Removal of Hg^0 from Containing-SO_2/NO Flue Gas by Ultraviolet/H_2O_2 Process in a Novel Photochemical Reactor

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A novel photochemical spray reactor is first developed and is used to remove Hg^0 and simultaneously remove Hg^0/SO_2/NO from flue gas by ultraviolet (UV)/H_2O_2 process. The effects of several parameters (UV wavelength, UV power, H_2O_2 concentration, Hg^0 inlet concentration, solution temperature, liquid–gas ratio, solution pH, SO_2 concentration, NO concentration, and O_2 concentration) on removal of Hg^0 by UV/H_2O_2 process were investigated. Removal mechanism of Hg^0 is proposed and simultaneous removal of Hg^0, NO, and SO_2 is also studied. The results show that the parameters, UV wavelength, UV power, H_2O_2 concentration, liquid–gas ratio, solution pH, and O_2 concentration, have significant impact on removal of Hg^0. However, the parameters, Hg^0 inlet concentration, solution temperature, SO_2 concentration, and NO concentration, only have small effect on removal of Hg^0. Hg^{2+} is the final product of Hg^0 removal, and Hg^0 is mainly removed by oxidations of H_2O_2, $\cdot OH$, $\cdot O$, O_3, and photoexcitation of UV. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 2275–2285, 2014

Keywords: ultraviolet/H_2O_2, flue gas, photochemical spray reactor, Hg^0, simultaneous removal

Introduction

Mercury has received more and more attention due to its persistence, bioaccumulation, and neurological toxicity. Coal combustion is considered as the largest source of anthropogenic mercury emission. Studying effective flue gas Hg^0 removal methods has become one of the hot topics in the field of environmental protection.[1,2] Recently, in all flue gas mercury control methods, adsorption and wet scrubbing are considered as two of the most promising mercury removal technologies.[1,2] Many results show that using wet chemical oxidation technologies or wet flue gas desulfurization systems combining with oxidizing additives ($KMnO_4$, $K_2S_2O_8$, $NaClO_2$, NaClO, H_2O_2, Fenton, and chlorine dioxide)[3–8] and dry pretreatment oxidation technologies (catalytic oxidation, plasma oxidation, ozonation, photochemical oxidation, and photocatalytic oxidation)[9–13] can achieve the simultaneous removal of SO_2, NO_x, and mercury, which is considered as a promising technology. Unfortunately, however, so far some technical problems such as development and application costs, safety and reliability, and secondary pollution of reaction products, can not be effectively solved yet.[4]

In addition, some studies show that Hg^{2+} and Hg^0 can be adsorbed by activated carbon and then are converted to particulate mercury, which can be captured using existing dust equipments. However, despite activated carbon has excellent adsorption performance for Hg^{2+} and Hg^0, the high using cost hinders its large-scale applications.[1,2] The other new adsorbents such as metal oxides, precious metals, activated coke, fly ash, calcium-based materials, molecular sieves, and natural mineral materials have shown potential development prospects, but because of the deficiencies in adsorbent's stability and reliability and high cost, they are still unable to obtain practical applications.[1,2] In summary, many flue gas mercury removal technologies have been developed, but so far, none of them is suitable for large-scale applications yet.

Ultraviolet (UV)/H_2O_2 process has been widely studied in degrading organic pollutants from wastewater due to having extremely strong oxidation ability, simple and secure process, and environmental protection.[14] Recently, our previous results[15,16] show that UV/H_2O_2 process can simultaneously oxidize SO_2 and NO_x from flue gas into available sulfuric acid and nitric acid by wet scrubbing in a photochemical bubble column reactor. In these works, the related process parameters were optimized and the reaction mechanism and kinetics were also investigated.[15–19] However, yet till now, using UV/H_2O_2 process for the removal of Hg^0 from flue gas by wet scrubbing is not reported yet. If UV/H_2O_2 process can also effectively remove Hg^0 in flue gas, it is expected that it may eventually be developed into an effective simultaneous removal technology of SO_2, NO_x, and Hg.

In addition, it is noteworthy that in the previous results, all of the reaction processes were studied in a photochemical bubble column reactor. However, it is well known that the spray tower is the most widely used wet scrubber in the field of flue gas purification. Therefore, in this work, a novel photochemical spray reactor is developed for the first time and is used to remove Hg^0 and simultaneously remove Hg^0/SO_2/NO from flue gas by combining with UV/H_2O_2 process. The effects of some important parameters such as UV wavelength, UV power per unit solution, H_2O_2 concentration, Hg^0 concentration, solution temperature, liquid–gas ratio, solution

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pH, SO_2 concentration, NO concentration, and O_2 concentration on removal of Hg^0 by UV/H_2O_2 process were investigated. The chemical reaction mechanism of Hg^0 removal by UV/H_2O_2 process was also proposed. Furthermore, a pre-experiment for simultaneous removal of Hg^0, NO, and SO_2 by UV/H_2O_2 process was carried out preliminarily. The results will provide some theoretical guidance for the follow-up studies and the industrial applications of this technology.

Experimental Section

Experimental system

It can be seen in Figure 1, the experimental system consists of flue gas preparation system, measuring system, and photochemical spray reactor. Cylinder gases 1–5, including N_2, NO, SO_2, O_2, and N_2 (Purity, 99.99%), are used to make simulated flue gas and carrier gas. The mercury generator 20, including U-tube and mercury permeation tube (VICI Metronics), is used to produce Hg^0 vapor. The photochemical spray reactor consists of spray reactor 17, jacket heat exchanger 18, mercury thermometer 16, nozzle 22, quartz tube 24, UV lamp 23, and gas distributor 19. The spray reactor 17 (High, 38 cm; Inside diameter, 9.0 cm) is made by plexiglass. The gas distributor 19 is installed at 8 cm away from the bottom of spray reactor 17 to distribute gas. The nozzle 22 is installed at 15 cm away from the top of spray reactor 17 to spray H_2O_2 solution by combining with using solution circulating pump 25 and H_2O_2 solution reservoir 26. The UV lamp 23 is placed in the spray reactor 17 to provide light source. To avoid the interference of photochemical reaction in gas phase, the UV lamp above part of spray liquid level is covered by black light-absorbing material. Constant temperature water bath 21 (HH-42, Changzhou GuoHua Co., China) with a thermal water circulating pump 27 is used to control solution temperature. Solution temperature is measured by the mercury thermometer 16. Flue gas analyzer (FGA-4100, Fuoshan Fuofen Instrument Co., China; MRU-VARIO PLUS, Germany) and flue gas mercury analyzer 28 (QM201H, Suzhou Qingan Instrument Co., China) are used to determinate concentrations of SO_2, NO, O_2, and Hg^0, respectively.

Experimental procedures

Simulated flue gas was made by opening the cylinders 1–5 and the mercury generator 20. Flows of simulated flue gas and concentrations of gas components were regulated by the rotameters 6–11. Inlet concentrations of SO_2, NO, O_2, and Hg^0 were measured by the flue gas mercury analyzer and flue gas analyzer 28 through the gas bypass line. 600 mL of H_2O_2, H_2O_2/NaOH, and $H_2O_2/Ca(OH)_2$ solutions were prepared using 30% commercial H_2O_2 solution, NaOH, and $Ca(OH)_2$ reagents (Guoyao Chemical Reagent Co., AR, China), and deionized water. Solution pH was adjusted by adding HCl and NaOH and was measured by an acidimeter (Kedida instrument Co., CT-6023, China). Solution temperatures were adjusted to the required temperatures by the combination use of the constant temperature water bath 21 and the mercury thermometer 16.

When the solution temperature reached required value and kept stable, the value 15 was closed and the value 14 was opened. Then, simulated flue gas entered the photochemical spray reactor to make a gas–liquid reaction after the UV lamp 23 was turned on. Both of the power and the wavelength of UV lamp 23 can be adjusted by replacing UV lamps with different powers and wavelengths. The outlet concentrations of Hg^0, SO_2, O_2, and NO were measured using the flue gas mercury analyzer and flue gas analyzer 28. Each experimental run was kept for 60 min. The concentrations of Hg^0, SO_2, and NO in reactor outlet were recorded once every 10 min. The average concentrations within 60 min were used as outlet concentrations of Hg^0, SO_2, and NO. Additionally, to study the removal pathways of Hg^0, the concentrations of Hg^0 and total mercury in solutions were measured using a fluorescence mercury analyzer. The possible active intermediates, O_3 and ·OH, were also identified and captured by the mass spectrometry (MS) detector of liquid-MS (LC-MS) and the ozone test paper.

Analysis and measurement methods

Determination of ·OH Free Radical. The ·OH is very difficult to directly detect by instruments because of having high reactivity and short life span. Currently, the commonly

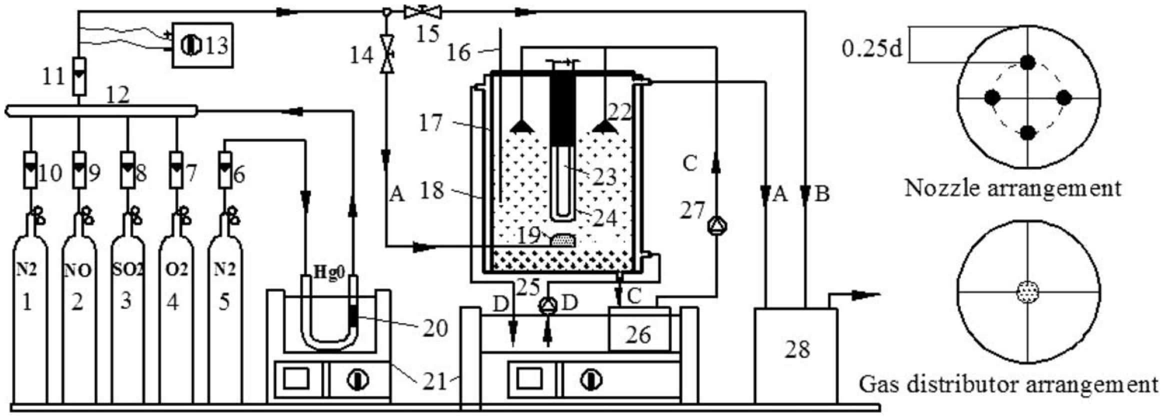
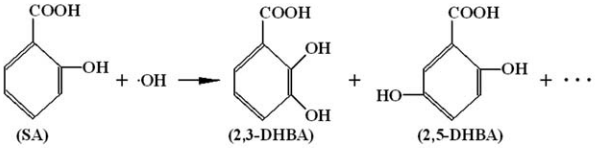


Figure 1. Schematic diagram of experimental system.

(1–5) N_2, NO, SO_2, O_2, and N_2 cylinders; (6–11) rotameters; (12) gas mixing tank; (13) electric heating thermostat (14–15) gas valves; (16) mercury thermometer; (17) spray reactor; (18) jacket heat exchanger; (19) gas distributor; (20) mercury generator; (21) constant temperature water bath; (22) nozzle (23) UV lamp; (24) quartz tube; (25) solution circulating pump; (26) H_2O_2 solution reservoir; (27) thermal water circulating pump; (28) flue gas analyzer and flue gas mercury analyzer; (A) gas main line (B) gas bypass line; (C) solution circulation loop (D) thermal water circulation loop; the right branch figure is the plan of nozzle and gas distributor in the spray reactor.

used method is adding capturing agent to react with ·OH to produce more stable intermediates, thereby indirectly detecting the presence of ·OH. In this, salicylic acid (SA) is used to capture ·OH by a hydroxylation reaction, which can produce more stable hydroxylated products, 2,3-DHBA and 2,5-DHBA. The 2,3-DHBA and 2,5-DHBA, with a relatively longer life than ·OH, can be determined by the MS detector of liquid-mass spectrometry (LC-MS). The related principles can be described by Eq. 1[19]



(1)

Determination of Hg^0 and Total Mercury Concentrations. When Hg^0 concentration in liquid phase was measured, 20-mL solution was transferred into a sealed reaction bottle, which was kept in a constant temperature water bath of 323 K without any pretreatments. Due to the high volatility of Hg^0 at above 303 K, the possible Hg^0 vapor would gasify and was directly blown into the fluorescence mercury analyzer by bubbling and carrying of N_2. However, unlike the Hg^0, when the concentration of total mercury was determined, to make possible solid mercury convert into soluble divalent mercury as completely as possible, 20-mL solution was first digested by adding 10% $H_2SO_4-10\%$ $KMnO_4$ solutions (mass fraction) in an Erlenmeyer flask and was heating in a constant temperature water bath of 353 K for 1 h. Before analysis, to reduce the redundant $KMnO_4$, several drops of hydroxylamine hydrochloride (mass fraction of 10%) were added into the Erlenmeyer flask until the color of solution turned clear. After holding for 10 min, 5 mL of the sample was transferred into the reaction bottle, and 1 mL $SnCl_2$ solution (mass fraction of 10%) was quickly added to reduce Hg^{2+} to Hg^0.[4,5] Then, the highly volatile Hg^0 vapor produced was carried by N_2 and flushed into the mercury analyzer to determine Hg^0 concentration.

Removal efficiency

The concentrations of Hg^0, SO_2, and NO measured by the bypass line are used as the inlet concentrations. The average concentrations within 60 min measured by the reactor outlet are used as the outlet concentrations. The removal efficiencies of Hg^0, SO_2, and NO in flue gas are calculated by the following Eq. 2

$$\mathrm{Hg}^0,\ \mathrm{SO}_2,\ \mathrm{NO\ removal\ efficiency} = \frac{C_{\mathrm{in}}-C_{\mathrm{out}}}{C_{\mathrm{in}}}\times 100(\%) \tag{2}$$

where C_{in} is the inlet concentration of Hg^0, SO_2, and NO in flue gas; C_{out} is the outlet concentration of Hg^0, SO_2, and NO in flue gas.

Results and Discussion

Effects of UV wavelength

UV wavelength often has a significant impact on photochemical reaction.[19] In this work, three most common UV wavelengths (185, 254, and 365 nm) are used to study the effects of UV wavelength on Hg^0 removal efficiency. Additionally, the visible light is also used to make a comparative experiment. All of the four lamps have the same shape, size, and power.

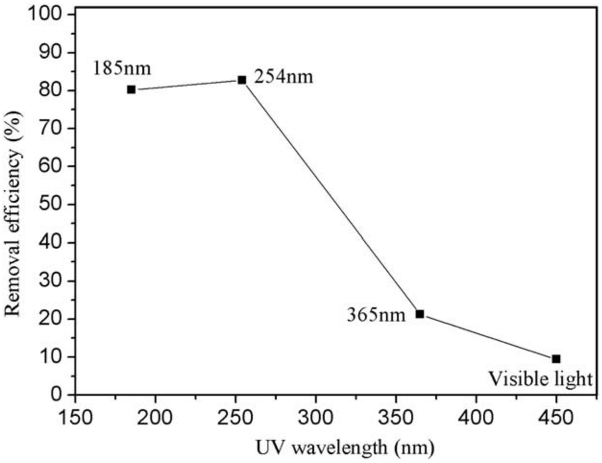


Figure 2. The effects of UV wavelength on Hg^0 removal efficiency.

Conditions: O_2 concentration, 6.0%; SO_2 concentration, 1500 ppm; NO concentration, 400 ppm; Hg^0 concentration, 30 μg/m^3; Liquid–gas ratio, 3.1; Solution temperature, 323 K; Solution pH, 3.97; H_2O_2 concentration, 0.50 mol/L; UV radiation power per unit solution, 0.0056 W/mL.

The effects of UV wavelengths on Hg^0 removal efficiency are studied and the results are shown in Figure 2. It can be seen that Hg^0 removal efficiency increases from 80.2 to 82.8% when wavelength increases from 185 to 254 nm, but reduces from 82.8 to 21.2% with the further increase of wavelength from 254 to 365 nm. In addition, comparing with the UV light, the visible light has almost no enhancement effect on the oxidation removal of Hg^0 by H_2O_2. The Hg^0 removal efficiency is only 9.8%, which is consistent with the removal efficiency of Hg^0 using single H_2O_2 oxidation.

There are two reasons to explain the experimental results. On the one hand, it is well known that the energy of UV photon can be calculated by the following Planck Eq. 3[20]

$$\varepsilon = h\nu = h\frac{c}{\lambda} \tag{3}$$

where ε-energy of photon, J; ν-UV frequency, 1/s; h-Planck constant, 6.626×10^{-34} J s; c-speed of light, 2.998×10^8 m/s; λ-UV wavelength, 100–380 nm.

From the Planck Eq. 3, it can be inferred that the shorter the UV wavelength, the bigger the UV photon energy, which can more fully destroy peroxide bond to produce more ·OH free radicals. However, the results[20] also show that the shorter the UV wavelength, the shorter the UV effective propagation distance. The effective propagation distance corresponds to the treatment capacity of pollutants in reactor, thus the shorter the UV effective propagation distance, the smaller the amount of pollutant treatment. So, synthetically considering the propagation distance and the photon energy, the 254 nm is the most effective UV wavelength in the photochemical reaction in this work, and achieves the highest Hg^0 removal efficiency. In addition, the results[12,13,21,22] of the other scholars also show that 254-nm UV light is highly effective in removing elemental mercury from various flue gases, and the longer wavelengths such as 365-nm UV light typically require a photocatalyst such as titanium oxide to capture mercury,[23] which are consistent with the present results in this work. Therefore, in the next works, the UV light of 254-nm wavelength is chosen as the excitation light source.

Effects of UV power per unit solution

As shown in Figure 3, Hg^0 removal efficiency is only 9.8% without UV radiation, showing that the oxidation capacity of H_2O_2 to Hg^0 is very limited in a spray reactor. When UV is added, the removal efficiency of Hg^0 greatly increases. When UV power per unit solution increases from 0 to 0.0056 W/mL, Hg^0 removal efficiency increases from 9.8 to 82.8%. But with the further increase of UV power per unit solution from 0.0056 to 0.0084 W/mL, the Hg^0 removal efficiency only slightly increases from 82.8 to 83.3%.

There are several reasons for explaining the above experimental results. For one thing, some results[10,12,15–19,22] show that under the radiation of UV, 1 mol of H_2O_2 can be decomposed and produce 2 mol of ·OH free radicals to oxidize Hg^0 according to the following Eqs. 4 and 5

$$H_2O_2+hv\xrightarrow{(\lambda<300\text{nm})}2\cdot OH \quad (4)$$

$$Hg^0+2\cdot OH \rightarrow Hg(OH)_2 \quad (5)$$

Additionally, several studies[12,21–26] have confirmed that under the radiation of UV with a less than 200- nm wavelength, O_2 can produce ·O free radicals and O_3 according to the following reactions (6) and (7) (In fact, during the experiment, the active substance O_3 has been identified using ozone test paper)

$$O_2+hv\xrightarrow{(\lambda<200\text{nm})}\cdot O+\cdot O \quad (6)$$

$$\cdot O+O_2 \rightarrow O_3 \quad (7)$$

Both of O_3 and ·O free radical have strong oxidizing property, and can oxidize and remove Hg^0 by the following reactions (8) and (9)[9,21–27]

$$Hg^0+O_3 \rightarrow HgO+O_2 \quad (8)$$

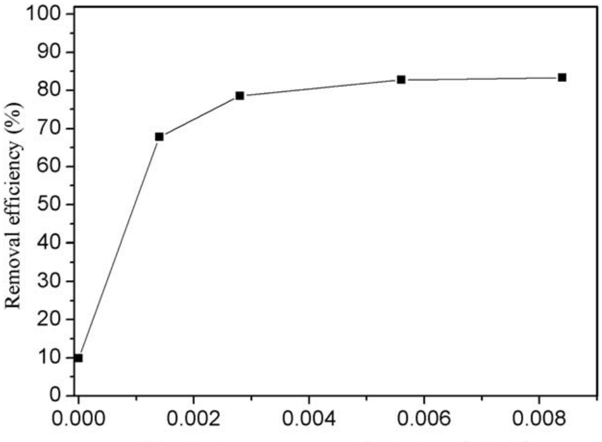


Figure 3. The effects of UV radiation power per unit solution on Hg^0 removal efficiency.

Conditions: O_2 concentration, 6.0%; SO_2 concentration, 1500 ppm; NO concentration, 400 ppm; Hg^0 concentration, 30 μg/m^3; Liquid–gas ratio, 3.1; Solution temperature, 323 K; Solution pH, 3.97; H_2O_2 concentration, 0.50 mol/L; UV wavelength, 254 nm.

$$Hg^0+\cdot O \rightarrow HgO \quad (9)$$

In addition, under the radiation of UV, O_3 can react with H_2O to produce H_2O_2 by the reaction (10).[27] The reaction product H_2O_2 can re-release ·OH free radicals to oxidize and remove Hg^0 by the above reactions (4) and (5)

$$O_3+H_2O+hv \rightarrow H_2O_2+O_2 \quad (10)$$

Some results[12,22,27] have proved that under the radiation of 254-nm UV, Hg^0 can also directly react with H_2O to produce HgO by the photoexcitation reaction (11)

$$Hg^0+H_2O+hv\xrightarrow{(\lambda=254\text{nm})}HgO+H_2 \quad (11)$$

The reaction product HgO can be captured through precipitation in water or dissolution in acidic solution. It can be judged from the above discussions that the growth in UV radiation power per unit solution can produce more effective UV photons, ·OH, ·O, and O_3, thereby being able to enhance the removal of Hg^0.

However, when UV radiation power per unit solution further increases and exceeds a certain maximum value, several side reactions such as the following reactions (12)–(19)[15–19,27] may also simultaneously occur in solution, which will result in the self-loss of ·OH, ·O, and O_3

$$H_2O_2+\cdot OH \rightarrow HO_2\cdot+H_2O \quad (12)$$

$$\cdot OH+\cdot OH \rightarrow H_2O_2 \quad (13)$$

$$HO_2\cdot+HO_2\cdot \rightarrow H_2O_2+O_2 \quad (14)$$

$$\cdot OH+HO_2\cdot \rightarrow H_2O+O_2 \quad (15)$$

$$O_3+\cdot OH \rightarrow HO_2\cdot+O_2 \quad (16)$$

$$\cdot O+\cdot O \rightarrow O_2 \quad (17)$$

$$\cdot O+O_3 \rightarrow O_2+O_2 \quad (18)$$

$$\cdot OH+\cdot O \rightarrow O_2+\cdot H \quad (19)$$

Furthermore, in addition to considering the changes in chemical reactions, it is also worth noting that as a gas–liquid heterogeneous reaction, the absorption rate of gas in liquid phase is often controlled by the mass transfer (fast reaction), the chemical reaction (slow reaction), or both (medium-speed reaction).[28] In this work, when the UV radiation power per unit solution is low and with its increase, Hg^0 removal efficiency has a great increase, which shows that the rate control step of Hg^0 removal may be the chemical reaction. However, with the further increase of UV radiation power per unit solution, the chemical reaction controlling may transfer to the mass transfer controlling. At this time, increasing the mass transfer rate may be more effective.[28] So, with the further increase of UV radiation power per unit solution, Hg^0 removal efficiency only has a very little increase.

Effects of H_2O_2 concentration

The effects of H_2O_2 concentration on Hg^0 removal efficiency are shown in Figure 4. It can be observed that Hg^0 removal efficiency increases from 57.1 to 82.8% when H_2O_2 concentration increases from 0 to 0.50 mol/L, but reduces from 82.8 to 69.5% when H_2O_2 concentration continues to increase from 0.50 to 1.50 mol/L. The above phenomenon may be attributed to the following reasons. On the one hand, according to the above listed reactions (4) and (5), H_2O_2 can be decomposed and produce ·OH free radicals to oxidize

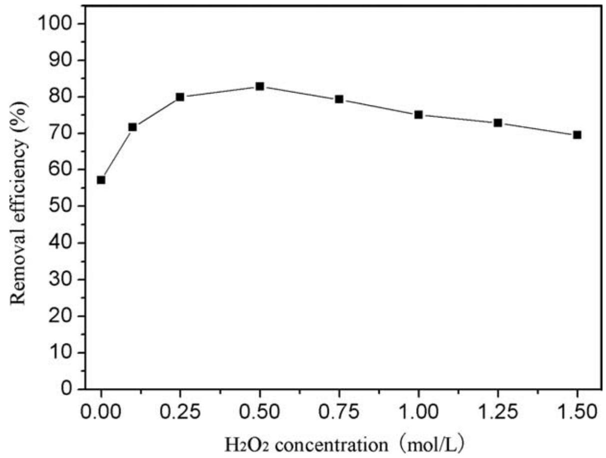


Figure 4. The effects of H_2O_2 concentration on Hg^0 removal efficiency.

Conditions: O_2 concentration, 6.0%; SO_2 concentration, 1500 ppm; NO concentration, 400 ppm; Hg^0 concentration, 30 μg/m^3; Liquid–gas ratio, 3.1; Solution temperature, 323 K; Solution pH, 3.97; UV radiation power per unit solution, 0.0056 W/mL; UV wavelength, 254 nm.

Hg^0. So, increasing H_2O_2 concentration can increase the yield of ·OH free radical, thereby enhancing the removal of Hg^0.

However, because H_2O_2 also has reducibility in addition to having strong oxidizing, it can become a scavenger of ·OH free radicals when it encounters the stronger oxidant ·OH,[18,19] so adding high concentration of H_2O_2 may cause the several side reactions (12)–(15). Therefore, adding excess H_2O_2 is not conducive to the removal of Hg^0 and the optimal H_2O_2 concentration is 0.50 mol/L.

Effects of solution temperature

The effects of solution temperature on Hg^0 removal efficiency are shown in Figure 5. It can be seen that the solution temperature has a small impact on removal of Hg^0. When it increases from 303 to 353 K, the removal efficiency of Hg^0 only reduces from 84.3 to 80.9%. The results[20] indicate that increasing solution temperature is able to improve chemical reaction rate to promote the removal of Hg^0. But in the present study, the activation energy of free radical reaction is so low[20] that increasing solution temperature can not play a significant role in enhancing the removal of Hg^0. However, increasing solution temperature can result in the reduction of Hg^0 solubility in solution,[28] thereby decreasing removal efficiency of Hg^0. In this work, with increasing solution temperature, the removal efficiency of Hg^0 slightly decreases, showing that with the increase of solution temperature, the reduction of Hg^0 solubility in liquid phase plays a major role.

Effects of Hg^0 concentration

The effects of Hg^0 concentration on Hg^0 removal efficiency were studied and the results are shown in Figure 6. With the increase of Hg^0 concentration, Hg^0 removal efficiency first has a slight increase and then has a slight decrease. For example, when Hg^0 concentration increases from 10 to 30 μg/m^3, Hg^0 removal efficiency increases from 80.1 to 82.8%. But, with the further increase of Hg^0 concentration from 30 to 60 μg/m^3, Hg^0 removal efficiency slightly decreases from 82.8 to 81.9%. There are two main reasons to explain the phenomena. On the one hand, some scholars argue that increasing Hg^0 concentration will increase the amount of Hg^0 through the reactor per unit time, which can decrease the relative molar ratio of ·OH, ·O, O_3, H_2O_2, and UV photons to Hg^0,[19] thereby reducing the removal efficiency of Hg^0. However, conversely, according to the two-film theory, the absorption rate of Hg^0 can be expressed by the following gas absorption rate Eq. 20[28]

$$N_{Hg^0}=k_{Hg^0,G}(p_{Hg^0}-p_{Hg^0,i}) \tag{20}$$

where N_{Hg^0} is the absorption rate of Hg^0, mol/m^2 s; $k_{Hg^0,G}$ is the gas phase mass-transfer coefficient of Hg^0, mol/m^2 s Pa; p_{Hg^0} is the Hg^0 partial pressure in gas body, Pa; $p_{Hg^0,i}$ is the Hg^0 partial pressure in phase interface, Pa.

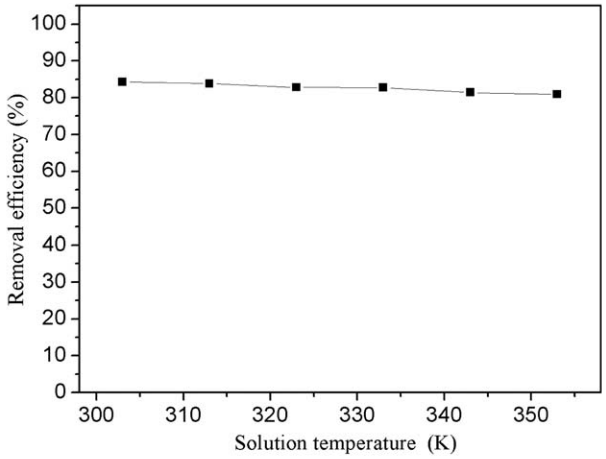


Figure 5. The effects of solution temperature on Hg^0 removal efficiency.

Conditions: O_2 concentration, 6.0%; SO_2 concentration, 1500 ppm; NO concentration, 400 ppm; Hg^0 concentration, 30 μg/m^3; Liquid–gas ratio, 3.1; Solution pH, 3.97; H_2O_2 concentration, 0.50 mol/L; UV radiation power per unit solution, 0.0056 W/mL; UV wavelength, 254 nm.

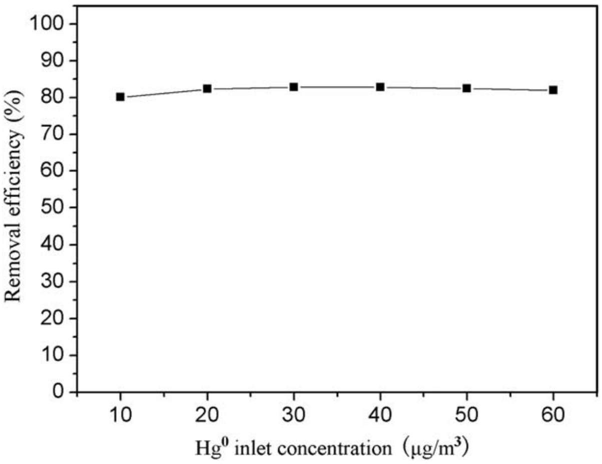


Figure 6. The effects of Hg^0 inlet concentration on Hg^0 removal efficiency.

Conditions: O_2 concentration, 6.0%; SO_2 concentration, 1500 ppm; NO concentration, 400 ppm; Liquid–gas ratio, 3.1; Solution temperature, 323 K; Solution pH, 3.97; H_2O_2 concentration, 0.50 mol/L; UV radiation power per unit solution, 0.0056 W/mL; UV wavelength, 254 nm.

It can be inferred from the above Eq. 20 that increasing Hg^0 concentration or Hg^0 partial pressure can increase the mass-transfer driving force of Hg^0, thereby promoting the removal of Hg^0. As shown in the above results, the back factor plays a main role when Hg^0 concentration is located between 10 and 30 μg/m^3. In contrast, the front factor plays a key role when Hg^0 concentration is located between 30 and 60 μg/m^3.

Effects of solution pH

The effects of solution pH on Hg^0 removal efficiency are shown in Figure 7. It can be observed that when solution pH increases from 1.27 to 11.23, Hg^0 removal efficiency sharply reduces from 85.9 to 37.3%. The effects of solution pH on Hg^0 removal include the following several reasons. The results show that H_2O_2 in solution can produce HO_2^-, which is a scavenger of ·OH free radical, by the hydrolysis reaction (21)[15,19]

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \tag{21}$$

The hydrolysis reaction (21) will result in an excessive self-consumption of H_2O_2, being not conducive to the oxidation removal of H_2O_2 for Hg^0 according to the following Eq. 22[3]

$$H_2O_2 + Hg^0 \rightarrow HgO + H_2O \tag{22}$$

In addition, the hydrolysis reaction product HO_2^- can consume ·OH free radicals though the following reaction (23),[15,19] thereby reducing the removal efficiency of Hg^0

$$\cdot OH + HO_2^- \rightarrow H_2O + O_2^- \tag{23}$$

It can also be observed from the reaction (21) that increasing solution pH can increase OH^- concentration and then OH^- can increase yield of HO_2^- by absorbing H^+ through acid–base neutralization reaction, thereby further reducing the utilization of H_2O_2 and ·OH free radicals.[15] Besides, some results[19] have shown that comparing with alkaline conditions, H_2O_2 has stronger oxidizing under acidic conditions. In summary, with increasing the solution pH, Hg^0 removal efficiency has a huge decline.

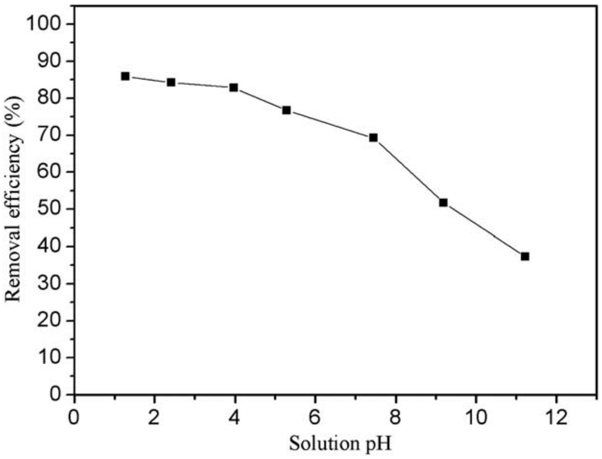


Figure 7. The effects of solution pH on Hg^0 removal efficiency.

Conditions: O_2 concentration, 6.0%; SO_2 concentration, 1500 ppm; NO concentration, 400 ppm; Hg^0 concentration, 30 μg/m^3; Liquid–gas ratio, 3.1; Solution temperature, 323 K; H_2O_2 concentration, 0.50 mol/L; UV radiation power per unit solution, 0.0056 W/mL; UV wavelength, 254 nm.

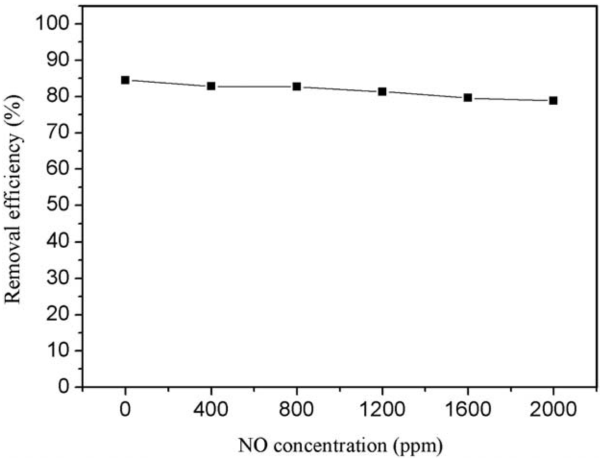


Figure 8. The effects of NO concentration on Hg^0 removal efficiency.

Conditions: O_2 concentration, 6.0%; SO_2 concentration, 1500 ppm; Hg^0 concentration, 30 μg/m^3; Liquid–gas ratio, 3.1; Solution temperature, 323 K; Solution pH, 3.97; H_2O_2 concentration, 0.50 mol/L; UV radiation power per unit solution, 0.0056 W/mL; UV wavelength, 254 nm.

Effects of NO concentration

The effects of NO concentration on the removal efficiency of Hg^0 are shown in Figure 8. It can be seen that when NO concentration increases from 0 to 2000 ppm, the removal efficiency of Hg^0 decreases from 84.5 to 78.8%. Some results[15–19] show that NO can react with and consume ·OH, ·O, O_3, and H_2O_2 by the following reactions (24)–(31), thus the increase of NO concentration can decrease the Hg^0 removal efficiency

$$NO + \cdot OH \rightarrow HNO_2 \tag{24}$$

$$HNO_2 + \cdot OH \rightarrow HNO_3 + \cdot H \tag{25}$$

$$NO + \cdot O \rightarrow NO_2 \tag{26}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{27}$$

$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O \tag{28}$$

$$NO_2 + \cdot OH \rightarrow HNO_3 \tag{29}$$

$$2NO_2 + H_2O_2 \rightarrow 2HNO_3 \tag{30}$$

$$2NO + 3H_2O_2 \rightarrow 2HNO_3 + 2H_2O \tag{31}$$

Effects of SO_2 concentration

The effects of SO_2 concentration on Hg^0 removal efficiency are shown in Figure 9. It can be seen that when SO_2 concentration increases from 0 to 3000 ppm, Hg^0 removal efficiency slightly decreases from 85.1 to 81.4%. Based on the following chemical reactions (32)–(39),[15–19] SO_2 can also react with and consume ·OH, ·O, O_3, and H_2O_2, thus with an increase in SO_2 concentration, Hg^0 removal efficiency also decreases

$$SO_2 + H_2O \leftrightarrow HSO_3^- + H^+ \tag{32}$$

$$HSO_3^- \leftrightarrow SO_3^{2-} + H^+ \tag{33}$$

$$HSO_3^- + \cdot OH \rightarrow \cdot SO_3^- + H_2O \tag{34}$$

$$SO_3^{2-} + \cdot OH \rightarrow \cdot SO_3^- + OH^- \tag{35}$$

$$HSO_3^- + H_2O_2 \rightarrow SO_4^{2-} + H^+ + H_2O \tag{36}$$

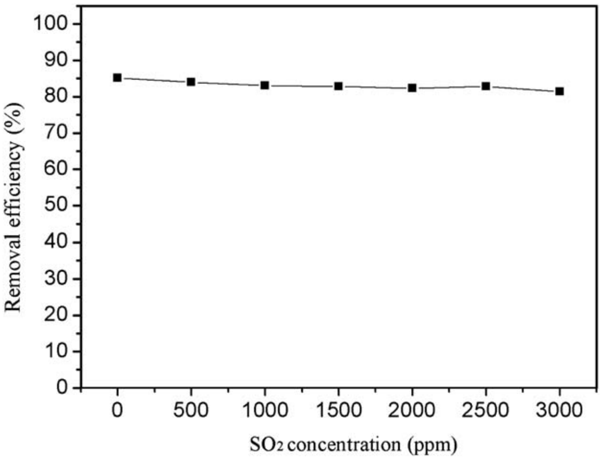


Figure 9. The effects of SO_2 concentration on Hg^0 removal efficiency.

Conditions: O_2 concentration, 6.0%; NO concentration, 400 ppm; Hg^0 concentration, 30 μg/m^3; Liquid–gas ratio, 3.1; Solution temperature, 323 K; Solution pH, 3.97; H_2O_2 concentration, 0.50 mol/L; UV radiation power per unit solution, 0.0056 W/mL; UV wavelength, 254 nm.

$$SO_3^{2-} + H_2O_2 \rightarrow SO_4^{2-} + H_2O \tag{37}$$

$$HSO_3^- + \cdot O \rightarrow SO_4^- \cdot + \cdot H \tag{38}$$

$$SO_3^{2-} + O_3 \rightarrow SO_4^{2-} + O_2 \tag{39}$$

Effects of liquid–gas ratio

The effects of liquid–gas ratio on Hg^0 removal efficiency are shown in Figure 10. It can be observed that liquid–gas ratio has an obvious impact on the removal efficiency of Hg^0. With the increase of liquid–gas ratio from 1.6 to 5.2, the removal efficiency of Hg^0 greatly increases from 65.9 to 92.2%. The total amount of ·OH, ·O, O_3, and H_2O_2 through the reactor per unit time will greatly increase with the increase of liquid–gas ratio, which can increase the relative molar ratio of ·OH, ·O, O_3, and H_2O_2 to Hg^0,[19] thereby being able to promote the removal of Hg^0. In addition, increasing liquid–gas ratio can increase the gas–liquid mass-transfer rate by strengthening the disturbance in gas–liquid two-phase, thereby being able to increase the absorption rate of Hg^0.[28] Therefore, the removal efficiency of Hg^0 increases with the increase of liquid–gas ratio.

Effects of O_2 concentration

The effects of O_2 concentration on Hg^0 removal efficiency were studied, and the results are shown in Figure 11. It can be seen that when O_2 concentration increases from 0 to 6.0%, Hg^0 removal efficiency greatly increases from 57.1 to 82.8%. The results[12,21–26] show that under radiation of UV, O_2 can decompose and produce strong oxidizing agents O_3 and ·O to oxidize Hg^0 by the above reactions (6)–(9). Thus, increasing O_2 concentration can raise Hg^0 removal efficiency. But, when O_2 concentration further increases from 6.0 to 15.0%, the removal efficiency of Hg^0 only raises from 82.8 to 85.8%, showing that O_2 concentration may have gradually become excess after exceeding 6.0%. In the actual flue gas, the common O_2 concentration is about 5.0–6.0%, which can basically meet the requirement of the photochemical reaction.

Comparison study of different systems

The comparison study in different systems was carried out and the results are shown in Figure 12. It can be seen that Hg^0 can achieve the removal efficiencies of 9.8, 22.8, 50.6, 31.2, 55.4, and 82.8% in O_2/H_2O_2, UV/H_2O, UV/H_2O_2, UV/O_2, UV/H_2O/O_2, and UV/H_2O_2/O_2, respectively, but even little Hg^0 can be removed in O_2/H_2O, which shows that all of UV, H_2O, H_2O_2, and O_2 play an important role in removal of Hg^0 and they have a significant synergistic effect each other.

·OH free radical, removal product, and material balance

To study the chemical reaction mechanism of Hg^0 removal, ·OH in liquid phase was captured by the combination use of SA and LC-MS, and the results are shown in Figure 13. It can be seen that both of the hydroxylated

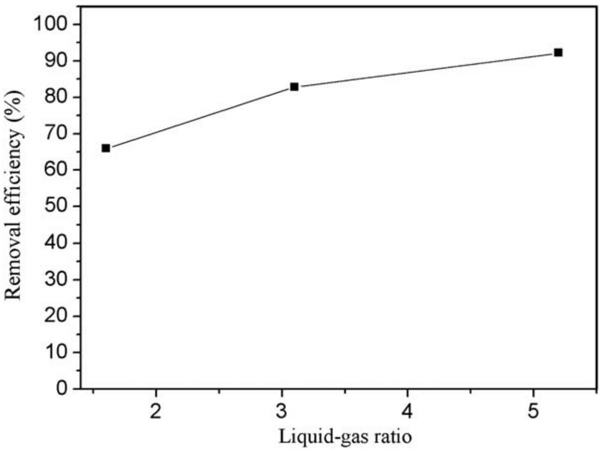


Figure 10. The effects of liquid–gas ratio on Hg^0 removal efficiency.

Conditions: O_2 concentration, 6.0%; SO_2 concentration, 1500 ppm; NO concentration, 400 ppm; Hg^0 concentration, 30 μg/m^3; Solution temperature, 323 K; Solution pH, 3.97; H_2O_2 concentration, 0.50 mol/L; UV radiation power per unit solution, 0.0056 W/mL; UV wavelength, 254 nm.

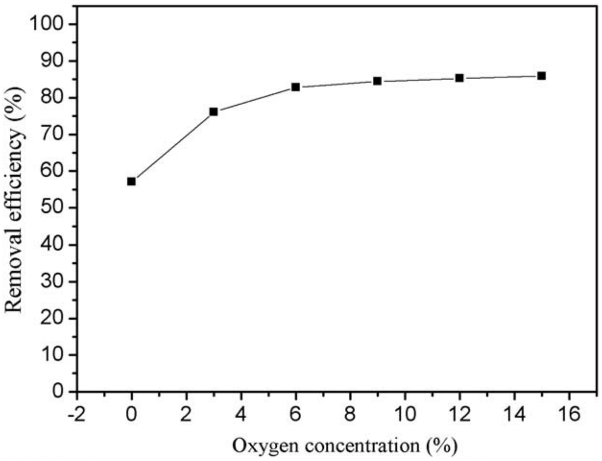


Figure 11. The effects of O_2 concentration on Hg^0 removal efficiency.

Conditions: SO_2 concentration, 1500 ppm; NO concentration, 400 ppm; Hg^0 concentration, 30 μg/m^3; Liquid–gas ratio, 3.1; Solution temperature, 323 K; Solution pH, 3.97; H_2O_2 concentration, 0.50 mol/L; UV radiation power per unit solution, 0.0056 W/mL; UV wavelength, 254 nm.

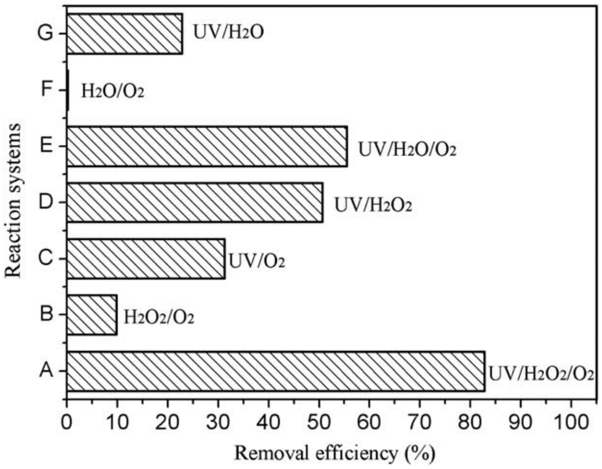


Figure 12. Comparison of different systems.

Conditions: O_2 concentration, 6.0%; SO_2 concentration, 1500 ppm; NO concentration, 400 ppm; Hg^0 concentration, 30 μg/m^3; Liquid–gas ratio, 3.1; Solution temperature, 323 K; Solution pH, 3.97; H_2O_2 concentration, 0.50 mol/L; UV radiation power per unit solution, 0.0056 W/mL; UV wavelength, 254 nm.

products, such as 2,3-DHBA and 2,5-DHBA can be measured by the MS detector of LC-MS, which show that ·OH has been produced in the solution and the removal process of Hg^0 by UV/H_2O_2 process is caused by the free radical chain reactions. In addition, the concentrations of Hg^0 and total mercury in liquid phase were also determined, and the results are shown in Figure 14. The results show that Hg^0 can not be detected, but the total mercury has been detected in the solution.

Additionally, on the basis of the measured results of total mercury concentration, the calculation of the mass balance for mercury element was also carried out. The results show that the calculated values of total mercury concentration are in good agreement with the determined values, with a relative error of 8.58%. The results suggest that Hg^{2+} is the final reaction product of Hg^0, and Hg^0 is mainly removed by oxidation reaction. The errors between the determined values and the calculated values may result from the mercury digestion process and the measurement errors.

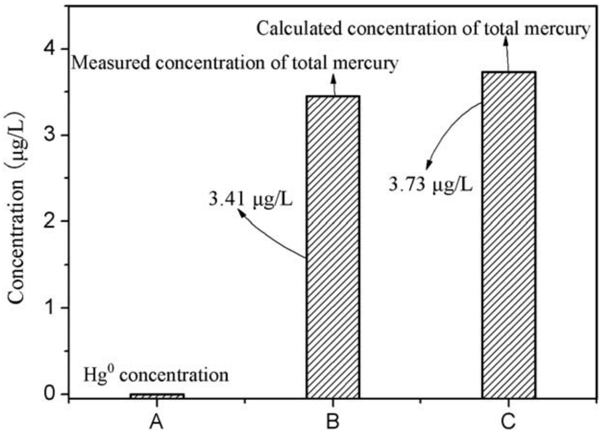


Figure 14. Removal products and mass balance of Hg^0 removal.

Conditions: O_2 concentration, 6.0%; SO_2 concentration, 1500 ppm; NO concentration, 400 ppm; Hg^0 concentration, 30 μg/m^3; Liquid–gas ratio, 3.1; Solution temperature, 323 K; Solution pH, 3.97; H_2O_2 concentration, 0.50 mol/L; UV radiation power per unit solution, 0.0056 W/mL; UV wavelength, 254 nm.

Chemical reaction mechanism of Hg^0 removal

The results of the comparison experiments in Figure 12 show that Hg^0 can achieve a removal efficiency of 9.8% in O_2/H_2O_2, but even little Hg^0 is removed by O_2/H_2O, showing that the removal of Hg^0 by the oxidation of H_2O_2 occurs in the reaction process. Hg^0 of 22.8% is removed by UV/H_2O, showing that the removal of Hg^0 by the photoexcitation reaction of Hg^0 with H_2O is one of the Hg^0 removal pathways. When O_2 is added, Hg^0 removal efficiencies significantly increase in UV/H_2O and UV/H_2O_2. For example, Hg^0 can achieve the removal efficiencies of 55.4 and 82.8% in UV/H_2O/O_2 and UV/H_2O_2/O_2, which are much higher than those in UV/H_2O (22.8%) and UV/H_2O_2 (50.6%), respectively. The Hg^0 removal efficiency of 31.2% in UV/O_2 also fully demonstrated that there is a synergistic effect between UV and O_2 and the chemical reactions (6)–(9) may occur in the reaction process. Besides, the presence of O_3 also further confirms that the removals of Hg^0 by the

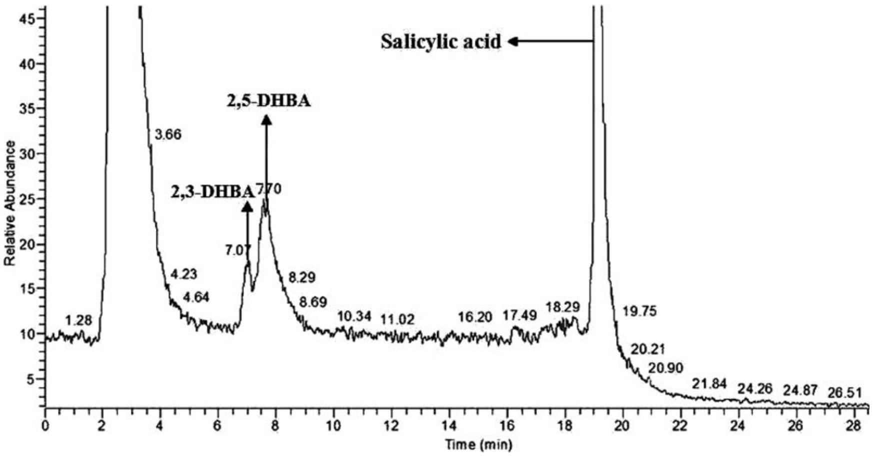


Figure 13. Determination of hydroxylated products 2,3-DHBA and 2,5-DHBA by the MS detector in LC-MS.

Conditions: SA, 0.05 mol/L; O_2 concentration, 6.0%; SO_2 concentration, 1500 ppm; NO concentration, 400 ppm; Hg^0 concentration, 30 μg/m^3; Liquid–gas ratio, 3.1; Solution temperature, 323 K; Solution pH, 3.97; H_2O_2 concentration, 0.50 mol/L; UV radiation power per unit solution, 0.0056 W/mL; UV wavelength, 254 nm.

oxidation of O_3 and ·O free radicals may be also part of the reaction pathways of Hg^0 removal.

When H_2O_2 is added into $UV/H_2O/O_2$ and UV/H_2O, Hg^0 can achieve the removal efficiencies of 82.8 and 50.6% in $UV/H_2O_2/O_2$ and UV/H_2O_2, which are higher than those in $UV/H_2O/O_2$ (55.4%) and UV/H_2O (22.8%), respectively. The successful capture of ·OH also further proves that the removal of Hg^0 by oxidation of ·OH is also one of the reaction pathways. Furthermore, the measured results of mercury removal products indicate that Hg^{2+} is the final reaction products of Hg^0, and Hg^0 is mainly removed by oxidation reaction in UV/H_2O_2 process in the presence of O_2, which can further prove that a variety of oxidation reactions and photoexcitation reactions aforementioned have occurred in the reaction process. In summary, based on the above Results and Discussions, although several other side reactions may also occur in liquid phase, the main reaction pathways of Hg^0 removal by UV/H_2O_2 process in the presence of O_2 can be presumably concluded as follows:

a. The ·OH, ·O, and O_3 are produced through UV photolysis of O_2 and H_2O_2 by the reactions (4), (6), and (7);
b. The removals of Hg^0 by the oxidations of ·OH, ·O, and O_3 by the reactions (5), (8), and (9);
c. The removal of Hg^0 by the photoexcitation reaction of Hg^0 with H_2O by the reaction (11);
d. The removal of Hg^0 by the direct oxidation of H_2O_2 by the reaction (22);
e. The termination of free radical chain reactions by the reactions (12)–(19).

Simultaneous removal of Hg^0, NO, and SO_2

The emissions of SO_2 and NO_x have been a major environmental concern because of their hazardous effects on human health and the ecosystems. So far, SO_2 and NO_x from flue gas are mainly controlled by simultaneously installing flue gas desulfurization and denitrification equipments, such as calcium-based wet flue gas desulfurization system and ammonium selective catalytic reduction denitrification system.[19] Furthermore, considering the potential requirement for mercury removal in the future, if coal-fired boiler continues to add mercury removal system, most of companies can not almost bear such a large economic burden. Recently, some results[4,9,19] show that simultaneous removal of NO_x, SO_2, and Hg in a reactor can effectively reduce the equipment space and complexity of systems and save the investment and operating costs. Therefore, studying new technologies and new theories about simultaneous removal of NO_x, SO_2, and Hg has become one of the hot issues in the field of energy and environment.

In this study, based on our previous results about removal of NO and SO_2 by UV/H_2O_2 process in a photochemical bubble reactor, the simultaneous removal of Hg^0, NO, and SO_2 by UV/H_2O_2 process in a novel photochemical spray reactor was preliminarily studied for the first time, and the

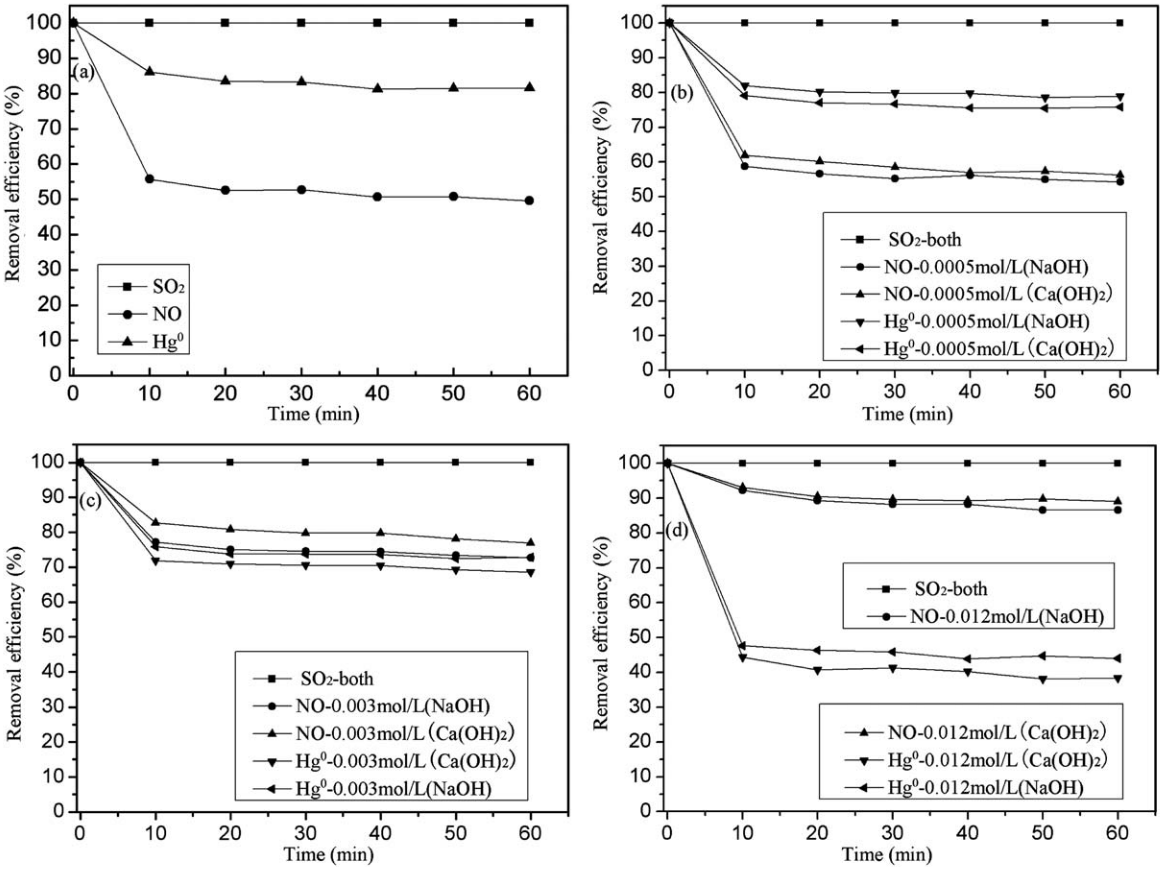


Figure 15. Simultaneous removal efficiencies of Hg^0, NO, and SO_2 by UV/H_2O_2 process and under the enhancement of $Ca(OH)_2$ and NaOH with different concentrations.

Conditions: O_2 concentration, 6.0%; SO_2 concentration, 1500 ppm; NO concentration, 400 ppm; Hg^0 concentration, 30 μg/m^3; Liquid–gas ratio, 3.1; Solution temperature, 323 K; Solution pH, 3.97; H_2O_2 concentration, 0.50 mol/L; UV radiation power per unit solution, 0.0056 W/mL; UV wavelength, 254 nm.

results are shown in Figure 15a. It can be seen that when NO, SO_2, and Hg^0 were simultaneously removed by UV/H_2O_2 process in the photochemical spray reactor, the simultaneous removal efficiencies of NO, Hg^0, and SO_2 are 52.0, 82.8, and 100%, respectively. The results indicate that Hg^0 and SO_2 can be effectively removed by UV/H_2O_2 process in the photochemical spray reactor. But, NO can not be efficiently removed by UV/H_2O_2 process because of its very low solubility in water. Therefore, it is very necessary that looking for effective measures to strengthen removal of NO in UV/H_2O_2 process.

In the past few decades, alkali-based wet flue gas desulfurization processes have been widely used because of the high desulfurization efficiency and the simple and reliable process.[19] Our previous results[15,19,29,30] have found that comparing with acidic conditions, neutral and alkaline conditions are more conducive to the removal of NO by UV/H_2O_2 process. Considering the wide applications of calcium-based and sodium-based absorbents in wet flue gas desulfurization processes, such as the most common calcium-based wet flue gas desulfurization and the dual-alkali wet flue gas desulfurization processes, thus here the experiments about simultaneous removals of Hg^0, NO, and SO_2 by UV/H_2O_2 process under enhancement of $Ca(OH)_2$ and NaOH with different concentrations (UV/H_2O_2/$Ca(OH)_2$ process and UV/H_2O_2/NaOH process) were conducted preliminarily, and the results are shown in Figures 15b–d.

It can be observed that after adding 0.0005, 0.003, 0.012 mol/L NaOH and 0.0005, 0.003, 0.012 mol/L $Ca(OH)_2$, respectively, SO_2 can still achieve complete removal. However, unlike the SO_2, both of the removal efficiencies of Hg^0 and NO significantly change. For example, after adding 0.0005, 0.003, 0.012 mol/L NaOH and 0.0005, 0.003, 0.012 mol/L $Ca(OH)_2$, the removal efficiencies of NO are 56.0, 74.5, 88.5% and 58.9, 79.7, 90.2% and the removal efficiencies of Hg^0 are 79.9, 73.7, 45.4% and 76.6, 70.3, 40.5%, respectively. The results show that the removal of NO is greatly improved, but the removal efficiencies of Hg^0 reduce by the addition of NaOH and $Ca(OH)_2$. Therefore, to ensure a good simultaneous removal efficiency of Hg^0, NO, and SO_2, the optimum concentration of NaOH and $Ca(OH)_2$ is 0.003 mol/L. In addition, the above studies further suggest that UV/H_2O_2 process may be used to simultaneously remove Hg^0, NO, and SO_2 by combining with or reforming the existing alkali-based wet flue gas desulfurization processes, which has been applied commercially in the coal-fired boilers. The related contents will be further studied in the next works.

Further research of this technology

It is well known that the mass-transfer reaction kinetics and kinetic parameters of gas absorption are the essential theoretical basis for the industrial design, the amplification of reactor and the numerical simulation of gas absorption process.[28] So, the mass-transfer reaction kinetics problems of Hg^0 removal by UV/H_2O_2 process will be further studied (determination of mass-transfer parameters of the photochemical spray reactor, obtaining the kinetic parameters, the rate controlling step, and the gas absorption kinetic models, and the optimized design of photochemical spray reactor) in the future works. The actual coal-fired flue gas composition is very complex, which often contains many acid gases, moisture, fly ash particles, and carbon monoxide.[12] Therefore, studying the potential impacts of these flue gas compositions on mercury removal are also the next important tasks. In addition, the feasibility about simultaneous removal of Hg^0, NO, and SO_2 using UV/H_2O_2 process combining with the existing alkali-based wet flue gas desulfurization processes has been proved, but the related basic theoretical issues such as optimization of process parameters, chemical reaction mechanism, and kinetic process still needs further study in the next works.

Conclusions

In this work, a novel photochemical spray reactor is developed for the first time and is used to remove Hg^0 and simultaneously remove Hg^0/SO_2/NO from flue gas by UV/H_2O_2 process. The effects of several parameters on removal of Hg^0 by UV/H_2O_2 process were investigated. The removal mechanism of Hg^0 by UV/H_2O_2 process is proposed. The results indicate that in four wavelengths (185 nm, 254 nm, 320 nm, and visible light), 254 nm is the most effective wavelength for the removal of Hg^0 by UV/H_2O_2 process. The removal of Hg^0 is significantly promoted by adding low concentration of H_2O_2, but is inhibited by adding high concentration of H_2O_2. Increasing solution pH obviously reduces Hg^0 removal efficiency. Increasing UV radiation power, liquid–gas ratio and O_2 can significantly promote the removal of Hg^0. Hg^0 removal efficiency slightly increases with the increase of Hg^0 inlet concentration in low concentration range (less than 30 $\mu g/m^3$), but slightly reduces with the increase of Hg^0 inlet concentration in high concentration range (more than 30 $\mu g/m^3$). With the increase of solution temperature, SO_2 concentration and NO concentration, Hg^0 removal efficiency slightly reduces. Hg^{2+} is the final reaction product of Hg^0 removal, and Hg^0 is mainly removed by the oxidations of H_2O_2, ·OH, ·O, O_3, and the photoexcitation of UV. In addition, in the last part of this work, simultaneous removal of Hg^0, NO, and SO_2 is also studied. The results show that Hg^0 and SO_2 can be effectively removed by UV/H_2O_2 process in the photochemical spray reactor. But NO can not be efficiently removed by UV/H_2O_2 process because of its very low solubility in water. The removal of NO is greatly improved, but the removal efficiencies of Hg^0 reduce by the addition of NaOH and $Ca(OH)_2$. To ensure a good simultaneous removal efficiency of Hg^0, NO, and SO_2, the optimum concentration of NaOH and $Ca(OH)_2$ is 0.003 mol/L. The above studies also suggest that UV/H_2O_2 process may be used to simultaneously remove Hg^0, NO, and SO_2 by combining with or reforming existing alkali-based wet flue gas desulfurization processes, which has been applied commercially in the coal-fired boilers.

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Literature Cited

1. Li P, Feng XB, Qiu GL, Shang LH, Li ZG. Mercury pollution in Asia: a review of the contaminated sites. *J Hazard Mater*. 2009;168: 591–601.

2. Xu MH, Yan R, Zheng CG, Qiao Y. Status of trace element emission in a coal combustion process: a review. *Fuel Process Technol.* 2003;85:215–237.
3. Martinez AI, Deshpande BK. Kinetic modeling of H_2O_2-enhanced oxidation of flue gas elemental mercury. *Fuel Process Technol.* 2007;88:982–987.
4. Ma XY. Experimental study on removal mercury from flue gas by aqueous solution, PhD thesis. Baoding, Hebei Province, China: North China Electric Power University (Baoding), 2008:6–16.
5. Xu XH, Ye QF, Tang TM, Wang DH. Hg^0 oxidative absorption by $K_2S_2O_8$ solution catalyzed by Ag^+ and Cu^{2+}. *J Hazard Mater.* 2008;158:410–416.
6. Fang P, Cen CP, Tang ZJ. Experimental study on the oxidative absorption of Hg^0 by $KMnO_4$ solution. *Chem Eng J.* 2012;102:198–199.
7. Lu D, Anthony EJ, Tan YW, Dureau R. Mercury removal from coal combustion by Fenton reactions—part A: bench-scale tests. *Fuel.* 2007;86:2789–2797.
8. Wang YJ, Liu Y, Wu ZB, Mo JS, Cheng B. Experimental study on the absorption behaviors of gas phase bivalent mercury in Ca-based wet flue gas desulfurization slurry system. *J Hazard Mater.* 2010; 183:902–907.
9. Wang ZH, Zhou JH, Zhu YQ, Wen ZH. Simultaneous removal of NO_x, SO_2 and Hg in nitrogen flow in a narrow reactor by ozone injection: experimental results. *Fuel Process Technol.* 2007;88:817–823.
10. Jeong J, Jurng J. Removal of gaseous elemental mercury by dielectric barrier discharge. *Chemosphere.* 2007;68:2007–2010.
11. Wang JW, Yang JL, Liu ZY. Gas-phase elemental mercury capture by a V_2O_5/AC catalyst. *Fuel Process Technol.* 2010;91:676–680.
12. Granite EJ, Pennline HW. Photochemical removal of mercury from flue gas. *Ind Eng Chem Res.* 2002;41:5470–547.
13. Li Y, Murphy P, Wu CY. Removal of elemental mercury from simulated coal-combustion flue gas using a SiO_2–TiO_2 nanocomposite. *Fuel Process Technol.* 2008;89:567–573.
14. Liu YX. Research progress of UV/H_2O_2 advanced oxidation process in the environmental protection and chemical industry field. *J Chem Ind Eng.* 2010;3:33–38.
15. Liu YX, Zhang J. Photochemical oxidation removal of nitric oxide and sulfur dioxide from simulated flue gas of coal-fired power plants by wet scrubbing using UV/H_2O_2 advanced oxidation process. *Ind Eng Chem Res.* 2011;50:3836–3841.
16. Liu YX, Zhang J, Sheng CD. Simultaneous removal of NO and SO_2 from coal-fired flue gas by UV/H_2O_2 advanced oxidation process. *Chem Eng J.* 2010;162:1006–1011.
17. Liu YX, Zhang J. A study on kinetics of NO removal from simulated flue gas by wet UV/H_2O_2 advanced oxidation process. *Energy Fuels.* 2011;6:1102–1107.
18. Liu YX, Zhang J. Kinetic model of NO removal from SO_2-containing simulated flue gas by wet UV/H_2O_2 advanced oxidation process. *Chem Eng J.* 2011;2:106–111.
19. Liu YX. Study on integrated desulfurization and denitrification by UV/H_2O_2 advanced oxidation process, PhD thesis. Nanjing, JiangSu Province, China: Southeast University, 2010;7:62–63.
20. Xu Y. *Chemical Reaction Kinetics*. Beijing: Chemical Industry Press, 2004.
21. McLarnon CR, Granite Evan J, Pennline HW. The PCO process for photochemical removal of mercury from flue gas. *Fuel Process Technol.* 2005;87:85–89.
22. Jia L, Dureau R, Ko V, Anthony EJ. Oxidation of mercury under ultraviolet (UV) irradiation. *Energy Fuels.* 2010;24:4351–4356.
23. Granite E, King W, Stanko D, Pennline H. The implications of mercury interactions with band-gap semiconductor oxides. *Main Group Chem.* 2008;7:227–237.
24. Granite EJ, Pennline HW, Hoffman JS. Effects of photochemical formation of mercuric oxide. *Ind Eng Chem Res.* 1999;38:5034–5037.
25. Goodsite ME, Plane JMC, Skov H. A theoretical study of the oxidation of Hg^0 to $HgBr_2$ in the troposphere. *Environ Sci Technol.* 2004; 38:1772–1776.
26. Chen ZY, Mannava DP, Mathur VK. Mercury oxidization in dielectric barrier discharge plasma system. *Ind Eng Chem Res.* 2006;45: 6050–6055.
27. Garoma T, Gurol M. Degradation of tert-butyl alcohol in dilute aqueous solution by an O_3/UV process. *Environ Sci Technol.* 2004; 38:5246–5252.
28. Zhang CF. *Gas-Liquid Reaction and Reactor*. Beijing: Chemical Industry Press, 1985.
29. Liu YX, Pan JF, Tang AK, Wang Q. A study on mass transfer–reaction kinetics of NO absorption by using UV/H_2O_2/NaOH process. *Fuel.* 2013;108:254–260.
30. Liu YX, Zhang J, Wang ZL. Simultaneous removal of NO and SO_2 from flue gas by UV/H_2O_2/CaO. *Chem Eng Technol.* 2012;10:1879–1884.

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