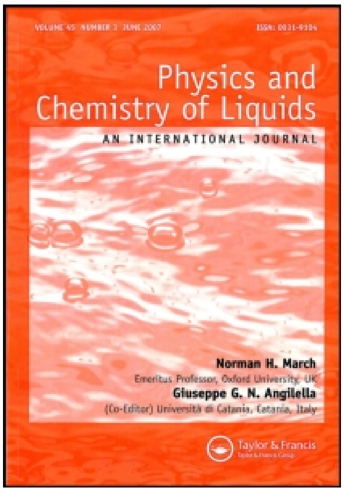

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Research on mechanism of gas liquid separation in SO_2 removal from flue gas by liquid absorption with catalysed reaction

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Research on mechanism of gas liquid separation in SO_2 removal from flue gas by liquid absorption with catalysed reaction

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The desulphurised experiment of an organic physical solvent of dimethyl sulphoxide (DMSO) mixed with a relatively small amount of Mn(II) catalyst, based on the novel desulphurisation technology using the organic solvent as absorbent, is studied. Results indicate that Mn(II) plays a significant catalytic role. Compared with pure physical solvent of DMSO, the purification efficiency of SO_2 with a small amount of catalyst has been much improved, and its absorption and reaction mechanism by liquid absorption with catalysed reaction are discussed.

Keywords: flue gas; desulphurisation; catalytic reaction; gas liquid separation; mechanism

1. Introduction

China ranks first in the world in the emission of sulphur dioxide from coal,which has been one of the main causes of acid rain pollution. At present, the environmental pollution from flue gases is becoming more and more serious. It has become particularly important to control the pollution because of sulphur dioxide. In order to find the effective method, various desulphurisation techniques [1–7], such as activated carbon, molecular sieve, electron-beam radiation technique, chemical method, physical solvents, etc. are all attempted. Compared with these methods, organic solvent absorption has some advantages, such as low investment, high SO_2 absorption efficiency and desorption efficiency, and therefore it is worth of further research. In this article, based on the studied organic absorbent with a high absorption and desorption efficiency for high selectivity to SO_2 with low toxicity and low price [8, 9], a small amount of Mn(II) catalyst is added to the system of organic solvent absorption. It is found that the purification efficiency of SO_2 with a small amount of Mn(II) catalyst has been much improved compared with pure physical solvent of DMSO; Mn(II) plays a significant catalytic role. Therefore, some laboratory measurements for increasing the purification efficiency of SO_2 from flue gas by catalytic oxidation have been carried out and the effect of transition metal ions on the catalytic reduction of SO_2 by the liquid catalysed oxidation is discussed primarily. The research provides a basis for the industrial production of flue gas desulphurisation technology.

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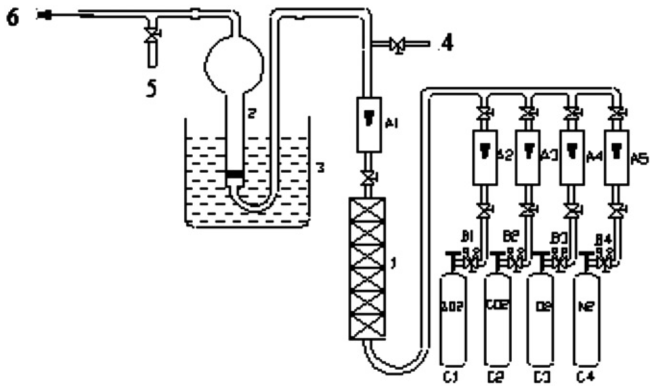

Figure 1. The technological process of SO_2 absorption. C1, SO_2 cylinder; C2, CO_2 cylinder; C3, O_2 cylinder; C4, N_2 cylinder; B1–B4, valve; A1–A5, flowrator; 1, a gas mixer with static agitation unit; 2, absorption tube; 3, constant temperature bath; 4, inlet gas to SO_2 analyser; 5, outlet gas to SO_2 analyser; 6, to fume hood.

2. Experimental

The technological process for SO_2 removal is shown in Figure 1. Sulphur dioxide with a mole fraction purity $\times (SO_2) \geq 0.997$, oxygen of purity $\times (O_2) \geq 0.99$, carbon dioxide with a mole fraction purity $\times (CO_2) \geq 0.99$ and nitrogen of purity $\times (N_2) \geq 0.99999$ are obtained from cylinders. Sulphur dioxide, carbon dioxide, oxygen and nitrogen are mixed by a gas mixer with static agitation to simulate the flue gas. A flowrator is used to control the gas flow. CO_2 is analysed by CO_2 analyser (type RD-7AG, Nanjing, China). O_2 is analysed with an AUS-gas analyser with gas absorption method. A SO_2 analyser (type NTS 100, Nanjing, China) is used for the SO_2 analysis of the gas phase from the inlet and tail gases. The SO_2 concentration in the gas phase before and after absorption is analysed by SO_2 analyser, and then the purification efficiency is calculated.

$$\text{The purification efficiency } (P) \text{ is } P = \frac{C_0 - C}{C_0} \times 100\%,$$

where C_0 is the SO_2 concentration before absorption and C the SO_2 concentration after absorption.

All the chemical reagents used are of AR grade. Purified and deionised water of conductivity $< 0.06\,\mu S\,cm^{-1}$ is used in the measurements.

3. Results and discussion

3.1. *Effect of different additives on the purification efficiency of SO_2*

In order to increase the purification efficiency of $SO_{2,}$ some additives such as Fe(III), Mn(II) and thiophene are added to liquid absorbents DMSO to test the effect of additives on SO_2 removal. The experimental results are shown in Figure 2.

Experimental conditions: temperature, 297.15 K; gas flow, $80\,ml\,min^{-1}$; and inlet SO_2 concentration, 0.1798% $SO_{2.}$

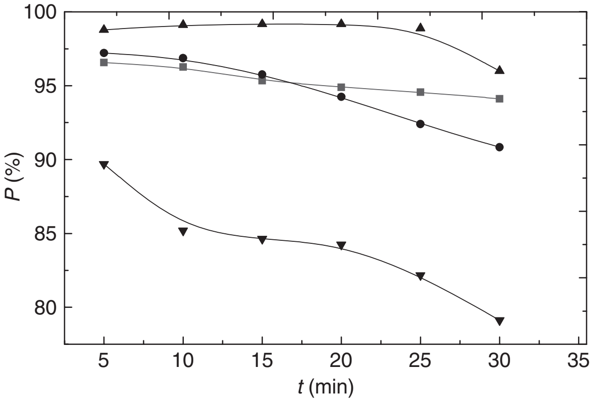

Figure 2. Effect of additives on the purification efficiency of SO_2. ▲, DMSO + Mn (II); ■, DMSO; •, DMSO + Fe^{3+}; ▼, DMSO + thiophene.

The results indicate that the addition of Mn(II) in DMSO can increase purification efficiency of SO_2; while the addition of Fe (III) can also increase purification efficiency of SO_2 only at the beginning of absorption, but decreases with the increase of absorbing time; the addition of thiophene to DMSO shows negative effect on the purification efficiency of SO_2 compared with pure DMSO. Compared the effect results of different additives on the purification efficiencies of SO_2, the addition of Mn (II) in DMSO can increase the purification efficiency of SO_2 significantly.

3.2. *Effect of Mn (II) concentration on purification efficiency of SO_2*

The effect result of Mn (II) concentration on purification efficiency of SO_2 is shown in Figure 3.

From Figure 3, it is found that the purification efficiencies of SO_2 with DMSO + Mn (II) are all better than pure DMSO, and Mn (II) concentration has great effect on the purification efficiency of SO_2. Although Mn (II) played a significant role in removing SO_2, it is not the high of the Mn (II) concentration, the better. The optimum Mn (II) concentration is about $0.03\,\mathrm{M\,l^{-1}}$.

3.3. *Effect of Mn (II) + DMSO on purification efficiency of SO_2*

The effects of $0.03\,\mathrm{M\,l^{-1}}$ Mn (II) and DMSO on purification efficiency of SO_2 are listed in Table 1.

From Table 1, it revealed that under the optimum Mn (II) concentration, the purification efficiencies of DMSO + Mn (II) are all over 95%.

3.4. *Effect of O_2 concentration in flue gas on the purification efficiency of SO_2 by catalytic system of Mn (II)*

The experimental conditions: $T = 303.15\,\mathrm{K}$, inlet SO_2 concentration, 0.1806%; gas flow rate, $80\,\mathrm{ml\,min^{-1}}$ and Mn (II) concentration; $0.03\,\mathrm{M\,l^{-1}}$. The effect of O_2 concentration in flue gas on the purification efficiency of SO_2 is shown in Figure 4.

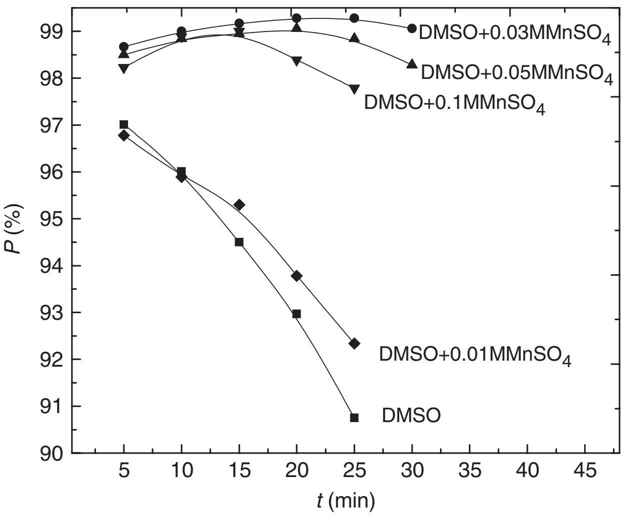

Figure 3. Effect of Mn (II) concentration on the purification efficiency of SO_2. ●, DMSO + 0.03 Mn (II); ▲, DMSO + 0.05 Mn (II); ▼, DMSO + 0.1 Mn (II); ◆, DMSO + 0.01 Mn (II); ■, DMSO. Experimental conditions: temperature 303.15 K, gas flow, 80 ml $min^{-1;}$ and inlet SO_2 concentration, 0.1806% SO_2.

Table 1. Effect of Mn (II) + DMSO on the purification efficiency of SO_2.

Number of experiment	Inlet SO_2 concentration ($\times 10^{-6}$)	Outlet SO_2 concentration ($\times 10^{-6}$)	Purification efficiency (%)
1	1806	34	98.12
2	1670	24	98.56
3	2608	95	96.36

Notes: Experimental conditions: absorption temperature, 303.15 K; and the gas flow, 80 ml min^{-1}.

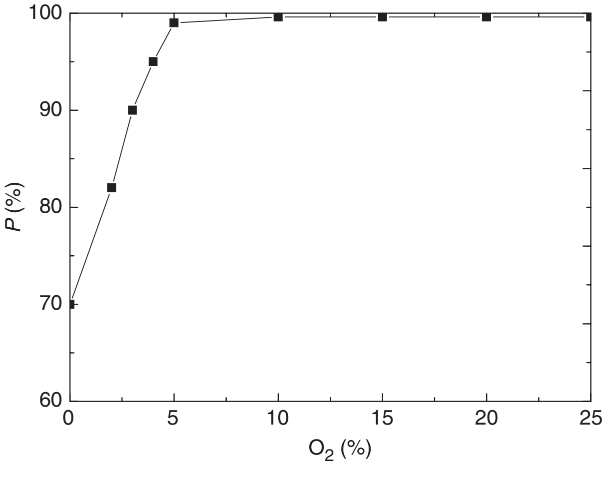

Figure 4. Effect of O_2 concentration in flue gas on the purification efficiency of SO_2.

From Figure 4, it can be found that O_2 has the greatest effect on manganese-catalysed autoxidation. When the O_2 content is less than 5%, the removal efficiency of SO_2 increases with the increased O_2 concentration; when the O_2 content is 5%, the removal efficiency of SO_2 is 99.5%; when the O_2 content is more than 5%, the removal efficiency of SO_2 is almost constant with the increased O_2 concentration; therefore, O_2 has an important effect in flue gas on the absorbing efficiency of SO_2 by the manganese-catalysed autoxidation.

3.5. *Selectivity absorption effect of Mn (II) + DMSO on the purification efficiency of SO_2 in the presence of CO_2*

There is not only sulphur dioxide, but also a lot of CO_2 in flue gas mixtures from industrial emissions. Both SO_2 and CO_2 are acidic gases, and the concentration of the former is much lower than the latter in the flue gas. If the absorbent is not selective for acid gases, such as SO_2 and CO_2, it will lead to a serious decrease in the efficiency of SO_2 purification because of absorbing a large number of CO_2. Therefore, a good selectivity for SO_2 and CO_2 is necessary in order to reach a higher efficiency of SO_2 purification.

Therefore, in order to further verify the selectivity absorption effect of Mn (II) + DMSO on the purification efficiency of SO_2 in the presence of CO_2, based on the gas mixture of SO_2, O_2 and N_2, CO_2 gas is mixed by gas mixing apparatus.

The selectivity absorption effects of Mn (II) + DMSO on the purification efficiency of SO_2 in the presence of CO_2 are listed in Table 2.

From Table 2, it can be shown that the purification efficiency of DMSO + Mn (II) mixed absorbent for SO_2 is over 98% in the presence of CO_2 within the absorption time of 0–30 min, but only 9–21% removal for CO_2; it can be found that DMSO + Mn (II) mixed absorbents have a good selective removal for SO_2 in the presence of CO_2.

Meanwhile, another experiment is also carried out to examine the absorption of SO_2 in the presence of CO_2 and SO_2 with pure DMSO, and similar results are obtained.

4. Mechanism analysis

The absorption process for SO_2 containing DMSO + Mn (II) is a complicated mechanism coexisting of physical and chemical absorptions.

Table 2. The selectivity absorption effect of Mn (II) + DMSO on purification efficiency of SO_2.

	Time (min)					
Purification efficiency (%)	5	10	15	20	25	30
SO_2	99.89	99.44	99.44	99.22	99.10	98.66
CO_2	21.23	18.58	16.81	15.04	13.27	9.73

Notes: Experimental conditions: absorption temperature, 301.15 K; gas flow, 140 ml min^{-1}; inlet CO_2 concentration, 11.3%; and inlet SO_2 concentration, 0.1893%.

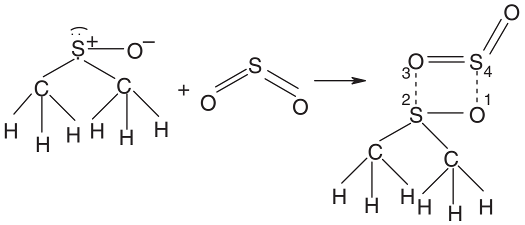

Figure 5. Absorption model of SO_2 in DMSO.

4.1. *Physical absorption*

DMSO is a polar organic solvent, whereas SO_2 is a polar gas molecule and CO_2 is a non-polar gas molecule. Therefore, DMSO has a better absorption capacity on the polar sulphur dioxide, but less absorption capacity on the non-polar carbon dioxide. It agrees with the principle that 'like dissolves like'. Accordingly, the absorption model of SO_2 in DMSO is shown in Figure 5.

4.2. *Chemical absorption*

After adding Mn(II) in DMSO, SO_2 is oxidised to H_2SO_4 and catalysed by $MnSO_4$. The chemical reaction is expressed as follows [10]:

$$SO_2 + \tfrac{1}{2}O_2 + H_2O \xrightarrow{M_nSO_4} H_2SO_4.$$

The reaction mechanism by liquid absorption with catalysed reaction may be the free-radical chain mechanism. Mn(II) in the liquid-phase catalysts for SO_2 oxidation mainly depends on valence state changes on its own to achieve [11,12].

Reactions involved in SO_2 oxidation may be:

Rapid pre-equilibrium:

$$SO_2(g) + H_2O \longleftrightarrow SO_2 \cdot H_2O$$
$$SO_2 \cdot H_2O \longleftrightarrow HSO_3^- + H^+$$
$$HSO_3^- \longleftrightarrow H^+ + SO_3^{2-}.$$

Catalytic reaction may be initiated after adding Mn (II) in aqueous solution:

$$Mn^{2+} + HSO_3^- \longleftrightarrow MnHSO_3^+$$
$$2Mn^{2+} \longleftrightarrow Mn_2^{4+}.$$

Initiation:

$$Mn_2^{4+} + HSO_3^- \longrightarrow Mn_2HSO_3^{3+}$$
$$Mn_2HSO_3^{3+} + O_2 \longrightarrow 2Mn^{2+} + OH\cdot + SO_4^{\bullet -}$$
$$OH\cdot + HSO_3^- \longrightarrow H_2O + SO_3^{\bullet -}.$$

Table 3. Desorption results of DMSO + Mn (II).

	Desorption temperature					
	333.15 K		343.15 K		353.15 K	
Time (min)	SO_2 concentration ($mol\,l^{-1}$)	Desorption efficiency (%)	SO_2 concentration ($mol\ l^{-1}$)	Desorption efficiency (%)	SO_2 concentration ($mol\,l^{-1}$)	Desorption efficiency (%)
Solution concentration before desorption	0.9700	0.00	1.204	0.00	1.2030	0.00
10	0.3200	67.01	0.3467	71.20	0.1336	88.89
20	0.1092	88.74	0.0680	91.61	0.0080	99.33
30	0.0227	97.66	0.0100	99.17	0.0018	99.85
40	0.0050	99.48	0.0045	99.63	0.0015	99.87
50	0.0043	99.56	0.0036	99.70	0.0014	99.88
60	0.0020	99.79	0.0020	99.83	0.0012	99.90

Propagation:

(1) Plays a major role chain:

$$\begin{aligned}&SO_4^{\bullet-} + HSO_3^- \rightarrow HSO_4^- + SO_3^{\bullet-}\\&SO_3^{\bullet-} + O_2 \rightarrow SO_5^{\bullet-}\\&SO_5^{\bullet-} + HSO_3^- \rightarrow SO_4^{\bullet-} + HSO_4^-.\end{aligned}$$

(2) Plays a secondary role chain:

$$\begin{aligned}&MnHSO_3^+ + HSO_3^- \rightarrow Mn(HSO_3)_2\\&Mn(HSO_3)_2 + O_2 \rightarrow Mn^{2+} + 2HSO_4^-.\end{aligned}$$

Termination:

$$SO_5^{\bullet-} + \text{organic substance} \rightarrow \text{inactive products}.$$

From the above analysis, we can find that the absorption process for SO_2 containing Mn (II) is a complicated manganese-catalysed autoxidation, in which O_2 has the effect of initiation and propagation.

4.3. *Experimental verification*

To test the above-mentioned conclusion, the presence of sulphur dioxide in the liquid phase is determined in the purification experiment with Mn (II) + DMSO as absorbent at 294.15 K, in which, the mole fraction of sulphur dioxide in the form of molecular state is 0.1016 and in the form of H_2SO_4 state is 0.1113. This is the direct evidence that physical and chemical absorptions coexist.

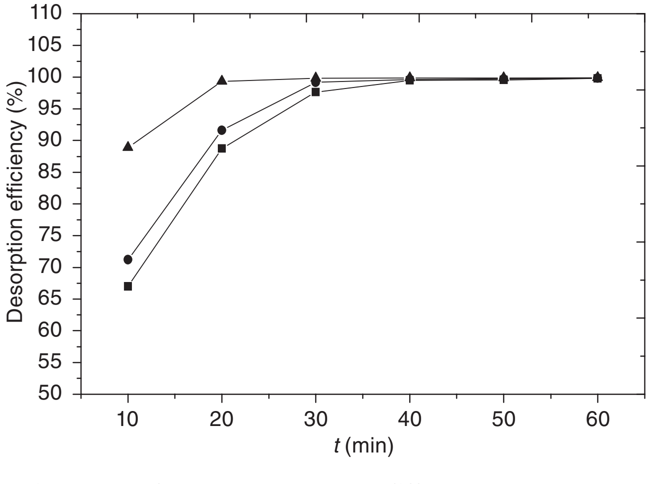

Figure 6. Desorption curve of DMSO + Mn (II) at different temperatures.
Notes: ■, 333.15 K; ●, 343.15 K; ▲, 353.15 K.

The physical absorption of sulphur dioxide in the form of molecular state has good desorption efficiency and the desorption result of DMSO + Mn (II) is shown in Table 3 and Figure 6.

Figure 6 shows that the desorption of DMSO + Mn (II) is influenced by the temperature. The higher the temperature, the higher the desorption efficiency. When the desorption time is near 60 min, the desorption efficiencies at different temperatures are all over 99%, so the absorbent of DMSO + Mn (II) has good desorption efficiency at a lower temperature.

5. Conclusions

The desulphurised experiment of an organic solvent of DMSO mixed with a relatively small amount of catalyst is studied. By theoretical analysis and experimental verification, the results show that the absorption process for SO_2 containing DMSO + Mn (II) is a complicated mechanism coexisting of physical and chemical absorptions.

The synergistic effect of Mn (II) in the sulphite-induced autoxidation of metal ions is investigated. The results indicate that Mn (II) has a significant catalytic effect and it is suggested that metal ions can oxidise Mn (II) to Mn (III) under the selected experimental conditions, which rapidly oxidises sulphite to SO_3 radicals to initiate the catalytic cycle. The results of this study are of direct importance to account for the synergistic effects observed in metal-catalysed autoxidation reactions of sulphur (IV)-oxides.

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