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HPA-BASED NEW LIQUID REDOX ABSORBENT SYSTEM FOR FLUE GAS TREATMENT

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Abstract

Using HPA (heteropoly acid), namely $Na_2HPMo_{12}O_{40}$, as absorbent in form of aqueous solution, a promising resolution to SO_2 containing gas purification was developed. In this study, experiments were conducted concerning the additive effect for maximizing the desulfurization efficiency of HPA absorbent system and the performance of absorbent regeneration. As a consequence, all additives including NaCl, H_3PO_4, $MnSO_4$, $CuSO_4$, $ZnSO_4$ and NH_4VO_3 were found to have positive effects on the improvement of the desulfurization efficiency of HPA solution. Among them, the effect of NaCl is the most significant. The following two couples i.e. NaCl vs H_3PO_4 and Zn^{2+} vs Mn^{2+}, were found to have interactions. Based on orthogonal experiments, the optimum additive/HPA molar ratio in multi-component absorbent system was gained. The process of HPA regeneration by air stream is strongly influenced by operation temperature, whereby the optimum regeneration temperature was found to be ca. 51°C. The desulfurization efficiency of single HPA shows excellent reproducibility during long time operation of 6 absorption-regeneration cycles. The resultant solution of single HPA after desulfurization can also be effectively regenerated by gas stream containing NOx, which shows better effect than that by air stream.

Key words: flue gas desulfurization, heteropoly acid, redox absorbent

1 Introduction

SO_2 is a main gaseous pollutant in the flue gases emitted from factories of various processes, and its treatment is an important step in controlling and preventing atmospheric pollution. The conventional methods for SO_2 removal include dry adsorption method and wet absorption method[1]. At present, dry method has not been widely used due to its limited sulfur loading capacity, most desulfurization processes industrialized are wet absorption methods, especially the wet $Ca(OH)_2$ slurry absorption methods with different modifications. The wet $Ca(OH)_2$ slurry absorption method is quite effective for SO_2 removal, but the solid waste disposal and the high capital investment and expensive operation cost of this method is still an unresolved problem, which has already confined its application. A new approach to flue gas desulfurization was developed using the aqueous solutions of heteropoly acid (HPA) as absorbent[2,3]. The HPAs investigated can easily gain one or more electrons when reacting with SO_2, oxidizing SO_2 to H_2SO_4 and making themselves changed into the reduction forms accordingly. The resultant HPAs may be changed reversibly to their original form in the presence of air by losing the electrons gained to oxygen. Hence, a circulating process of SO_2 conversion with HPAs can be formed in the presence of air. This is the basic principle of the new process for SO_2 removal, where the desulfurization effect is based on the redox property of HPA.

Compared to the wet $Ca(OH)_2$ slurry absorption methods for SO_2 removal, no secondary pollutant arises in the new process with HPA, the absorbent can be regenerated rather than be used only once. Hence, the new process for SO_2 removal deserves systematic investigations so as to provide basic proof for further application.

In the past years, however, HPA has long been used mainly to act as catalyst for organic material synthesis or reagent for chemical analysis, few report has been given on the new application of HPA in gaseous pollutant control. Most HPAs are quite chemically stable, it would be of great importance to harness the redox property of HPA to develop new technique in the field of gas purification and air pollution control. In light of the method developed previously for SO_2 removal[2,3], a further study was made concerning the performance of the new absorbent system comprising HPA and one or more additives, additive interactions and absorbent regeneration, which will be discussed in this paper.

2 Materials and Methods

Scheme of the experiment flow sheet is shown in Fig. **1**. A multiorifice plate glass gas-scrubber containing the absorbent solution was used to investigate the performance of the absorbent system. The experimental data gained are the SO_2 and NO_x concentrations in the feed gas and outlet gas stream. The HPA investigated in this study, namely $Na_2HPMo_{12}O_{40}$, was commercially available, and of reagent grade. The feed gas stream with constant SO_2 concentration, flowing at the rate of 0.5L/min, was prepared by mixing two gas streams of dilute SO_2 and pure nitrogen after passing through mass flow controller and rotameter, respectively. The resultant absorbent solution after desulfurization can be regenerated by an air stream or the mixed gas stream from NO_x and N_2. The SO_2 concentration was analyzed with a Dioxor II SO_2 detector. The NO_x concentration was analyzed by colorimetry. All chemicals used were of reagent grade and deionized water was used throughout.

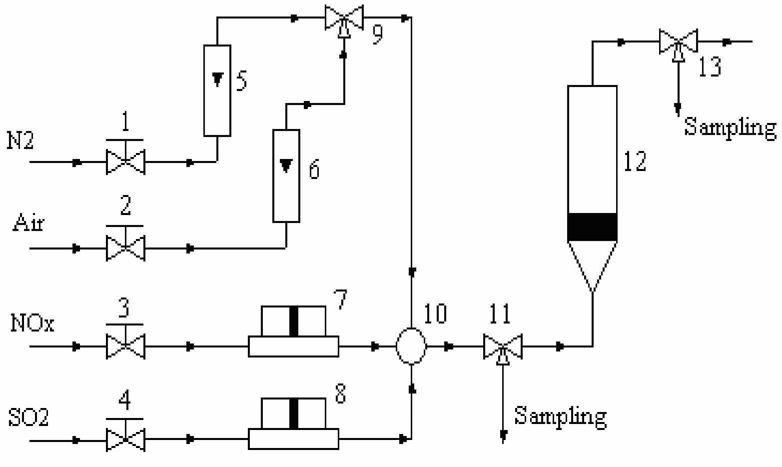

Figure 1. Scheme of the experimental flow sheet

1, 2, 3, 4 Relief valve 5, 6 Rotameter 7, 8 Mass flow controller 9, 11, 13 Three-way valve,10 Gas mixer ,12 Hole-plate gas scrubber (hole diameter: 50~70μm)

3 Results and Discussion

3.1 The enhancement effects on desulfurization by additives

3.1.1 Effects of single additives

Additives having positive effect on the desulfurization performance of HPA solution were found. These additives include NaCl, H_3PO_4, $MnSO_4$, $CuSO_4$, $ZnSO_4$ and NH_4VO_3. The experiment results are listed in Table **1**. It is evident that, for all additives investigated, two different types of dosage-effectiveness relation exist. One of them, manifested in H_3PO_4, $CuSO_4$ and NH_4VO_3, is the so-called cumulative effect, where the enhancement effect of additive on desulfurization efficiency of HPA solution increases with the increase of additive dosage. The other, with an optimum additive dosage corresponding to the maximum desulfurization efficiency, is embodied in NaCl, $MnSO_4$ and $ZnSO_4$. It appears that all of H_3PO_4, $CuSO_4$ and NH_4VO_3 can make the SO_2 removal efficiency of HPA solution approach asymptotic value as the additive/HPA molar ratio exceeds 1/2. As to the effect of NaCl, $MnSO_4$ and $ZnSO_4$, the optimum additive/HPA molar ratios for the first one and the last two could be found to be 1/4 and 1/8 respectively.

To illustrate the enhancement effects of the additives, the following mechanisms were proposed: The effects of $CuSO_4$, NaCl, $MnSO_4$ and $ZnSO_4$ lie in the cations they possess, this has been proved by contrast experiments using the same salts with different anions. Hence, if we let Me^{n+} (n=1,2) represent any of the cation in these salts, what happens during the process of desulfurization can then be expressed as:

$$Me^{n+}+SO_2+2H_2O+Na_2HPMo(VI)_{12}O_{40}\rightarrow nNa^{+}+H_2SO_4+Na_{2-n}H_3MePMo(VI)_{10}Mo(V)_2O_{40}$$

Table 1. The effect of single additives on SO_2 removal efficiency of HPA

Additive	Molar ratio of additive to HPA & SO_2 removal efficiency (%)*			
	0	1/8	1/4	1/2
H_3PO_4	95.5	97.6	98.2	98.5
$CuSO_4$	95.5	97.6	97.9	97.9
NH_4VO_3	95.5	97.3	97.9	98.2
NaCl	95.5	95.7	97.3	96.1
$MnSO_4$	95.5	98.2	95.8	95.8
$ZnSO_4$	95.5	98.1	97.6	96.2

* $[SO_2]_{in}$=985.40mg/m^3, [HPA]=1.2×10^{-4}mol/L, G=0.5L/min, V=100mL, T=28 ^{o}C, absorption time: 20min.

In contrast, in the absence of saline additives, the following reaction occurs:

$$SO_2+2H_2O+Na_2HPMo(VI)_{12}O_{40}\rightarrow H_2SO_4+Na_2H_3PMo(VI)_{10}Mo(V)_2O_{40}$$

It should be noted that $Na_2H_3PMo(VI)_{10}Mo(V)_2O_{40}$ is a strong acid, maybe stronger than that of common mineral acids. Hence, the acidity of the solution is predominated by HPA. In this case, as the chemical absorption proceeds, the acidity of the resulting solution will be increased, which is unfavorable to the subsequent absorption. That is why the chemical absorption is relatively slow if no saline additive is added.

Compared to $Na_2H_3PMo(VI)_{10}Mo(V)_2O_{40}$, the acidity of the resultant HPA in the presence of saline additives, viz. $Na_{2-n}H_3MePMo(VI)_{10}Mo(V)_2O_{40}$, is lower. As a consequence, the decrease of pH value during the reaction is retarded in the presence of saline additives. Hence, the absorption process was improved in the presence of saline additive.

The effect of H_3PO_4 may arise from the improvement of the redox property of HPA solution, which overwhelms the negative effect of acidity herein.

The effect of NH_4VO_3 is due to the following reaction:

$$H_2O + 2SO_2 + 4NH_4VO_3 \rightarrow (NH_4)_2V_4O_9 + H_2SO_4 + (NH_4)_2SO_4$$

3.1.2 Contrast contribution of additives and multi-component system optimization

In view of the foregoing positive effects of the additives, precursory experiments were conducted to determine if additive interactions exist so as to provide basic understanding for absorbent system optimization. After many experiments concerning all the possible additive combinations, the following two couples, i.e. NaCl vs H_3PO_4 and $ZnSO_4$ vs $MnSO_4$, were found to have interactions (Fig.**2** and Fig.**3**). The common characteristic that could be found in Fig.**2** and Fig.**3** is that, concerning the effect of one additive (i.e. NaCl in Fig.**2** or $ZnSO_4$ in Fig.**3**), you can’t simply tell which dosage is optimal without considering the effect of the other additive. This phenomenon reflects the fact that, besides working independently, the two additives may work together. That is what the interaction refers to. Taking Fig.**2** as an example, a turning point with a H_3PO_4 dosage of 1.35ml can be found. When the dosage of H_3PO_4 is below 1.35ml, the optimal dosage for NaCl is 0.6ml; when the dosage of H_3PO_4 exceeds 1.35ml, the optimal dosage for NaCl is 1.5ml. Apparently, within the dosage range of H_3PO_4 used, the interaction between NaCl and H_3PO_4 is not remarkable and can be ignored. Similar case can be found in the interaction between $ZnSO_4$ and $MnSO_4$ (Fig.**2**).

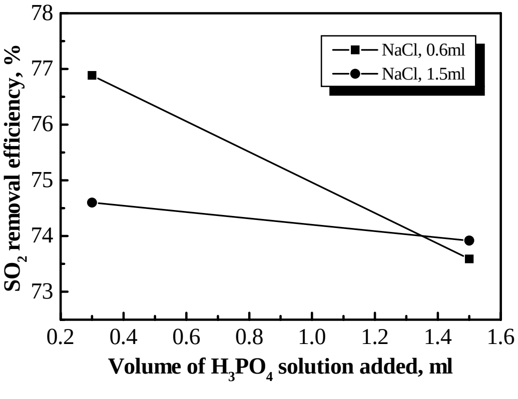

Figure 2. The interactions between NaCl and H_3PO_4

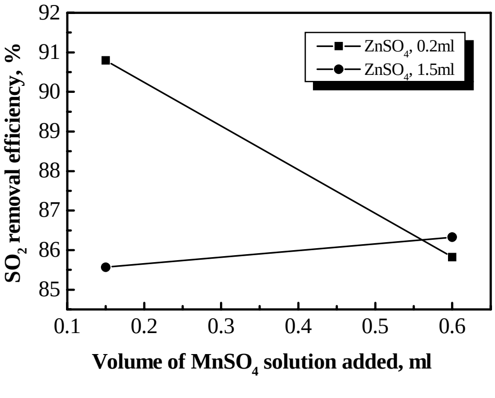

Figure 3. The interactions between $ZnSO_4$ and $MnSO_4$

[HPA]=1.2×10^{-4}mol/l, $[SO_2]_{in}$=1858.1mg/m^3, G=0.5l/min, T=31°C, V=100ml, absorption time: 20min. Concentration of all additive solutions: 5.0×10^{-3}mol/l

With an aim to obtain an optimized multi-component absorbent system, further experiments were conducted according to the orthogonal layout. The experiments were conducted under conditions as follows: $[SO_2]_{in}$=714.6mg/m^3, [HPA]=1.2×10^{-4}mol/L, G=0.5L/min, V=100ml, T=28^{o}C, absorption time: 50min.. The dosages of H_3PO_4 and $MnSO_4$ were set to be within the range where the additive interactions are negligible. The SO_2 removal efficiency after absorption for 50minutes was chosen to be the evaluation parameter. The experiment results are listed in Table **2**.

Table 2. The experimental results based on orthogonal layout

No.	Factors investigated (the molar ratios of additives to HPA)						SO_2 removal efficiency at t=50min, %
	NaCl /HPA	H_3PO_4 /HPA	$ZnSO_4$ /HPA	$MnSO_4$ /HPA	NH_4VO_3 /HPA	$CuSO_4$ /HPA	
1	0	0	0	0	0	0	73.41
2	0	1/8	1/12	1/16	1/8	1/8	68.36
3	0	1/4	1/6	1/8	1/4	1/4	82.10
4	0	1/2	1/4	3/16	1/2	1/2	70.97
5	0	5/8	1/3	1/4	5/8	5/8	81.57
6	1/12	5/8	1/12	1/8	1/2	0	82.97
7	1/12	0	1/6	3/16	5/8	1/8	78.97
8	1/12	1/8	1/4	1/4	0	1/4	74.27
9	1/12	1/4	1/3	0	1/8	1/2	76.01
10	1/12	1/2	0	1/16	1/4	5/8	80.01
11	1/6	1/2	1/6	1/4	1/8	0	73.41
12	1/6	5/8	1/4	0	1/4	1/8	66.28
13	1/6	0	1/3	1/16	1/2	1/4	65.41
14	1/6	1/8	0	1/8	5/8	1/2	62.80
15	1/6	1/4	1/12	3/16	0	5/8	65.58
16	1/4	1/4	1/4	1/16	5/8	0	69.93
17	1/4	1/2	1/3	1/8	0	1/8	76.88
18	1/4	5/8	0	3/16	1/8	1/4	77.06
19	1/4	0	1/12	1/4	1/4	1/2	73.75
20	1/4	1/8	1/6	0	1/2	5/8	73.93
21	1/3	1/8	1/3	3/16	1/4	0	74.27
22	1/3	1/4	0	1/4	1/2	1/8	81.75
23	1/3	1/2	1/12	0	5/8	1/4	82.97
24	1/3	5/8	1/6	1/16	0	1/2	73.41
25	1/3	0	1/4	1/8	1/8	5/8	77.05

Based on the range analysis of the influences of the six factors in Table **2**, the effects of the six additives on the absorbent system were determined to decrease in turn as follows: NaCl>H_3PO_4>$MnSO_4$>$CuSO_4$>$ZnSO_4$>NH_4VO_3. The optimum additive/HPA molar ratio in multi-component system comprising all additives was determined to be: NaCl/HPA: H_3PO_4/HPA: $ZnSO_4$/HPA: $MnSO_4$/HPA: NH_4VO_3/HPA: $CuSO_4$/HPA=1/12: 1/4: 1/6: 1/4: 1/4: 1/2.

3.2 Absorbent regeneration

3.2.1 Effect of temperature

The process of HPA regeneration by air stream is strongly influenced by operation temperature (Fig.**4**), whereby the optimum operation temperature was found to be ca. 51^{o}C. In nature, the regeneration process is a gas-liquid reaction subjecting to the influence of mass-transfer. From the viewpoint of chemical reaction, the increase of regeneration temperature can facilitate the chemical reaction and thus may improve the overall process when such contribution predominates. However, when the temperature for regeneration increases to a certain degree, the effect of mass-transfer may be remarkable. In this case, owing to the decrease of the solubility of oxygen in solution, the process of oxygen transfer from bulk air stream to solution may be retarded considerably and thus slows down the overall process.

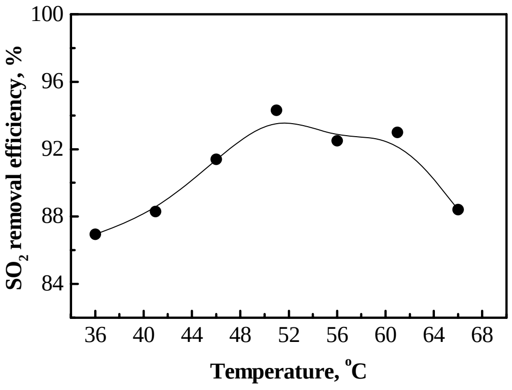

Figure 4. The influence of temperature on regeneration

Absorption: $[SO_2]_{in}$=1839.9mg/m^3, G=0.5l/min, T=28°C, [HPA]=1.2×10^{-3}mol/l, V=100ml, t =15 min
Regeneration: G_{air}=1.2 l/min, t = 45min

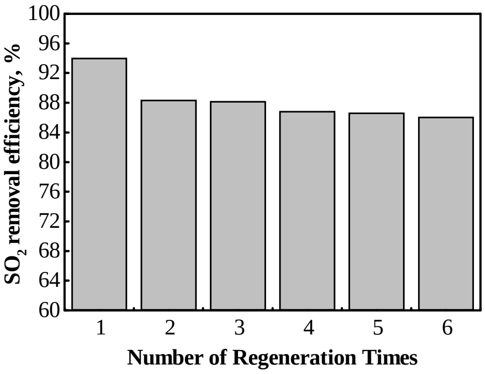

Figure 5. Reproducibility of the regeneration performance

Absorption: $[SO_2]_{in}$=1839.9mg/m^3, G=0.5l/min, T=28 °C, [HPA]=1.2×10^{-3}mol/l, V=100ml,
t =15 min. Regeneration: G_{air}=1.2 l/min, T=51 °C, t = 45min

3.2.2 Reproducibility of the regeneration performance

It is evident that the desulfurization efficiency of single HPA has excellent reproducibility during long time operation of 6 absorption-regeneration cycles (Fig. **5**). The resultant solution after the second time of regeneration maintains nearly the same desulfurization capability, with the SO_2 removal efficiency being around 87%.

3.2.3 Effectiveness of regeneration by NO_x

Table 3. Effect of HPA regeneration by NO_X

Regeneration time (min)	SO_2 removal efficiency, %
30	85.8 / (83.0*)
60	99.9 / (87.3*)
120	99.9 / (87.8*)

*Contrast result of regeneration by air.

As NO_x is another gaseous pollutant in the flus gases, the effectiveness of NO_x on HPA regeneration was investigated to determine the feasibility of simultaneous removal of SO_2 and NO_x. The experiment conditions for SO_2 removal is: $[SO_2]_{in}$=1839.87mg/m^3, G=0.5l/min, T=24°C, [HPA]=1.2×10^{-3}mol/l, V=100ml, absorption time: 15min. The HPA solution after desulfurization was regenerated at 24°C in the same reactor by NO_x- enriched nitrogen gas stream, containing 1237.09 mg/m^3 of NO_x, flowing at the rate of 0.75L/min. From the results shown in Table 3, it is evident that, besides air/O_2, NO_x is also an effective oxidant for HPA regeneration. Moreover, the process of simultaneous removal of SO_2 and NO_x is also proved to be feasible. The role of NO_x can be illustrated by the reactions proposed in the previous study [3]. Compared to air/O_2, the effect of NO_x is much better (Table **3**).

As a whole, HPA-based absorbent is hopeful in the application of flue gas treatment.

4 Acknowledgements

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