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Removal of nitric oxide from simulated gas by the corona discharge combined with cobalt ethylenediamine solution

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ABSTRACT

The effects of the water flow rate, absorbent concentration, supply power voltage, pH, additive, NO concentration and gas flow rate on the NO removal efficiency were investigated, and the synergic mechanism of NO removal in the corona discharge combined with cobalt ethylenediamine (CEDA) solution was discussed. The results show that the NO removal efficiency remarkably increases with the increasing of the supply power voltage, the CEDA concentration and the water flow rate. However, the NO removal efficiency slightly decreases with the increasing of the concentration of NO and the gas flow rate. Both pH and the additive have a significant effect on the NO removal. The optimum pH for the absorbent $Co(en)_3^{3+}$ and $H_2O_2/Co(en)_3^{3+}$ were 12.0 and 10.0 respectively. The CEDA greatly increased the NO removal efficiency up to 76.5% at 25 kV, the $[Co(en)_3^{3+}]$ 0.02 M and $[H_2O_2]$ 4.0%. The NO is oxidized into NO_2 partially with active particles produced by the corona discharge in the gas, and then the mass-transfer of the NO_2 and the remaining NO in the gas phase are enhanced due to the directcorona discharge effect and catalytic reactions in solution in the reactor.

1. Introduction

The nitrogen oxide (NO) is a poisonous contaminant, which is released to the atmosphere from combustion processes such as coal-fired power plants, ferrous and non-ferrous smelters, hazardous-waste combustors and co-combustion processes of coal and biomass [1,2], to give rise to acid deposition and hazy weather, and respiratory problems to mankind. Hence, it is urgent to reduce the emission of NO to control atmospheric pollution [3,4]. The selective catalytic reduction (SCR) with ammonia is applied widely to the flue gas denitration in the large-scale industrial boiler [5,6], and the reduction rate of NO reaches 80% above. However, the disadvantages of this method are a relatively high operating costs and the ammonia escapes from the reactor to form secondary pollution. So, it is unsuitable for the flue gas denitration of the small and medium scale industrial boiler.

The possibility of NO_x reduction from exhaust gases by means of the corona discharge is intensively studied [7–12]. It reveals that the chemically active radicals produced in the ionized gaseous media interact with pollutant molecules, converting them to non-hazardous substances. The corona discharge method for the NO removal has a higher NO reduction rate by the addition of NH_3 [9]. However, compared with the corona discharged with ammonia absorption, a single corona discharge for the NO removal gains low removal efficiency. Moreover, a single corona discharge for treatment of the exhaust gases has a low energy efficiency, and generates by-products pollutants (O_3, NO_x etc).

The conventional absorption methods (chemical scrubbing) have the advantages of eliminating NO_x [13]. However, NO, the main component of NO_x, has a very low solubility in aqueous solutions, which leads to difficultly to remove NO by the conventional absorption methods. The successful use of the metal chelates or oxidant additives in the wet scrubbing systems for the NO removal is widely reported [14–27]. These methods have a high removal efficiency of NO, but most of the methods are too expensive for practical purposes, and also, oxidant additives (e.g. $KMnO_4$) are known to be a secondary pollution. $Co(en)_3^{3+}$ acts as a chelate catalyst to oxidize NO into soluble NO_2, which can increase the absorption rate of NO [16,17]. Compared with other absorption solutions, $Co(en)_3^{3+}$ is a low toxic chelate and self-regenerating, and is regarded as a good absorbent for NO removal. Some works reveal that the corona discharge combined with additional catalyst or additives (such as hydrocarbons, H_2O_2 or Mn^{2+}) increases the removal efficiency of NO_x and avoids ammonia escape [28–32]. The corona discharged with CEDA solution for treatment of the flue gas will gain economically high NO removal efficiency. However, few works focus on using the corona discharge combined with CEDA solution to remove NO from the simulated gas, and literatures on this subject are scarce.

In this work, an innovative technique of the corona discharge combined with CEDA solution was applied to remove NO from the simulated gas in the column reactor. The objective of this work was to investigate the NO removal with hybrid system consisting of a corona discharge and ethylenediamine complex solution at room temperature with no

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ammonia and to improve the energy efficiency. The effects of the water flow rate, the concentration and types of the absorbent, the supply power voltage, the pH, the NO concentration and the gas flow rate on the removal efficiency of NO were investigated. The synergic mechanism of the NO removal using the corona discharge combined with $Co(en)_3^{3+}$ in the reactor was discussed.

2. Experimental methods

As shown in Fig. 1, the experimental setup was composed of a gas supply system, corona discharge reactor, high voltage supply, water cycling system and gas measurement. The gas supply system contained NO cylinder, pump and air mixer. The reactor was a wire-cylinder electrode type and was made of polymethyl methacrylate with a length and internal diameter of 1300 mm and 140 mm, respectively. In addition, the central stainless bur wire (diameter 4 mm, length 1000 mm, bur length 3 mm) and the outer cylinder (water film) were applied to cathode and anode, respectively.

Measured amounts of cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) and ethylenediamine (abbreviated as en) ($CoCl_2 \cdot 6H_2O$/en = 1/3, *w*/*w*) were dissolved in 1000 ml distilled water, a stable complex ion $Co(en)_3^{3+}$ was formed after $CoCl_2$ dissolved in aqueous solution by simple stirring. Glutamate ethylenediamine (GEN) and cobalt GEN (CGEN) solutions were obtained in the same way. A pH-electrode was immersed into the liquid to check the pH value, which was adjusted by adding NaOH or H_2SO_4. Taking into account the HNO_3 and NO_3^- generated in the synergic reaction of NO removal in the reactor, which decreased the pH value with the increasing of reaction time, the pH-electrode was deemed to be necessary to control unchanged pH in the absorbent solution and ensure the homogeneity of the NO removal efficiency during the treatment of NO. In fact, it was observed that the controlled pH value was nearly unchanged with the increasing of the reaction time of the NO removal.

A high voltage (0–35 kV) was used for the central wire needle with the outer cylinder grounded. A feed gas stream composed of NO and atmospheric air was introduced into the inlet of the reactor. The composition of atmospheric air consists of 78.08% (V/V) nitrogen, 20.94% (V/V) oxygen, and trace components. Complex ion solution or water circulated into the inner wall of the reactor to form a water film. Treated gas was emitted through a gas-absorbing device. Except for the especial introduction, the initial NO concentration was 300 mg m^{-3}, the gas flow rate and the water flow rate were controlled in 1 m^3 h^{-1} and 60 L h^{-1} respectively, and the experiments were performed at room temperature (293 ± 1 K). The NO concentration at the inlet and outlet of the reactor was analyzed by a flue gas analyzing apparatus (Testo 350XL, Germany). The monitored range of the NO concentration was from 0 to 1000 mg m^{-3} and the precision was ±5 mg m^{-3}.

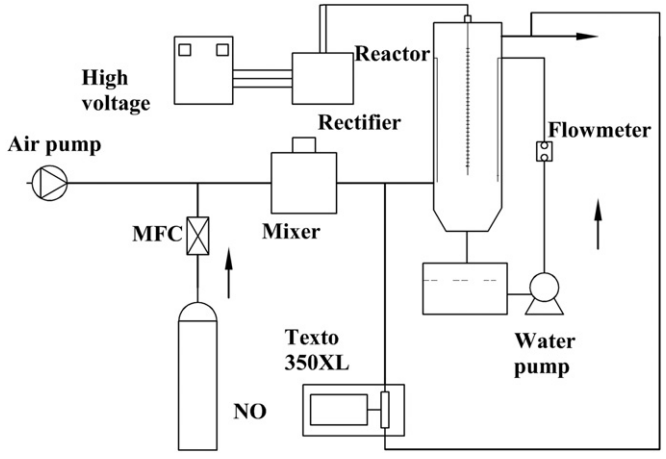

Fig. 1. The experiment schematic diagram.

The NO removal efficiency is expressed as NO conversion percentage (η) which was obtained with the inlet and outlet concentrations of NO in the reactor.

3. Results and discussion

3.1. Effect of water flow rate

As shown in Fig. 2, the corona discharge began with the needle and then tended to the water film. The corona discharge produced ion wind that interfered with the water film on the inner wall of the reactor [32].

As displayed in Fig. 2, the η increased with the increasing of the water flow rate in the range from 20 to 120 L h^{-1} at the voltage range from 0 to 30 kV. However, the large water flow rate produced high humidity which might cause spark over to affect the stabilization of the discharge corona. The η only reached 1–4% in the experiments without water, which is consistent with previous works [33]. It finds that the η had a large difference between with discharge voltage and without discharge voltage. The η was 3.7% at 100 L h^{-1} of the water flow rate without discharge voltage, while it could reach 22.7% at 100 L h^{-1} of the water flow rate and at 30 kV of the discharge voltage. It explains that the NO in the gas stream are oxidized into NO_2 by radicals and active species produced by the corona discharge, such as •O, •OH, $•HO_2$ and O_3 [34]. As Fig. 2 exhibits, the η was little with the aqueous solution, in other words, the corona discharge made nearly all contribution to reduce NO.

3.2. Effect of absorbent concentration

As shown in Fig. 3, compared with the other absorbent, the η for $Co(en)_3^{3+}$ solution was as maximum up to 70.2% at same experimental condition. It illustrates that the combining corona discharged with $Co(en)_3^{3+}$ solutions may greatly increase the NO removal efficiency. It is due to that $Co(en)_3^{3+}$ acts as an oxidation catalyst, which reacts with NO and improves the NO absorbing rate in the solution.

As displayed in Fig. 4, the η increased with the increasing of the absorbent concentration which was less than 0.02 M at 0–30 kV of the discharge voltage, and then slowly rose while the absorbent concentration exceeded 0.02 M at 25–30 kV of the discharge voltage. It seems that the higher the discharge voltage is, the larger the η is at same CEDA concentration.

Further, as exhibited in Fig. 4, the NO removal efficiency rapidly increased from 56.6% to 61.4% with the voltage range from 20 to 30 kV at [$Co(en)_3^{3+}$] 0.01 M, while only about 45.5% of NO was removed without corona discharge. It indicates that the corona discharge generates non-thermal plasma, which has a significant effect on the NO removal.

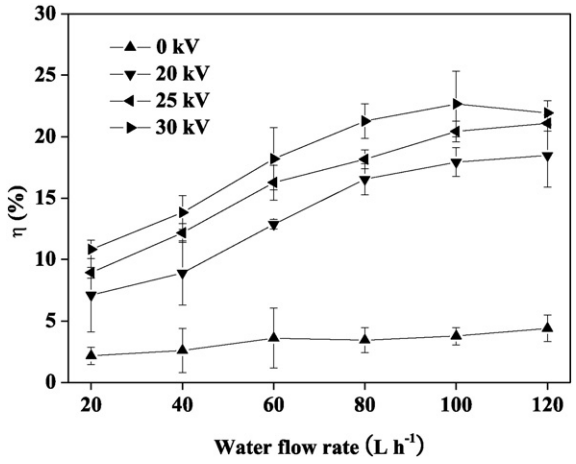

Fig. 2. Effect of the water flow rate on the NO removal (the absorbent, H_2O; the initial concentration of NO, 300 mg m^{-3}; the gas flow rate, 1 m^3 h^{-1}; the temperature, 293 ± 1 K).