



New insights into synergistic effects and active species toward Hg^0 emission control by Fe(VI) absorbent



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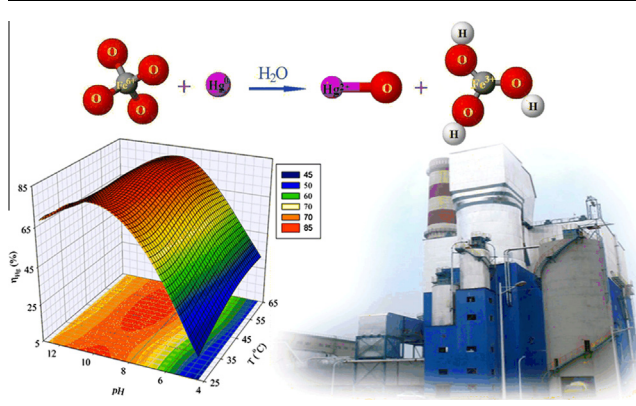
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HIGHLIGHTS

- Fe(VI) is a promising agent for Hg^0 control.
- Removal of Hg^0 was optimized with the response surface methodology.
- Synergic effect of pH and temperature is considerable.
- Species analysis and thermodynamics revealed Hg^0 removal mechanism.

GRAPHICAL ABSTRACT



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ABSTRACT

With the timelines for implementation of the U.S. Environmental Protection Agency's mercury emission control rules approaching soon, finding an innovative and cost-effective mercury removal technology has become increasingly important. The most challenging species in all the mercury forms is gaseous elemental mercury (Hg^0). The objective of this work is to inspect the absorption behavior and removal of Hg^0 by Fe(VI). The synergistic effects of various factors were investigated and the optimization for Hg^0 removal by Fe(VI) was achieved based on the response surface methodology. The speciation of Fe(VI) and Hg reaction species was emphatically analyzed in the entire pH range in order to clarify the possible Fe(VI)-based Hg^0 removal mechanism in depth. According to the thermodynamics calculation, the Gibbs free energies for the reaction between Fe(VI) and Hg^0 in the weak alkaline/acid medium are determined as -120.03 kJ/mol and -235.42 kJ/mol, respectively, implying the oxidation of Hg^0 by Fe(VI) is spontaneous and thorough. Finally, industrial feasibility analysis indicates that Fe(VI) has the practical potential to be a promising removal agent for Hg^0 emission control from coal-fired flue gas, which might be integrated into the existing mainstream flue gas desulfurization scrubber to achieve the removal of multi-pollutants simultaneously, in prospect.

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1. Introduction

People have become increasingly concerned about the toxic effect of Hg^0 since it was first recognized in the early 1950s [1].

With the breakneck development of the energy industry in the last few decades, mercury emission has become more problematic to the atmosphere, water and soil [2]. The Global Mercury Assessment reported that approximately 1,960 tons of mercury was emitted to the atmosphere in 2010 as a direct result of human activity. In order to cope with the serious environmental and health issues incurred by the increase in mercury emission, a global treaty for mercury emission control was recently signed in Geneva in early 2013. Coal combustion is responsible for about 475 tons of annual mercury emissions [3]. Mercury emission regulation will be implemented in the United States soon [4].

Mercury in coal-derived flue gas exists in three forms: particulate-bound mercury (Hg_p), vapor-phase oxidized mercury (Hg^{2+}), and vapor-phase elemental mercury (Hg^0) [5,6]. The majority of Hg_p and Hg^{2+} can be easily captured by existing pollution control technologies including electrostatic precipitators (ESP) or fabric filters (FF) [7], activated carbon injection [7,8] and wet flue gas desulfurization (WFGD) systems [9]; however, the removal of Hg^0 is challenging due to its high volatility and low solubility [10]. Clearly, the strategy for effective removal of Hg^0 is to quickly convert Hg^0 to Hg^{2+} since the latter is soluble and hence can be easily absorbed by WFGD. Many oxidizing absorbents, including $KMnO_4$, $K_2S_2O_8$, $K_2Cr_2O_7$, $NaClO_2$, and H_2O_2 , have been investigated [11–15]. Unfortunately, these classical oxidants either have lower economical efficiencies or may generate hazardous byproducts which can lead to secondary pollution. Specifically, $KMnO_4$, $K_2Cr_2O_7$ and $NaClO_2$ are often considered as the effective reagents for removal of Hg^0 , but they will bring a large number of heavy metal, manganese, chromium and chlorine species that remain in the removal products from the process, which can bring serious threats to the environment and human health [16,17]. Although H_2O_2 is an environmentally benign reagent, this approach is very inefficient without UV radiation, and as such its commercialization application is seriously restricted. Therefore, the development of efficient and environmentally friendly technologies for the removal of Hg^0 from flue gas is imperative.

Ferrate(VI), or Fe(VI), because of its strong oxidation and coagulation abilities, has been used to treat wastewater [18–20], particularly in removing heavy metals such as As^{3+} , Mn^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Cr^{3+} , and Hg^{2+} in water and wastewater [21]. Recently, limited efforts have been devoted to introduce this emerging green multifunctional chemical, Fe(VI), into flue gas treatment [22–24]. An Fe-based absorbent shows more potential to simultaneously control multi-pollutants including mercury [24–26], however, to the best knowledge, the study focused on Hg^0 removal by Fe(VI) is not thorough, especially with regards to the synergistic effects on the Hg^0 absorption behavior by Fe(VI) absorbent, which is crucial for further optimizing to suit a wide range of industrial applications. Meanwhile, the Hg^0 removal mechanism of Fe(VI) is far from being clearly studied and analyzed. This work aimed at filling this gap. In conventional multifactor experiments, optimization is usually performed by varying a single factor while keeping all other factors fixed at a specific set of conditions. It is not only time-consuming, but also usually incapable of reaching the true optimum due to ignoring the interactions among factors. Compared with other statistical experimental design methods, the main advantage of response surface methodology (RSM) is the reduced number of experiment trials needed to evaluate multiple parameters and their interactions [27,28]. For this reason, RSM was employed to investigate the independent and synergistic effects of main operating conditions on the Hg^0 removal capability, respectively, in order to optimize the process and provide parameters suitable for a pilot-scale trial. In addition, the Hg^0 removal mechanism of Fe(VI) was explored in detail by species analysis and thermodynamics calculation under various pH conditions.

Finally, the industrial implementation and its feasibility were discussed and analyzed.

2. Experimental

2.1. Materials

Potassium ferrate (K_2FeO_4 , purity 92%) was supplied by the Tianshun Chemical Co. in Xi'an, China. All the other reagents were analytical grade and purchased from the Tianjin Chemical Reagents Co., in Tianjin, China. Ferrate(VI) solutions were prepared by mixing predetermined amounts of K_2FeO_4 powder and deionized water along with a pH regulator, in which 0.2 M KOH or 0.1 M H_2SO_4 solution acted as a pH regulator to control the initial pH of the reaction solution.

2.2. Apparatus and methods

The experimental apparatus used for removal of Hg^0 with Fe(VI) is illustrated in Fig. 1. It has three units: inlet flue gas simulation, removal of Hg^0 , and outlet gas analysis and treatment, corresponding to parts 1–7, 8–12, and 13–14 in Fig. 1, respectively. Teflon (PTFE) lined tubing and fittings were employed to connect all parts in the apparatus. The first step of mercury removal test is to flow N_2 from its cylinder (1) at 1 L/min controlled by a regulator (2) and a meter (3', LZB, Tianjin Flow Meter Co.) into the Hg^0 generator, which consists of glass beads (4a), a membrane veneer (4b), and a mercury permeation tube (4c, VICI Metronics Co.). The temperature of the Hg^0 generator was controlled by a HD120-T12 thermostatic water bath with the four-bit LED display (5', ± 0.02 °C, Prima Co., British). Then the gas from the Hg^0 generator set was mixed with the balance N_2 controlled by a flow meter (3'') in a gas mixer (6). The gas mixture passed through a valve (7) and then entered the Hg^0 removal reactor (10), through a gas diffuser (8), and the Hg^0 reacted with Fe(VI) loaded through an injector (9). In order to improve the applicability, the reactor was designed with a reduced scale ratio of 1:40 to mimic a pilot-scale bubble column tower in an actual power plant (600 MW, MATOU power plant, Hebei, China). The capacity and the height of the reactor were determined as 1 L and 15 cm, respectively, in accordance with the E-S1 and E-S2 (Supplementary data). The gas velocity in vacant reactor was kept down to 4.5–6 cm/s, to avoid back-mix flow. The pH values of the reaction solution were tested by a waterproof pH meter (± 0.01 , PHS-3G type, Shanghai LEICI Co., China). Part of the outlet gas from the reactor (10) was monitored with a PHSJ-5 Hg^0 analyzer (11, Suzhou, Qingan Instrument Co.) and a computer (12), while the remaining part passed through a three-way-valve (13) for complete removal of Hg^0 with a solution containing 10 wt.% H_2SO_4 and 4 wt.% $KMnO_4$ in a scrubber (14) before it was vented to hood.

2.3. Experimental design

Considering many unparalleled advantages, including minimization of the number of experiments and analysis of potential interaction of factors [27,28], response surface methodology (RSM) was applied to find out the relationship between the removal efficiencies of Hg^0 and the associated factors, to evaluate the significance of each factor and their synergistic effects, and therefore to determine the optimal industrial operating conditions for the Hg^0 removal. The output response is the removal efficiency of Hg^0 (%), which was calculated as below

$$\eta_{Hg} = \left(1 - \frac{C_{Hg}}{C_{Hg0}} \right) \times 100\% \quad (E1)$$

where C_{Hg0} and C_{Hg} stand for the inlet and outlet concentrations of Hg^0 , respectively. Many factors will affect the removal efficiency of

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