Adsorb-Catalytic Removal of PH$_3$ and H$_2$S in Yellow Phosphorus Off-Gas by Metallic Modified Activated Carbon

Rui Li$^{1,a}$, Botao Wang$^{1,b}$, Mei Yao$^{1,c}$, Fang Wang$^{1,d}$, Tiancheng Liu$^{1,e}$, Chenhui Liu$^{1,f}$, Jiyun Gao$^{1,g}$, Ping Ning$^{2,h}$ and Lijuan Jia$^{1,*}$

$^1$School of Chemistry and Environment, Yunnan Minzu University, Kunming 650500, Yunnan, P. R. China
$^2$Faculty of Environment Science and Engineering, Kunming University of Science and Technology, Kunming 650093, Yunnan, P. R. China

*Corresponding author e-mail: LeegyerKM@163.com, $^a$2965655279@qq.com, $^b$wangbotao0309@163.com, $^c$2020067110@qq.com, $^d$451077062@qq.com, $^e$liutiancheng76@163.com, $^f$591090347@qq.com, $^g$407048137@qq.com, $^h$Ningping86@163.com

Abstract. Activated carbon modified with Cu$^{2+}$ and Co$^{2+}$ was used to remove PH$_3$ and H$_2$S from yellow phosphorus off-gas. An orthogonal experiment was carried out to identify the superiority order of influencing factors and the optimal experimental parameters. For PH$_3$, the superiority order was temperature $>$ oxygen content $>$ parch temperature $>$ impregnant concentration (Cu$^{2+}$) $>$ flow rate $>$ diameter, whereas, for H$_2$S, it was reaction temperature $>$ oxygen content $>$ impregnant concentration $>$ parch temperature $>$ diameter $>$ flow rate. Following were the optimal experimental parameters for both PH$_3$ and H$_2$S: reaction temperature, 95°C; impregnant concentration (Cu$^{2+}$), 0.25 mol/L; diameter of metallic modified activated carbon (MMAC), 3.5 mm; oxygen content, 1%; parch temperature, 300°C; and flow rate, 0.4 L/min. Regeneration of MMAC was effective for PH$_3$ but not compelling for H$_2$S. The activation energy and reaction orders were calculated, and the transmission process was evaluated to assess the characteristics of the dynamics of the adsorb-catalytic reaction. The reaction orders were -0.8 and -0.76 for PH$_3$ and H$_2$S and the average activation energies were 1247.6 and 134.4 J/mol for PH$_3$ and H$_2$S, respectively. The adsorb-catalytic reaction was fast, and decreasing transmission resistance can play a key role in improving the performance of MMAC.

1. Introduction

A substantial amount of off-gas containing ample carbon monoxide (CO) is produced during the production of yellow phosphorus. It could be used as raw material in the mono-carbon chemical industry for the production of methane (CH$_4$), methanol (CH$_3$OH), and other valuable products. Ning Ping [1] reported that 3000 Nm$^3$ of off-gas can be produced during production per ton of manufactured yellow phosphorus. There are many ingredients in the off-gas of yellow phosphorus, among which is CO representing 85% to 95% (V/V) with some impurities, such as dust, phosphorus, and sulfur. The impurity of phosphorus exists mainly in the form of hydrogen phosphide (PH$_3$) and phosphorus...
molecules (P₄), and sulfur in form of hydrogen sulfide (H₂S) [2]. Because of the toxic effects of these impurities on catalysts in the chemical industry and on human health [3], purification methods should be developed for the further utilization of yellow phosphorus off-gas.

Adsorption is a common and effective method for the removal of PH₃ and H₂S. Teresa and her colleague demonstrated that a more acidic environment promoted the formation of sulfur oxides and sulfuric acid, despite yielding small H₂S removal capacities, while a basic environment favored the formation of elemental sulfur (sulfur radicals) and yielded high capacities in several cases on virgin AC [4-7]. Tsai evaluated the H₂S adsorption capacity on alkaline impregnated AC and showed that it was five times that of a corresponding fresh AC [8]. Magnetron sputtering and electron-beam evaporation techniques were used by Alexeeva to impregnate Mo, W, Ni, Ti, and Cu on carbon fiber to improve its thermal and chemical stability for adsorption-catalytic removal of H₂S [9]. Junji found that toluene and ethanol could compete with H₂S for adsorption on AC [10]. With X-ray photoelectron photoemission spectroscopy, Dudzik and Shimomura reported that H₂S, in the form of molecules, was combined with surface atoms on semiconductors [11, 12]. Also, there were some reports that H₂S adsorption occurred on adsorbent of solid base [13, 14] and zinc titanate [15]. Gonchshrova et al. investigated PH₃ adsorption on Cu and concluded that PH₃ adsorption at a low temperature produced a molecular overlayer structure with short-range order, while annealing resulted in decomposition but not desorption of the adsorbed PH₃ [16].

In this investigation of the adsorb-catalytic removal of PH₃ and H₂S from the off-gas of yellow phosphorus, the following results were obtained. First, the superiority order of the influencing factors, the relative optimal parameters of the adsorb-catalytic reaction, and the regeneration effect of metallic modified activated carbon (MMAC) were identified. Then, some characteristics of dynamics were found through calculation of the activation energy and reaction order and through transmission analysis.

2. Experiment

2.1. Preparation of MMAC

The raw material was industry 4# AC, whose basic properties are partly listed in Table 1. First, approximately 20 g of AC with a certain diameter was washed three times in distilled water. Then, it was dipped into a 100-mL solution of 0.1mol/L Co²⁺ and Cu²⁺ with a certain concentration for 24h. Next, it was dried at 110°C for 15h. Finally, it was parched in a muffle at a certain temperature for 6h to get the MMAC.

| εp /cm³·g⁻¹ | pB/g·L⁻¹ | q/mm | s/m²·g⁻¹ | Ads.cap. of iodine /mg·g⁻¹ | Intens./kg·cm²⁻² |
|-------------|----------|------|----------|---------------------------|-----------------|
| 0.7         | 450~550  | 3.5±0.5 | >800     | >900                      | >7              |

2.2. Adsorb-catalytic experiments

Fig 1 presents a schematic flow chart of the adsorb-catalytic experiments. PH₃ and H₂S were provided through a steel cylinder with N₂ as the carrier to simulate the off-gas of yellow phosphorus. First, PH₃ and H₂S were mixed with air in a blender at a certain flow rate; then, with an approximate concentration of 1000-mg/m³ PH₃ and 1000-mg/m³ H₂S, these gases flowed through an adsorber in which there was a certain amount of MMAC, and the adsorb-catalytic reaction occurred. Finally, it was discharged into the air after determination of the PH₃ and H₂S concentration through gas chromatography (GC-14C), and the residual PH₃ and H₂S were absorbed with a solution of CuSO₄. With the concentration of PH₃ and H₂S, Equation (1) was used to calculate the PH₃ and H₂S capacity of MMAC.

\[ q = \left( Q_{C_i} - Q \int_0^t C_i dt \right) / m \]
The regeneration of MMAC was as follows. First, hot air was used to oxidize the remnant, if any, sulfur or phosphorus into their oxides for 2h; then, sulfur and phosphorus oxides were respectively regenerated by NH$_3$ and (NH$_4$)$_2$S solution in a container vibrated for 3h at 30℃. Finally, after activation through water steam for 30min, regenerated MMAC was acquired by drying at 110℃ for 6h.

3. Results and discussion

3.1. Adsorb-catalysis

An orthogonal experiment was carried out to identify the adsorb-catalytic performance of MMAC. The experimental design, experimental result, and orthogonal analysis are respectively presented in Table 2, Table 3, Table 4, and Table 5. According to the values of range in Table 4 and Table 5, the superiority orders of the influencing factors of the adsorb-catalytic reaction for PH$_3$ and H$_2$S were, respectively, reaction temperature > oxygen content > parch temperature > impregnant concentration (Cu$^{2+}$) > flow rate > diameter and reaction temperature > oxygen content > impregnant concentration > parch temperature > diameter > flow rate. Furthermore, for both PH$_3$ and H$_2$S, within the experimental range, the optimal adsorb-catalytic reaction parameters were: reaction temperature, 95℃; impregnant concentration (Cu$^{2+}$), 0.25mol/L; diameter of MMAC, 3.5mm; oxygen content, 1%; parch temperature, 300℃; and flow rate, 0.4L/min.

![Figure 1. Schematic flow chart of experiment.](image)

| Factor               | Rec.Temp./℃ | Impreg.Conc./mol.L$^{-1}$ | Diameter/mm | Oxy.Cont./vol% | Parch Temp./℃ | Flow Rate/L.min$^{-1}$ |
|----------------------|-------------|---------------------------|-------------|----------------|---------------|------------------------|
| Level 1              | 20          | 0.05                      | 0.25        | 0.5            | 300           | 0.2                    |
| Level 2              | 40          | 0.1                       | 0.5         | 1              | 350           | 0.3                    |
| Level 3              | 60          | 0.2                       | 1           | 2              | 400           | 0.4                    |
| Level 4              | 80          | 0.25                      | 3.5         | 3              | 450           | 0.5                    |
| Level 5              | 95          | 0.3                       | 5           | 3.5            | 500           | 0.6                    |

Table 3 Adsorb capacity of PH$_3$ and H$_2$S on MMAC.

| Experim     | PH$_3$ | H$_2$S |
|-------------|--------|--------|
| Work Station|        |        |
Table 4. Orthogonal analysis of PH$_3$ (mg.g$^{-1}$).

| Factor   | Rec.Temp. | Impreg.Conc. | Diameter | Oxy.Cont. | Parch.Temp. | Flow Rate |
|----------|-----------|---------------|----------|-----------|-------------|-----------|
| Aver.Cap. 1 | 3.656     | 11.916        | 5.046    | 3.214     | 14.817      | 7.320     |
| Aver.Cap. 2 | 4.235     | 5.569         | 9.064    | 14.167    | 7.413       | 7.110     |
| Aver.Cap. 3 | 9.205     | 3.688         | 9.612    | 7.959     | 7.085       | 12.954    |
| Aver.Cap. 4 | 9.212     | 9.784         | 11.606   | 11.409    | 5.322       | 5.442     |
| Aver.Cap. 5 | 16.876    | 12.227        | 7.856    | 6.434     | 8.547       | 9.189     |
| R         | 13.220    | 8.53          | 11.38    | 17.43     | 7.36        | 9.94      |

3.2. Regeneration
A comparison of the adsorb-catalytic effects between fresh MMAC (Number 2 in Table 3) and regenerated MMAC is displayed in Fig. 2. In Fig. 2, the breakthrough time for PH$_3$ did not shorten obviously, and it even was prolonged a little, whereas that of H$_2$S shortened dramatically. It is clear that the regeneration process was effective for PH$_3$ while not compelling for H$_2$S. S (from (NH$_4$)$_2$S) deposition on the surface of MMAC during regeneration was the main reason for the unsuccessful regeneration of H$_2$S.

Table 5. Orthogonal analysis of H$_2$S (mg.g$^{-1}$).

| Factor   | Rec.Temp. | Impreg.Conc. | Diameter | Oxy.Cont. | Parch.Temp. | Flow Rate |
|----------|-----------|---------------|----------|-----------|-------------|-----------|
| Aver.Cap. 1 | 4.213     | 10.489        | 5.601    | 3.764     | 12.474      | 7.025     |
| Aver.Cap. 2 | 4.631     | 6.039         | 8.358    | 12.361    | 6.838       | 6.509     |
| Aver.Cap. 3 | 8.528     | 4.152         | 8.858    | 8.072     | 7.280       | 10.948    |
| Aver.Cap. 4 | 8.513     | 9.641         | 10.493   | 10.195    | 6.693       | 6.745     |
| Aver.Cap. 5 | 15.325    | 10.891        | 7.901    | 6.820     | 7.926       | 9.097     |
| R         | 11.112    | 6.739         | 4.892    | 8.597     | 5.781       | 4.439     |

3.3. Activation energy
For the calculation of the average adsorb-catalytic activation energy, first, it was assumed that the reaction rate was closely related to the adsorb capacities of PH$_3$ and H$_2$S on MMAC. This is
demonstrated through Equations (2) and (3). Then, with Equations (2) and (3), one can obtain the rate constant \( k \) of different temperatures and reaction order \( n \) through relevant calculation, and this is shown in Fig. 3. Finally, through the Arrhenius equation and its derivative, as shown by Equations (4) and (5), one can acquire the average adsorb-catalytic activation energy, as shown in Fig. 4. According to the calculation, the reaction orders were -0.8 and -0.76 for \( \text{PH}_3 \) and \( \text{H}_2\text{S} \), respectively. The average activation energies were 1247.6 and 134.4 J/mol for \( \text{PH}_3 \) and \( \text{H}_2\text{S} \), respectively. For the lower value of average activation energy, the adsorb-catalytic rate was very fast for \( \text{PH}_3 \) or \( \text{H}_2\text{S} \) [17].

\[
\frac{dq}{dt} = k q^n \tag{2}
\]

\[
\ln r = \ln k + n \ln q \tag{3}
\]

\[
K = K_0 \exp \left( \frac{E}{RT} \right) \tag{4}
\]

\[
\ln K = \ln K_0 - \left( \frac{E}{RT} \right) \frac{1}{T} \tag{5}
\]

**Figure 2.** Comparison of adsorb-catalytic effects between fresh MMAC and regenerated MMAC.

**Figure 3.** Dynamics curve of \( \text{PH}_3 \) and \( \text{H}_2\text{S} \).
3.4. Transmission
Markedly with the increase of diameter and increased obviously with the increase of flow rate.

![Figure 4](image)

**Figure 4.** Resolving curve of activation energy of PH₃ and H₂S.

3.4. Transmission
Markedly with the increase of diameter and increased obviously with the increase of flow rate.

![Figure 5](image)

**Figure 5.** Influence of transmission on average reaction rate of MMAC.

4. Conclusion
(1) The superiority orders of influencing factors and optimal experimental parameters were identified through an orthogonal experiment.
(2) Regeneration of MMAC was effective for PH₃, but it was not compelling for H₂S.
(3) The characteristics of the dynamics of the adsorb-catalytic reaction were assessed through both the calculation of average activation energy and reaction orders and the evaluation of the transmission process.

**Nomenclature**

- $Q$: flow rate of off-gas, L/min
- $q$: adsorb capacity on base of H₂S or PH₃, mg/g
- $C$, $C_0$: outlet and initial concentration of H₂S or PH₃, mg/m³
- $r$: adsorb-catalytic reaction rate on base of H₂S or PH₃, mg/(g.min)
- $k$: constant of adsorb-catalytic reaction rate, unit related with the value of $n$
- $k_o$: transmission coefficient, mg/(g.min)
- $t$: time of adsorb-catalytic reaction, min
- $m$: weight of MMAC, g
- $T$: Temperature, K
\( n \) adsorb-catalytic reaction order
\( s \) specific area of MMAC, m\(^2\)/g
\( \varepsilon_p \) pore ratio of raw AC
\( \rho_B \) stack density of AC or MMAC, kg/m\(^3\)
\( \phi \) diameter of AC or MMAC, mm

Acknowledgments
This study was supported by the National Natural Science Foundation of China (51568067, 51568068), and the Applied Basic Research Fund Project of Yunnan Province (2016FB100, 2018FD053, 2018FD054).

References
[1] P.Ning, X.Wang, Bart.H.J, S.Tian, Y.Zhang, X.Q.Wang: Removal of Phosphorus and Sulfur from Yellow Phosphorus Off-Gas by Metal-modified Activated Carbon. J. of Cleaner Production, 19 (13), 1547-1552 (2011).
[2] H.Xiong, X.L.Yang, X.G.Li: Removal of Sulfur and Phosphorus from Tail Gas of In Yellow Phosphorus Production by Sodium Hypochlorite Oxidation Process. Environmental Protection of Chemical Industry, 22 (3), 161-164 (2002).
[3] Y.W.Wang, Q.Lin, P.Ning, C.Wang, X.Sun, K.Li: Preparation of Ce0.6-Cu60/Al40-[O] Catalyst and Role of CeO2/CuO In Simultaneous Removal of H2S and PH3.J.of the Taiwan Institute of Chemical Engineers, 87, 44-54 (2018).
[4] Andrey.B, Habibur.R, Teresa.J.B: Study of H2S Adsorption and Water Regeneration of Spent Coconut-Based Activated Carbon. Environmental Science & Technology, 34 (21), 4587-4592 (2000).
[5] Teresa.J.B: Effect of Pore Structure and Surface Chemistry of Virgin Activated Carbons on Removal of Hydrogen Sulfide. Carbon, 37 (3), 483-491 (1999).
[6] Teresa J.B: On the Adsorption/Oxidation of Hydrogen Sulfide on Activated Carbons at Ambient Temperatures. J. of Colloid and Interface Science, 246 (1), 1-20 (2002).
[7] Andrey.B, Habibur.R, Teresa: Wood-Based Activated Carbons as Adsorbents of Hydrogen Sulfide: A Study of Adsorption and Water Regeneration Processes. Industrial & Engineering Chemistry Research, 39 (10), 3849-3855 (2000).
[8] Tsai, J.H, Jeng.F.T, Chiang.H.L, Removal of H2S from Exhaust Gas by Use of Alkaline Activated Carbon, Adsorption, 7 (4), 357-366 (2001).
[9] Alexeeva.O.K, Klebanov.Y.D, Safonova.A.M, Sidorov.G.L: Preparation of Adsorption-Catalytic and Protective Coatings on Carbon Fibers Used for Hydrogen Purification. International Journal of Hydrogen Energy, 24 (24), 241-246 (1999).
[10] Masuda.J, Fukuyama.J, Fujii.S: Influence of Concurrent Substance on Removal of Hydrogen Sulfide on Activated Carbon, Chemosphere, 39 (10), 1611-1616 (1999).
[11] Shimomura.M, Moller.P.J, Nerlov.J, Christensen.S.V, Guo.Q, Ananda.N: Adsorption of H2S on InP (001) Studied by Photoemission Spectroscopy. Applied Surface Science, 121 (none), 237-240 (1997).
[12] Dudzik.E, C.Muller, McGovern.I.T, LloydD.R, Patchett.A, Zahn, D.R.T: H2S Adsorption on the (110) Surface of III-V Semiconductors. Surface Science, 34 (1-2), 1-10 (1995).
[13] Y.Duan, Y.Xiang, D.Xia: Removal of Hydrogen Sulfide from Light Oil with Solid Base. Fuel Processing Technology, 86 (3), 237-244 (2004).
[14] Y.F.Duan, D.Xia, Y.Z.Xiang, X, Zhang: Solid Base for Hydrogen Sulfide Removal In Light Oil.J. of Colloid and Interface Science, 281 (1), 197-200 (2005).
[15] Ozdemir.S, Bardakci.T: Hydrogen Sulfide Removal from Coal Gas by Zinc Titanate Sorbent. Separation and Purification Technology, 16 (3), 225-234 (1999).
[16] Goncharova.L.V, Clowes.S.K, Fogg.R.R, Ermakov.A.V, Hinch.B.J: Phosphine Adsorption and the Production of Phosphide Phases on Cu (001), Surface Science 515 (1), 553-566 (2002).
[17] Zhu B.C, Chemical Engineering, third ed. (Chemical Industry Press, 2002).