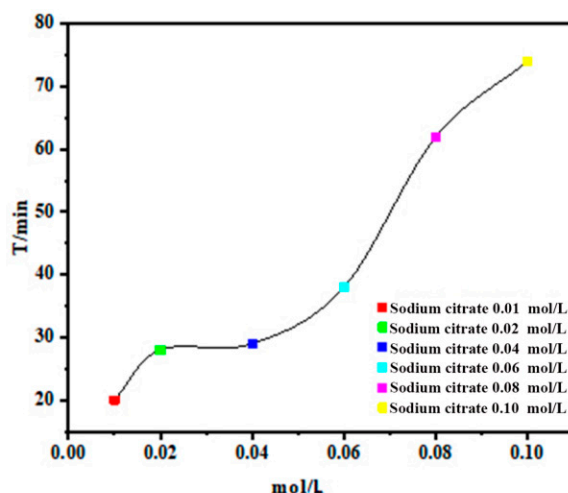

Figure 2. The effect of Ci-Na concentration on desulfurization time. SO_2 = 2300 ppm, gas flow = 1.68 L/min and absorption solution = 60 mL and 25 °C.

3.2. Effect of HA–Na Concentration

The different quantity of HA–Na was a significant factor on the reduction of SO_2 concentration, hence a series of experiments were carried out to study the effect of quantity on desulfurization efficiency [31]. The desulfurization efficiency using only HA–Na solution was shown in Figure 3. With the quantity increasing of HA–Na, the SO_2 absorption efficiency increased from 82% to 98%, which also had a certain impact on the break-through time. In addition, as the amount of HA–Na quantity increased (from 0.05 to 2.4 g), the

desulfurization time also was enhanced and almost remained above 40 min when HA–Na mass was 2.4 g. The reason is as follows: the HA–Na solution is alkaline (generally the PH value is 10), and the hydroxide (OH^-) in the solution is rapidly neutralized with the generated H^+. Moreover, a large number of acid ions ionized by HA–Na (such as COO- and OH^-), which will interact with a large number of H^+. The H^+ combines with HA–Na to generate HA precipitation, which moves the dissolution balance to the right and promotes the dissolution of more SO_2 into the HA–Na solution.
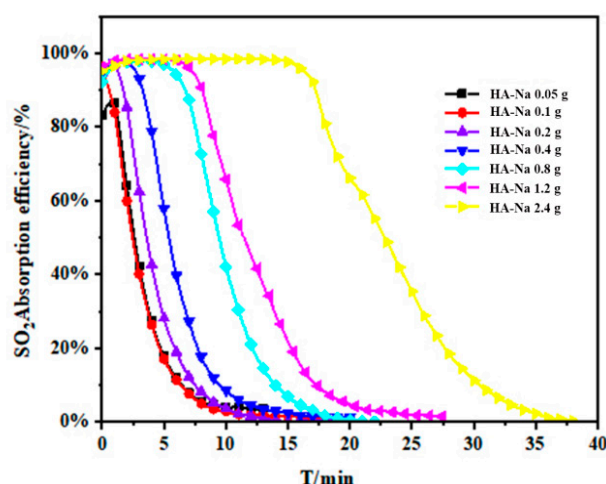

Figure 3. The effect of different quality HA–Na on desulfurization efficiency. SO_2 = 2300 ppm, gas flow = 1.68 L/min and absorption solution = 60 mL and 25 °C.

3.3. Effect of the Additive Amount of HA–Na on the Desulfurization Performance of Ci-Na

The addition of a different quantity of HA–Na may be one of the factors affecting the desulfurization efficiency of Ci-Na [32]. HA–Na was added into Ci-Na solution as an additive, such as 0.05 g, 0.1 g, 0.2 g, 0.4 g, 0.8 g, 1.2 g and 2.4 g, respectively, and the desulfurization effect was shown in Figure 4. The SO_2 absorption efficiency increased as the adding amount of HA–Na, and the saturation time also was improved, from 40 to 70 min. The reason may be that the addition of HA–Na increases the hydroxide ion (OH^-) in the solution, promoting more SO_2 absorption. Ci-Na and HA–Na had a synergistic effect for SO_2 absorption. This is more clearly confirmed in Figure 5.
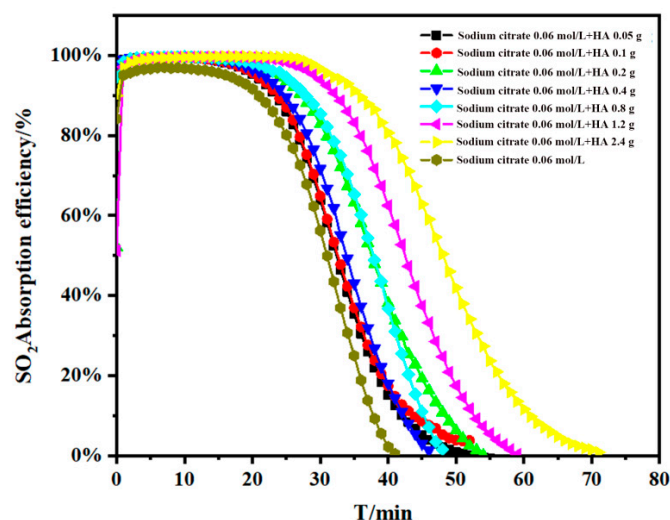

Figure 4. Effect of HA–Na additive on the desulfurization effect. SO_2 = 2300 ppm, gas flow = 1.68 L/min, absorption solution = 60 mL and Ci-Na = 0.06 mol/L and 25 °C.
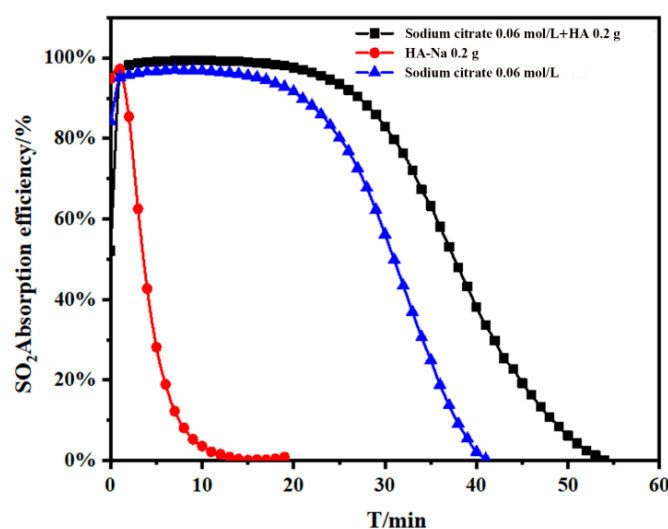
Figure 5. Comparison of HA–Na and Ci-Na solution. SO_2 = 2300 ppm, gas flow = 1.68 L/min, absorption solution = 60 mL and Ci-Na = 0.06 mol/L and 25 °C.

It is evident from Figure 5 that the addition of HA–Na can remarkably enhance the desulfurization efficiency and saturation time of Ci-Na. It was also found that the SO_2 absorption efficiency was close to 0% at 40 min when there was no HA–Na added, but it was still about 50% after adding HA–Na. Moreover, the desulfurization time increased by 15 min. The causes of this phenomenon are various [33]. In addition to the hydrolysis of HA–Na to generate hydroxide ions, it can also ionize the acid radical ions (carboxylate), thus consuming H^+ to move the dissolution balance to the right and cooperating with Ci-Na to absorb more SO_2.

3.4. Effect of the Inlet SO_2 Concentration

The concentration of SO_2 is different in the actual industrial flue gas. Hence, it might be necessary to research the influence of SO_2 concentration on SO_2 absorption efficiency. The influence of different SO_2 concentrations on the SO_2 removal efficiency as illustrated in Figure 6. Simulated flue gas with the SO_2 concentrations of 1000 ppm, 2300 ppm and 3000 ppm were used for the desulfurization experiment. The results are represented in Figure 6 that with the increase of SO_2 concentration, the desulfurization time of reaching saturation decreased from 92 to 40 min and diminished by 2.3 times. Moreover, the desulfurization time decreased significantly at 40 min, only about 5% under the high SO_2 concentration condition, while the desulfurization time was still close to 100% under the condition of low SO_2 concentration. The result shows that the inlet SO_2 concentration had a certain influence on the removal efficiency.

The main reason is that the driving force of mass transfer increased with the increasing of SO_2 concentration, which is beneficial to the absorption reaction [34]. However, the SO_2 capacity per unit volume of the solution was constant. As the inlet SO_2 concentration increased, the mass transfer rate was heightened while the time of SO_2 absorption saturation was shortened. So, the SO_2 absorption rate will be accelerated and the desulfurization time will be reduced.
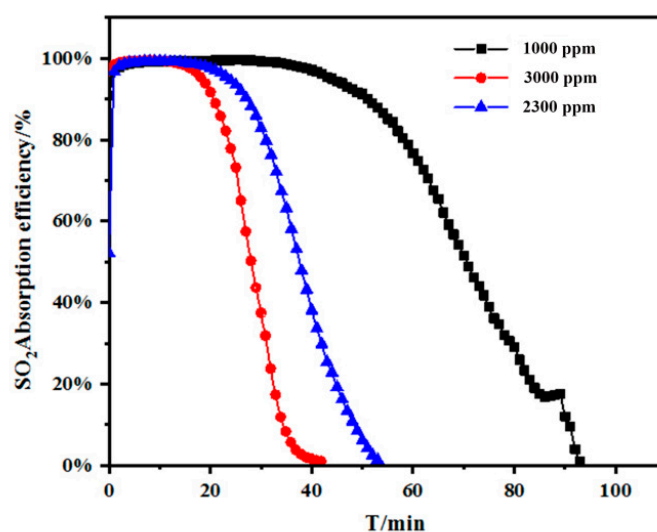
Figure 6. Effect of SO_2 concentration on desulfurization efficiency. Gas flow = 1.68 L/min, absorption solution = 60 mL, Ci-Na = 0.06 mol/L and HA–Na = 0.2 g and 25 °C.

3.5. Effect of the Gas Flow Rate

Most of the experiments were discussed as the influence of the gas flow rate on SO_2 removal efficiency. The initial inlet gas flow rate were respectively set as 1.0 L/min, 1.3 L/min and 1.6 L/min in the experiment. The results was presented in Figure 7. It is proved by the experiment that the removal efficiency of SO_2 increased as the initial inlet gas flow decreased. The increasing of the gas flow rate reduced the driving force of the absorption reaction, which is unfavorable for the desulfurization reaction. At the same time, the gas flow rate increased and the gas–liquid reaction time was reduced. A part of SO_2 was released before the reaction, which affected the absorption efficiency. In general, increasing gas flow had only some negative consequences.
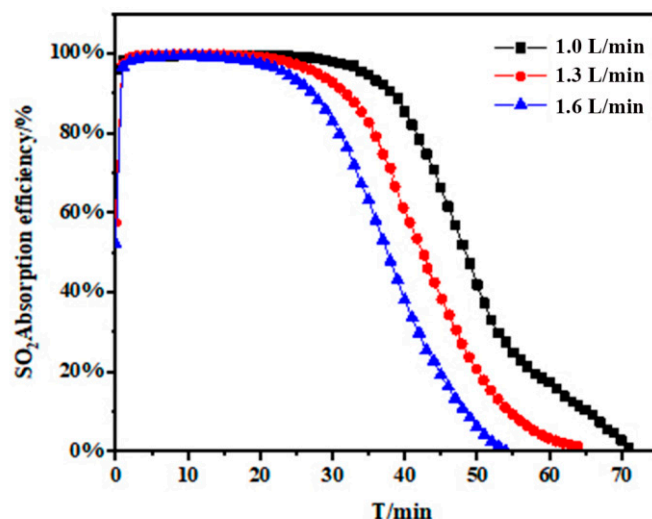

Figure 7. Effect of the gas flow rate. SO_2 = 2300 ppm, absorption solution = 60 mL, Ci-Na = 0.06 mol/L and HA–Na = 0.2 g and 25 °C.

3.6. Effect of O_2

The actual industrial flue gas contains a variety of ingredients, such as O_2. For instance, the flue gas of coal-fired power plant typically contains about 5–15 vol% O_2 [35]. Therefore, the existence of O_2 in the simulated flue gas was also explored. Figure 8 shows the effect of the presence of O_2 on the SO_2 removal efficiency. The experimental results indicated that SO_2 absorption efficiency at 50 min was improved significantly from 5% to 95% by the

addition of 15% O_2. It can be seen that the existence of O_2 increased the desulfurization efficiency noticeably and also prolonged the desulfurization time from 55 to 80 min. The possible reasons were as follows [36]. The presence of O_2 could be more effective in improving O_2 dissolving into water so that the centration of dissolved O_2 into the solution was far higher than before, which is conducive to the oxidation of sulfite. According to Equation (9), it can infer that dissolved O_2 could accelerate the oxidation of sulfate. This reduces the concentration of HSO_3^- in the liquid phase and makes Equation (10) shift to the right. The liquid phase mass transfer coefficient was reduced.
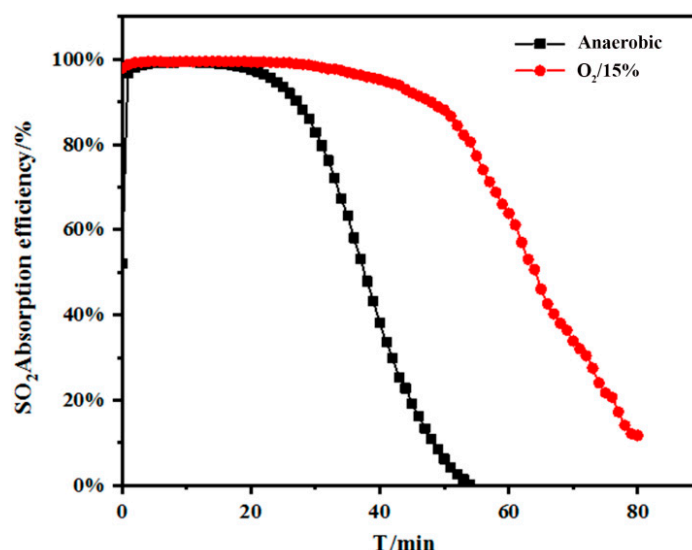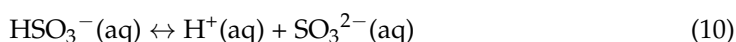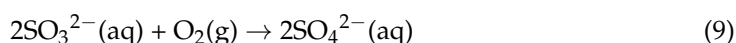

Figure 8. Effect of O_2. SO_2 = 2300 ppm, gas flow = 1.68 L/min, absorption solution = 60 mL, Ci-Na = 0.06 mol/L and HA–Na = 0.2 g and 25 °C.

After the addition of O_2, the desulfurization process will be accompanied by the following reactions.

$$2SO_3{}^{2-}(aq) + O_2(g) \rightarrow 2SO_4{}^{2-}(aq) \tag{9}$$

$$HSO_3{}^-(aq) \leftrightarrow H^+(aq) + SO_3{}^{2-}(aq) \tag{10}$$

It could be deduced that more O_2 in the solution participated in the desulfurization reaction and both the amount of SO_2 absorbed and desulfurization time were increased.

4. Materials and Methods

4.1. Sample Preparation

Ci-Na, sodium hydroxide, sodium acetate, acetic acid solution, anhydrous ethanol and sodium carbonate were from Sino pharm Chemical Reagent Co., Ltd., in Shanghai, China. HA–Na was from Shanghai Jincheng Biochemical Co., Ltd, in Shanghai, China. Deionized water was made in the laboratory.

4.2. Desulfurization Test

A principle diagram of the experimental devices are represented in Figure 9 below. Absorption experiments of the SO_2 in the laboratory consisted of SO_2, O_2 and balance N_2 as simulated flue gas. The SO_2, O_2 and N_2 gases were provided by cylinders. The experiment adopted SO_2 with a concentration range of 1000–3000 ppm. The total flow rate of the simulated flue gas was controlled with a mass flow controller (MFC). The flue gas analyzer was used to monitor the change of SO_2 concentration at the inlet and outlet of the reactor (KANE-9506, UK) [29].
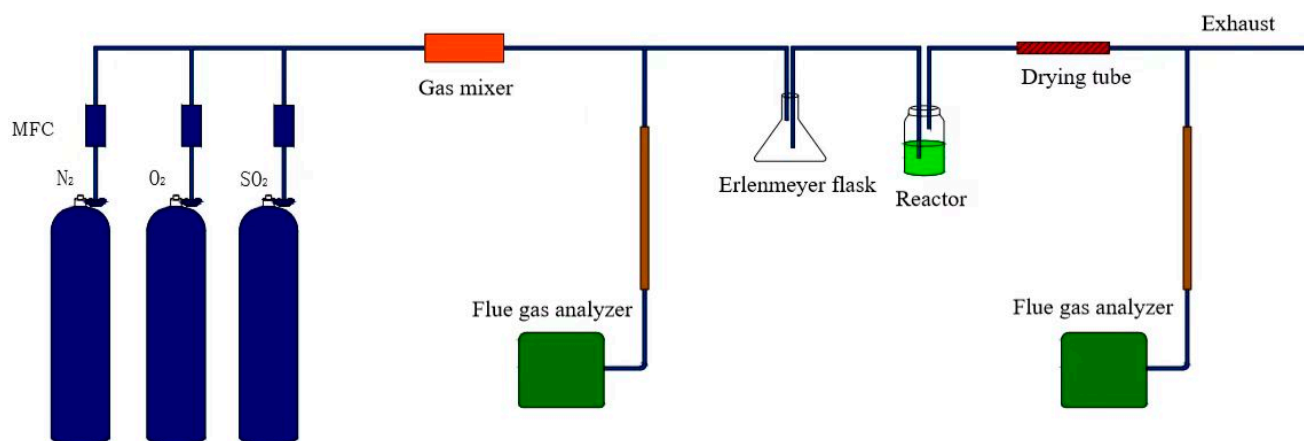
Figure 9. Schematic diagram of the experimental apparatus.

The absorption efficiency SO_2 can be obtained by the following formula:

$$\eta = \frac{(C_{in} - C_{out}) \times 100\%}{C_{in}} \tag{11}$$

where η is the SO_2 absorption efficiency and C_{an} and C_{oot} are the inlet and outlet of the SO_2 concentration, respectively.

5. Conclusions

The new desulfurization method with Ci-Na/HA–Na solution was put forward. The influence of different Ci-Na concentration, inlet SO_2 concentration, flow rate and other elements on the desulfurization performance were studied. The mechanism of HA–Na as an addition agent to improve the desulfurization performance of Ci-Na was discussed. For the absorption process, the higher the Ci-Na concentration and the lower the inlet flue gas flow, the more conducive to the SO_2 absorption. The presence of O_2 had a slight influence on the desulfurization efficiency. HA–Na played a key role during SO_2 absorption by the Ci-Na solution and can improve obviously the desulfurization performance of the Ci-Na solution.

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References

1. Mohd, M.; Hayyiratul-Fatimah, Z.; Chong, K.; Khairulazhar, J.; Lim, Y.; Sarrthesvaarni, R. Futuristic advance and perspective of deep eutectic solvent for extractive desulfurization of fuel oil: A review. *J. Mol. Liq.* **2020**, *306*, 112870.
2. Akyalçın, L.; Kaytakoğlu, S. Flue gas desulfurization by citrate process and optimization of working parameters. *Chem. Eng. Process.* **2009**, *49*, 199–204. [CrossRef]
3. Antony, R.; Tian, C.; Hong, F.; Zhi, Y.; Jie, F.; Wen, L. A comprehensive review on oxidative desulfurization catalysts targeting clean energy and environment. *J. Mater. Chem. A* **2020**, *8*, 2246.

4. Yong, Y.; Zhong, M.; Jin, L.; Ru, D.; Jia, L. Simultaneous removal of SO_2, NO_x and Hg^0 by O_3 oxidation integrated with bio-charcoal adsorption. *Fuel Chem. Technol.* **2020**, *48*, 1452–1460.

5. Guo, H.; Zhi, S.; Han, G. Novel Process of Simultaneous Removal of SO_2 and NO_2 by sodium humate solution. *Environ. Sci. Technol.* **2010**, *44*, 6712–6717.

6. Wei, S.; Jia, Z.; Bao, W.; Shu, L.; Jun, H. New insight into investigation of reduction of desulfurization ash by pyrite for clean generation SO_2. *J. Clean. Prod.* **2020**, *253*, 120026.

7. Jia, L.; Zhi, Y.; Si, L.; Qi, J.; Jian, Z. Review on oxidative desulfurization of fuel by supported heteropolyacid catalysts. *J. Ind. Eng. Chem.* **2020**, *82*, 1–16.

8. Lu, C.; Zhi, S.; Jin, X.; Meng, W.; Jia, F.; Li, Z. Reactivity Improvement of Ca-Based CO_2 Absorbent Modified with Sodium Humate in Cyclic Calcination/Carbonation. *ACS Omega* **2020**, *5*, 8867–8874.

9. Yi, Z.; Run, H.; Tian, W.; Chun, Y. Follow-up research for integrative process of pre-oxidation and post-absorption cleaning flue gas: Absorption of NO_2, NO and SO_2. *Chem. Eng. J.* **2015**, *273*, 55–65.

10. Castillo-Villalón, P.; Jorge, R.; Vargas-Luciano, J.A. Analysis of the role of citric acid in the preparation of highly active HDS catalysts. *J. Catal.* **2014**, *320*, 127–136. [CrossRef]

11. Budukva, S.V.; Klimov, O.V.; Noskov, A.S. Effect of citric acid and triethylene glycol addition on the reactivation of CoMo/γ-Al_2O_3 hydrotreating catalysts. *Catal. Today* **2019**, *329*, 35–43. [CrossRef]

12. Gao, L.; Yuan, L.; Jun, H. Intensifying effects of zinc oxide wet flue gas desulfurization process with citric acid. *J. Environ. Chem. Eng.* **2018**, *7*, 102831.

13. Xiu, J.; You, L.; Meiduo, G.U. Absorption of Sulphur Dioxide with Sodium Citrate Buffer Solution in a Rotating Packed Bed. *Chin. J. Chem. Eng.* **2011**, *19*, 687–692.

14. Kazakova, M.O.; Kazakova, M.A.; Vatutina, Y.V.; Larina, T.V.; Noskov, A.S. Comparative study of MWCNT and alumina supported CoMo hydrotreating catalysts prepared with citric acid as chelating agent. *Catal. Today* **2020**, *357*, 221–230. [CrossRef]

15. Zhang, W.; Yu, H.; Wei, W.; Shu, R.; Kai, Z. Efficient Removal of Sulfuric Acid from Sodium Lactate Aqueous Solution Based on Common-Ion Effect for the Absorption of SO_2 of Flue Gas. *Energy Fuels* **2019**, *33*, 4395–4400.

16. Fateme, R.; Rownaghi, A.; Saman, M.; Ryan, P.; Christopher, W. SO_x/NO_x Removal from Flue Gas Streams by Solid Adsorbents: A Review of Current Challenges and Future Directions. *Energy Fuels* **2015**, *29*, 5467–5486.

17. Zheng, X.; Deng, L.; Fei, W.; Zhi, S.; Zheng, L. Simultaneous removal of NO and SO_2 with a new recycling micro-nano bubble oxidation-absorption process based on HA-Na. *Sep. Purif. Technol.* **2020**, *242*, 116788.

18. Motta, F.L.; Santana, A. Production of humic acids from oil palm empty fruit bunch by submerged fermentation with Trichoderma viride: Cellulosic substratesand nitrogen sources. *Biotechnol. Prog.* **2013**, *29*, 631–637. [CrossRef] [PubMed]

19. Hong, D.; Tong, S.; Ting, H.; Xiang, L.; Ze, G.; Xing, W.; Yong, C. Interactions between cerium dioxide nanoparticles and humic acid: Influence of light intensities and molecular weight fractions. *Environ. Res.* **2021**, *195*, 110861.

20. Shu, X.; Ya, X.; Guo, W.; Zhen, M. Adsorption of heavy metals in water by modifying Fe_3O_4 nanoparticles with oxidized humic acid. *Colloid Surf. A* **2021**, *616*, 126333.

21. Kun, Y.; Xin, Y.; Jia, X.; Ling, J.; Wen, W. Sorption of organic compounds by pyrolyzed humic acids. *Sci. Total Environ.* **2021**, *781*, 146646.

22. Trckova, M.; Lorencova, A.; Hazova, K.; Sramkova, Z. Prophylaxis of post-weaning diarrhea in piglets by zinc oxide and sodium humate. *Vet. Med.* **2015**, *63*, 351–360.

23. Hashish, K.I.; Fatma, E.M.; Azza, M.M. Influence of potassium humate on growth and chemical constituents of Jatropha Curcus L. *Int. J. Chemtech. Res.* **2015**, *8*, 279–283.

24. Fábio, O.; Natália, A.; Raul-Castro, C.R.; Luciano, C. Substrate biofortification in combination with foliar sprays of plant growth promoting bacteria and humic substances boosts production of organic tomatoes. *Sci. Hortic.* **2015**, *183*, 100–108.

25. Wen, C.; Zhong, L.; Yan, L.; Xiao, X.; Qiang, L.; Xun, Z. Improved electricity generation, coulombic efficiency and microbial community structure of microbial fuel cells using sodium citrate as an effective additive. *J. Power Sources* **2021**, *482*, 228947.

26. Yan, Z.; Xue, Z.; Yong, S.; Jiang, W. Enhanced performance of calcium-enriched coal ash for the removal of humic acids from aqueous solution. *Fuel* **2015**, *141*, 93–98.

27. Guo, D.; Zhi, J. Preparation of Sodium Humate-Modified Biochar Absorbents for Water Treatment. *ACS Omega* **2019**, *4*, 536–542.

28. Zhi, S.; Han, G.; Guo, H.; Yan, L. Preparation of Sodium Humate/α-Aluminum Oxide Adsorbents for Flue Gas Desulfurization. *Environ. Eng. Sci.* **2009**, *26*, 1249–1255.

29. Zhi, S.; Yu, Z.; Han, G.; Guo, H. Removal of SO_2 from Flue Gas by Sodium Humate Solution. *Energy Fuels* **2010**, *24*, 1013–1019.

30. Biswa, B.; Sung, J. Oxidative desulfurization and denitrogenation of fuels using metal-organic framework-based/-derived catalysts. *Appl. Catal. B* **2019**, *259*, 118021.

31. Guo, D.; Zhi, J. Sodium humate as an effective inhibitor of low-temperature coal oxidation. *Thermochim. Acta* **2019**, *673*, 53–59.

32. Kentaro, K.; Masatoshi, N. Active sites of sulfided NiMo/Al_2O_3 catalysts for 4, 6-dimethyldibenzothiophene hydrodesulfurization-effects of Ni and Mo components, sulfidation, citric acid and phosphate addition. *Catal. Today* **2017**, *292*, 74–83.

33. Kutus, B.; Dudás, C.; Friesen, S.; Peintler, G.; Pálinkó, I.; Sipos, P.; Buchner, R. Equilibria and Dynamics of Sodium Citrate Aqueous Solutions: The Hydration of Citrate and Formation of the Na_3Cit^0 Ion Aggregate. *J. Phys. Chem.* **2020**, *124*, 9604–9614. [CrossRef] [PubMed]

34. Nadeesha, H.K.; Patricio, X.P.; Dionysios, D.D.; Al-Abed, S.R. Recent advances in flue gas desulfurization gypsum processes and applications—A review. *J. Environ. Manag.* **2019**, *251*, 109572.
35. Seong-Pil, K.; Huen, L. Recovery of CO_2 from Flue Gas Using Gas Hydrate: Thermodynamic Verifification through Phase Equilibrium Measurements. *Environ. Sci. Technol.* **2000**, *34*, 4397–4400.
36. You, L.; Jia, L.; Tian, Y. Surface modification of SiC powder with HA-Na: Adsorption kinetics, equilibrium and mechanism. *Langmuir* **2018**, *34*, 9645–9653.