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Sustainable removal of N_2O by mediated electrocatalytic reduction at ambient temperature electro-scrubbing using electrogenerated Ni(I) electron mediator

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Highlights

- A single step ambient temperature reductive electroscrubbing method was established for N_2O removal
- Nearly 95% N_2O removal efficiency was achieved by electrogenerated Ni(I)
- A new valuable product NH_3 was achieved in the electroscrubbing process.

Abstract

Direct catalysis is generally proposed for nitrous oxide (N_2O) abatement but catalysis is expensive, requires high temperatures, and suffers from media fouling, which limits its lifetime. In the present study, an ambient temperature electroscrubbing method was developed, coupling wet-scrubbing with an electrogenerated Ni(I) ($[Ni(I)(CN)_4]^{3-}$) mediator, to enable N_2O reduction in a single process stage. The initial studies of 10 ppm N_2O absorption into 9 M KOH and an electrolyzed 9 M KOH solution showed no removal. However, 95% N_2O removal was identified through the addition of Ni(I) to an electrolyzed 9 M KOH. A change in the oxidation/reduction potential from -850 mV to -650 mV occurred following a decrease in Ni(I) concentration from 4.6 mM to 4.0 mM, which confirmed that N_2O removal was mediated by an electrocatalytic reduction (MER) pathway. Online analysis identified the reaction product to be ammonia (NH_3). Increasing the feed N_2O concentration increased NH_3 formation, which suggests that a decrease in electrolyzed solution reactivity induced by the increased N_2O load constrained the side reaction with the carrier gas. Importantly, this study outlines a new regenerable method for N_2O removal to commodity product NH_3 at ambient temperature that fosters process intensification, overcomes the limitations generally observed with catalysis, and permits product

transformation to NH_3.

Keywords: N_2O removal, NH_3 formation, electroscrubbing process, electrocatalytic reduction.

1. Introduction

Nitrous oxide (N_2O) is stable in the atmosphere for prolonged periods, and is an approximately 310 times more potent greenhouse gas than carbon dioxide (CO_2) [1]. Therefore, N_2O has been categorized as the greatest contributor to stratospheric ozone depletion, and is regarded as the third most significant anthropogenic greenhouse gas [2-6]. The projected growth in N_2O emissions is estimated to reach 14.49 Mt/y by 2020. The industrial sector is regarded as the most significant emission source after agriculture, where N_2O is produced as a by-product during the manufacture of adipic acid and nitric acid, or as an intermediate in the biological nitrification of wastewater [7,8].

A range of abatement solutions can be used to control N_2O emissions, such as thermal decomposition, adsorption, and direct catalysis [9]. Catalysis is generally favored, where N_2O is reduced to nitrogen and oxygen. Although numerous catalysts have been trialed, high operating temperatures coupled with interference from the presence of other gases [10-22], and catalyst deactivation (or fouling), increase the process complexity, which can lead to technology failure, resulting in the need for frequent replenishment of the catalyst [6]. N_2O is highly soluble because of the dipole-dipole interactions with water [23], which has led to the study of N_2O absorption (or scrubbing) using packed column technology [24]. Whilst effective for gas phase separation, the absorbed N_2O is concentrated in the liquid phase but not transformed. Synergy between technologies has been investigated to provide process intensification, in which absorption is first employed to separate and concentrate N_2O from the gas phase, after which N_2O is then desorbed and exposed to a catalytic treatment to facilitate N_2O conversion (a three-stage process). Weißbach et al. [23] used desorption technology to separate and concentrate liquid phase N_2O emissions from wastewater, after which N_2O was blended with biogas (rich in methane) and combusted within a combined heat and power engine. This enables the control of N_2O emissions, whilst also increasing power generation by 37% through the exothermal release of energy from N_2O (82 kJ mol^{-1}). This method avoids the limitations attributed to catalysis, and proposes a new value to the final gaseous product. On the other hand, its application is limited explicitly to applications in which N_2O emissions and biogas generation facilities are co-located (i.e. large centralized wastewater treatment facilities).

Besides catalytic removal operated at high temperature, electrochemical technique provided room temperature degradation of many greenhouse gases by green catalyst ‘electron’, though the works done by fundamental cyclic voltammetry (CV) technique. At first step development to minimize the potential (or energy), electron mediators or catalyst were started to use because of many pollutants contain high oxidation/reduction potential such as N_2O has thermodynamic potential of +1.77 V (vs SHE) [25]. The transition or noble metals as catalyst, here as electrode, have reduce the reduction potential of N_2O to N_2 to -0.8 V (vs Ag/AgCl) [26]. On the other side, a solution phase electron mediators have used to reduce the N_2O to N_2 reduction potential to -1.15 V (vs NHE) [27] with the help of Ni^{2+} complex of [I5 or 14]aneN4 {[I5 or 14]aneN4 = 1,4,8,12(or 11)-tetra-azacyclopenta(or tetra)decane} in aqueous solution. Similar way, Ni or Pt catalyst modified gas diffusion electrode and Co(II)/Co(I) redox process of tetraaminophthalocyaninatocobalt(II) (Co(II)TAPc) adsorbed on a graphite electrode were applied on N_2O degradation to N_2 [28,29]. Note that the published works so far on electrochemical reduction of N_2O done by basic CV method to understand the fundamental electron transfer and ended up N_2 as a product. In recent investigations, the electrochemical technique stepped towards industrial practice for air pollutants removal by adopting paired electrolysis with wet scrubber column. Through the combination of paired electrolysis and wet scrubbing (electroscrubbing), many gas pollutants, such as benzene [30] and odorous gases [31] have been removed using electrogenerated oxidative mediators by MEO (mediated electrochemical oxidation). In addition, homogeneous $[Ni(I)(CN)_4]^{3-}$ was generated electrochemically on a Cu metal electrode at cathodic half-cell by constant current electrolysis for the first time and used to remove gaseous CCl_4 by MER (mediated electrochemical reduction) at electroscrubbing [32]. In a very recent study on carbon tetrafluoride (CF_4) degradation, electrochemical production of mediator Cu^{1+} facilitated a regenerative chemical reaction at room temperature, resulting in product transformation to trifluoroethane and ethanol without HF using $Cu^{1+}[Ni^{2+}(CN)_4]^{1-}$ [33]. Hence, electroscrubbing enables process intensification through the provision of separation and product transformation within a single stage, simultaneously generating a product of commercial value that can improve the return on investment.

This paper proposes to build upon the successful development of MER, and introduces Ni(I) as a new reductive electrochemical mediator, that can facilitate the effective abatement of N_2O through chemical transformation into a comparatively benign final product. The subsequent integration of MER into an electroscrubber, to form a single stage process introduces considerable process intensification versus conventionally applied methods and since MER can be operated at ambient temperature, as well as being comparatively insensitive to fouling, this proposition overcomes the limitations commonly associated with gas phase catalysis. The nickel based complexes, mostly organic/aqueous mixture solvents or modified electrodes due to insolubility, are good in effective water splitting at reduced potential [34,35]. In similar way, high potential organic compounds are reduced at less potential of electrogenerated Ni(I) complexes [36]. In addition, a planar type orientation of electrogenerated Ni(I) complexes are more reactive either by nucleophilic vs radical type reactivity depending upon the ligand [37] and more specifically, a chemically reduced $[Ni(I)(CN)_4]^{3-}$ used as hydrogenation catalysts in organic reactions [38]. Because of solubility restriction in aqueous medium, many nickel complexes used as modified electrode or dissolved in non-aqueous medium [39-42]. In reverse, $[Ni(II)(CN)_4]^{2-}$ is quite soluble in alkaline media [32] and yields a reduction potential of -900 mV(vs Ag/AgCl) [43]. Therefore, use of aqueous soluble nickel based complex such as $[Ni(II)(CN)_4]^{2-}$ may open possibilities in generation of commodity products during reduction of N_2O. Ammonia is a critical building block for many industrial and pharmaceutical chemicals, foods, and fertilizer formulations. Currently, ammonia (NH_3) is manufactured primarily through the Haber-Bosch process, which utilizes 19.3 kWh kgN^{-1} and is believed to consume 7% of natural gas globally [44]. Significant focus has recently been placed on identifying new sustainable sources of ammonia, to generate high value products from waste streams, such as the production of single cell protein [45].

This study introduces and examines the reaction pathway of MER based $[Ni(II)(CN)_4]^{2-}$, specifically to identify the potential to transform N_2O to NH_3 as a high value end product that can improve both the return on investment and sustainability criteria of the process. The specific objectives of this study were as follows: (i) demonstrate N_2O removal at room temperature in a single stage using electro-scrubbing; (ii) identify and quantify the N_2O reduction products and propose a possible reaction pathway; (iii) determine the mass transfer coefficient to describe the separation and conversion rate; and (iv) evaluate a sustainable operation in the form of reduced electron mediator Ni(I) regeneration.

2. Experimental

The supporting information section outlines the following: complete experimental details for the preparation of nickel cyanide complex reported elsewhere [46]; electrolytic cell setup with a wet scrubber for the active electron mediator generation and removal of N_2O gas (based on our experience [47,48] along with a schematic presentation (Fig.SI 1)); and the analysis type and conditions used in the present investigation.

3. Results and discussion

3.1 Identification of N_2O removal at the electroscrubber

The absorption of N_2O into KOH was initially evaluated in the recycle from the catholyte tank but without activation of the electrochemical cell or inclusion of Ni(I) to observe only the physical separation of N_2O (Fig.1). Gondal [49] reported that the solubility of N_2O was higher in KOH (7817 kPa m^{-3} $kmol^{-1}$, 1.79M KOH, 25°C) than in water (4199 kPa m^{-3} $kmol^{-1}$, 25°C). In this study, despite the initial N_2O separation of >99%, a significant decrease in removal efficiency was observed after 5 minutes operation (Fig. 1A curve a), which can be attributed to the short empty bed residence time of the column (EBRT, 0.32 min.), subsequently promoting a high N_2O solvent loading following a number of solution recycles. Although N_2O reduction has been identified on Pt [26], metal complex adsorbed electrodes [50], gas diffusion electrodes [51], and cyclic voltammetry in acidic or basic pH, the reduction of N_2O has never been evaluated in an electrolyzed solution (without an electron mediator in solution) using a metal cathode. Electrolyzation of the 9 M KOH was undertaken to discern the impact of N_2O reduction within the electroscrubber (Fig.1A, curve b). Because no dissolved electrogenerated electron mediator was present, the results are described in the form of a direct electrochemical reduction (DER). Similar to physical absorption, DER is described as the initial removal of approximately 60% N_2O (10 ppm removal in 5 min), followed by a rapid decline toward 0% removal, following continued recirculation of the solvent. A decrease in N_2O removal to 60% (Fig.1A curve b) during use of only 9 M KOH electrolyzed solution could be due a prevention of N_2O absorption into liquid, here possibly by electrogenerated molecular H_2 gas. Therefore, limited N_2O reduction occurred in the electrolyzed 9 M KOH solution, which showed that DER did not occur at the Cu electrode under the specified conditions.

In contrast, the presence of an electrogenerated electron mediation $[Ni(I)(CN)_4]^{3-}$ (Ni(I)) in 9 M KOH resulted in the near consistent 95% removal of N_2O (Fig.1A curve c) from the initiation of the experiment and for more than an hour of operation, which shows that N_2O removal is facilitated by MER (Eq. 5 and 6). A significant change in the ORP (oxidation/reduction potential) and Ni(I) concentration was observed while N_2O removal or injection to the bottom of the electro-scrubber was undertaken (Fig.1B). The decrease in Ni(I) concentration from 4.6 mM to 4.0 mM initially observed at approximately 175 minutes, which then declined further to 3.3 mM (Fig.1B curve a), indicates the consumption of Ni(I) sufficient to limit its reactivity. This was derived through changes in ORP measurements from -850 mV to -650 mV (Fig.1B curve b) while N_2O gas added.

3.2 Product analysis

Online FTIR revealed an ammonia peak in the spectrum produced from the exit gas of the electroscrubber during the MER treatment (Fig.2 curve c). Although the moisture peak dominated the spectrum, the NH_3 region (768-1190 cm^{-1}, the primary region for NH_3 evaluation) observed is coincident with that of the reference spectrum (provided in the MIDAC library, Fig. 2 curve a). Over the corresponding period, the N-O- symmetry region for N_2O gas (2158-2271 cm^{-1}, the primary region fixed to monitor N_2O) decreased; an observation compounded when referenced to the feed FTIR spectrum (Fig.2, curve d; or N_2O reference spectrum, Fig. 2, curve b). To the best of the authors' knowledge, this is the first study to report the production of NH_3 during the degradation of N_2O, which includes methods, such as catalytic decomposition [52], dielectric plasma discharge [53], and cyclic voltammetry (electrochemical) [26]. In these comparative technologies, molecular N_2 and O_2 or OH^- was confirmed as the final product [26,52,53] depending on the method used. In the gas phase, catalytic decomposition forms N_2 and O_2 (eqn. 1-3), whereas in the solution phase, N_2 and OH^- are produced through electrochemical reduction (eqn. 4) [26,52,53]:

$$\text{Catalyst}^{+1} + \text{ONN} \longrightarrow \text{Catalyst}^{+1}\text{-ONN} \quad \text{-- (1)}$$

$$\text{Catalyst}^{+1}\text{-ONN} \longrightarrow \text{Catalyst}^{+2}\text{-O}^{-} + N_2 \quad \text{-- (2)}$$

$$\text{Catalyst}^{+2}\text{-O}^{-} \longrightarrow 2\text{Catalsyt}^{+1} + O_2 \quad \text{-- (3)}$$

$$N_2O + H_2O + 2e^{-} \longrightarrow N_2 + 2OH^{-} \quad \text{-- (4)}$$

To confirm NH_3 formation, online GC-BDI-TCD was employed to analyze the exit gas produced from MER. Confirmatory analysis was complementary to that of FTIR and identified NH_3 and nitrogen dioxide (NO_2) as products (Fig 3, curve a). The NO_2 peak was evidently more intense than NH_3. This suggests that the column temperature (280 °C) coupled with carrier gas (N_2) selection for GC analysis could initiate further chemical reactions because in the photochemical removal of N_2O with air as the carrier gas, HNO_3

was identified as an additional product to N_2 and O_2 [54] via OH and NO_2 as potential intermediates. To investigate this further, the GC column temperature was reduced to 100°C, resulting in a decrease in NO_2 peak intensity (Fig.3 curve b). The carrier gas was also changed to Argon (Ar), which resulted in further minimization of the NO_2 peak (Fig.3, curve c). This suggests that NO_2 formation was an artefact of the GC analytical methodology. For corroboration, online FTIR analysis was conducted, in which no carrier gas or high temperature profile is required to facilitate analysis; only NH_3 was identified as the product with no NO or NO_2 (Fig.4). A potential explanation for NH_3 formation during N_2O reduction could be H^+ ions or $H^{+\bullet}$ radicals formed at the cathode through water splitting. The applied current density of 25 mA cm^{-2} and high cell potential (5.6 V) may promote water splitting to generate H_2 via a radical reaction at the cathode. On the other hand, pure molecular H_2 is not necessary for NH_3 formation during MER because catalytic degradation in the presence of molecular H_2 as the carrier gas identified only N_2 and O_2 as products [55]. The NH_3 concentration observed by FTIR spectroscopy at 95% N_2O removal was approximately 500 ppm (average), which is around 50 times higher than that of the feed N_2O concentration (10 ppm) when N_2 was used as the carrier gas (Fig.SI 2 curve a). GC recorded a comparable NH_3 concentration of approximately 400 ppm (average) NH_3 under analogous conditions (Fig.SI 2 curve b). This elevated NH_3 concentration from a comparatively small N_2O (10 ppm) feed concentration suggests that further chemical reactions are facilitated with N_2, H^+ ion or $H^{+\bullet}$ radicals (Eq. 5 and 6):

$$[Ni(II)(CN)_4]^{2-} + H_2O + e^- \longrightarrow [Ni(I)(CN)_4]^{3-} + 2H^{+ \text{ or } \bullet+} + O^{2-} \quad \text{-- (5)}$$

$$[Ni(I)(CN)_4]^{3-} + 12H^{+ \text{ or } \bullet+} + O^{2-} + N_2O + N_2 \longrightarrow [Ni(II)(CN)_4]^{2-} + 4NH_3 + O_2 \quad \text{-- (6)}$$

Additional, detailed analyses to confirm this will be reported elsewhere.

3.3 Efficiency analysis

Following an increase in N_2O feed gas concentration, the N_2O removal efficiency declined from almost 90% at 10 ppm N_2O feed gas to 50% at 20 ppm N_2O (Fig. 5) and further to 35% at 50 ppm N_2O. To determine the rate limiting mechanism, mass transfer analysis was undertaken and demonstrated a linear increase in the rate of N_2O conversion with increasing feed concentration (Fig. 6). An analysis of NH_3 in the exit gas produced from N_2O feed gas concentrations ranging 20 to 50 ppm N_2O showed that an increased NH_3 yield was achieved at higher feed gas concentrations (Fig. SI 3). This provides confirmatory evidence for the increased reactivity achieved at higher feed gas concentrations; the linear increase in mass transfer with feed gas concentration suggests that the reaction and subsequent conversion of N_2O to NH_3 may be pseudo first order with respect to [N_2O]. In packed column technology, mass transfer is generally described using two-film theory [56]. Although an increase in gas flow rate resulted in a small improvement in the mass transfer rate, the data suggests that the liquid phase may have exerted greater resistance to mass transfer. This was evidenced by the transient curves for the exit NH_3 gas, which exhibited a larger decline at higher gas flow rates (Fig.SI 4), and is analogous to a higher solvent loading. The faster decline in conversion efficiency at higher gas flow rates was attributed to the combination of a shorter gas phase residence time and higher solvent loading (Fig. 7 and Fig SI 4). The overall mass transfer coefficient was approximately 0.017 s^{-1}. Although this cannot be compared directly with other studies on N_2O due to the paucity of data in the literature, to contextualize the absorption rate determined in this study, this is analogous to the lower region of chemically reactive mass transfer recorded for CO_2 separation in a similarly designed packed column technology [57]. The increasing resistance to mass transfer identified in the liquid phase could be solved by increasing the solvent recirculation rate to promote replenishing of the reactant (i.e. Ni(I) complex) at the gas-liquid interface whilst simultaneously reducing the concentration boundary layer to improve N_2O transport into the bulk solution. More study will be needed to confirm this. Regenerability of the Ni(I) complex was confirmed through consecutive electroscrubbing cycles for N_2O removal (Fig.8). After each regeneration cycle, the Ni(I) concentration was recovered to the initial concentration through solution electrolysis induced after each batch N_2O removal cycle. The energy required to remove N_2O under the given conditions was 6.3 x 10^{-7} kg kWh^{-1}, which is the energy also produced to form 1.38 x 10^{-5} kg h^{-1} NH_3. Therefore, the energy spent can be minimized in the form of valuable product NH_3.

4 Conclusions

The continuous removal of N_2O at room temperature was demonstrated by integrating a mediated electrocatalytic mediator (MER) Ni(I) into the alkaline absorption solvent of a packed column. Absorption using only an alkaline or electrolyzed alkaline KOH solution showed that N_2O absorption was unsustainable, which indicated that electrogenerated Ni(I) successfully mediates N_2O removal in this electroscubber MER process. An extensive evaluation of the reaction pathway showed that MER can facilitate the transformation of N_2O to NH_3 in the presence of excess nitrogen. Therefore, such transformation is made possible only through a solution phase reaction; this provides an explicit advantage compared to conventional gas-phase technologies, and affords an opportunity to realize a new value proposition through NH_3 product recovery. As MER is applied directly to the solution phase at ambient temperature, limitations, such as fouling and substantive thermal loads, are largely obviated and it should be simple to retrofit scrubbing technology to a conventional packed column, which is applied ubiquitously for industrial scale gas-liquid separation.

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References

[1]. M.A. Zamudio, S. Bensaid, D. Fino, N. Russo, Influence of the $MgCo_2O_4$ preparation method on N_2O catalytic decomposition, Ind. Eng. Chem. Res. 50 (2011) 2622-2627.

[2] R. W. Portmann, J. S. Daniel, and A. R. Ravishankara, Stratospheric ozone depletion due to nitrous oxide: influences of other gases, Philos. Trans. R. Soc. Lond. B. Biol. Sci. 367 (2012) 1256–1264

[3] W. Wang, W. Tian, S. Dhomse, F. Xie, J. Shu, J. Austin, Stratospheric ozone depletion from future nitrous oxide, Atmos. Chem. Phys. 14 (2014) 12967–12982

[4] Richard S. Stolarski, A.R. Douglass, L.D. Oman, D.W. Waugh, Impact of future nitrous oxide and carbon dioxide emissions on the stratospheric ozone layer, Environ. Res. Lett. 10 (2015) 034011

[5] D.R. Kanter, S.P. McDermid, L. Nazarenko, Nitrous oxide's ozone destructiveness

under different climate scenarios, Proceedings of the 2016 International Nitrogen Initiative Conference, "Solutions to improve nitrogen use efficiency for the world", 4 – 8 December 2016, Melbourne, Australia

[6] R. Zhang, C. Hua, B. Wang, Y. Jiang, N_2O Decomposition over Cu–Zn/γ–Al_2O_3 Catalysts, Catalysts, 6 (2016) 200.

[7] Atomic Energy Agency (AEA), Options to Reduce Nitrous Oxide Emissions: A report produced for DGXI, AEA Technology Environment, AEAE-4180: Issue 3, Nov., 1988.

[8] International Energy Agency (IEA) (2000). Abatement of other greenhouse gases – nitrous oxide. IEA Greenhouse Gas R&D Programme, No. PH3/29, Sept., 2000.

[9] S. Kumar, A. Vinu, J. Subrt, S. Bakardjieva, S. Rayalu, Y. Teraoka, N. Labhsetwar, Catalytic N_2O decomposition on $Pr_{0.8}Ba_{0.2}MnO_3$ type perovskite catalyst for industrial emission control, Catal. Today 198 (2012) 125-132.

[10] N. Russo, D. Fino, G. Saracco, V. Specchia, N_2O catalytic decomposition over various spinel-type oxides, Catal. Today 119 (2007) 228-232.

[11] J. Haber, M. Nattich, T. Machej, Alkali-metal promoted rhodium-on-alumina catalysts for nitrous oxide decomposition, Appl. Catal. B: Environ. 77 (2008) 278-283.

[12] Q. Shen, L. Li, J. Li, H. Tian, Z. Hao, A study on N_2O catalytic decomposition over Co/MgO catalysts, J. Hazard. Mater. 163 (2009) 1332-1337.

[13] M. Hussain, D. Fino, N. Russo, N_2O decomposition by mesoporous silica supported Rh catalysts, J. Hazard. Mater. 211-212 (2012) 255-265.

[14] B.M. Abu-Zied, W. Schwieger, A. Unger, Nitrous oxide decomposition over transition metal exchanged ZSM-5 zeolites prepared by the solid-state ion-exchange method, Appl. Catal. B: Environ. 84 (2008) 277-288.

[15] G. Pekridis, N. Kaklidis, M. Konsolakis, E.F. Iliopoulou, I.V. Yentekakis, G.E. Marnellos, Correlation of surface characteristics with catalytic performance of potassium promoted Pd/Al_2O_3 catalysts: The case of N_2O reduction by alkanes or alkenes, Top. Catal. 54 (2011) 1135.

[16] N. Russo, D. Mescia, D. Fino, G. Saracco, V. Specchia, N_2O Decomposition over perovskite catalysts, Ind. Eng. Chem. Res. 46 (2007) 4226-4231.

[17] L. Xue, C. Zhang, H. He, Y. Teraoka, Catalytic decomposition of N_2O over CeO_2 promoted Co_3O_4 spinel catalyst, Appl. Catal. B: Environ. 75 (2007) 167-174.

[18] N. Pasha, N. Lingaiah, P. Siva Sankar Reddy, P.S. Sai Prasad, An investigation into the effect of Cs promotion on the catalytic activity of NiO in the direct decomposition of N_2O, Catal. Lett. 118 (2007) 64-68.

[19] E. Iwanek, K. Krawczyk, J. Petryk, J.W. Sobczak, Z. Kaszkur, Direct nitrous oxide decomposition with CoO_x-CeO_2 catalysts, Appl. Catal. B: Environ. 106 (2011) 416-422.

[20] M. Zabilskiy, P. Djinović, E. Tchernychova, O.P. Tkachenko, L.M. Kustov, A. Pintar, Nanoshaped CuO/CeO_2 Materials: Effect of the exposed ceria surfaces on catalytic activity in N_2O decomposition reaction, ACS Catal. 5 (2015) 5357-5365.

[21] X. Zhang, Q. Shen, C. He, Y. Wang, J. Cheng, Z. Hao, CoMOR zeolite catalyst prepared by buffered ion exchange for effective decomposition of nitrous oxide, J. Hazard. Mater. 192 (2011) 1756-1765.

[22] N. Pasha, N. Lingaiah, P.S.S. Reddy, P.S.S. Prasad, Direct decomposition of N_2O over cesium-doped CuO catalysts, Catal. Lett. 127 (2009) 101-106.

[23] M. Weißbach, F. Gossler, J.E. Drewes, K. Koch, Separation of nitrous oxide from aqueous solutions applying a micro porous hollow fiber membrane contactor for energy recovery, Sep. Purif. Technol. 195 (2018) 271-280.

[24] J. Kuropka, Removal of nitrogen oxides from flue gases in a packed column, Environ. Prot. Eng. 37 (2011) 13-22.

[25] K. Kanazawa, H. Yamamura, M. Nakayama, K. Ogura, Electrochemical reduction of nitrous oxide by the protons transported through polyelectrolyte-coated porous glass, J. Electroanal. Chem. 521 (2002) 127-131.

[26] K.E. Johnson, D.T. Sawyer, The electrochemical reduction of nitrous oxide in alkaline solution, J. Electroanal. Chem. 49 (1974) 95-103.

[27] I. Taniguchi, T. Shimpuku, K. Yamashita, H. Ohtaki, Electrocatalytic reduction of nitrous oxide to dinitrogen at a mercury electrode using Ni(II) complexes of macrocyclic polyamines, J. Chem. Soc. Chem. Comm. (1990) 915-917.

[28] K. Nozomi, H. Kohjiro, K. Akihiko, S. Tadayoshi, Electrochemical Reduction of N_2O on Gas-Diffusion Electrodes, B. Chem. Soc. Jpn. 69 (1996) 2159-2162.

[29] J. Zhang, Y.-H. Tse, A.B.P. Lever, W.J. Pietro, Electrochemical reduction of nitrous oxide (N_2O) catalysed by tetraaminophthalocyanatocobalt(II) adsorbed on a graphite electrode in aqueous solution, J. Porphyr. Phthalocya. 1 (1997) 323-331.

[30] M. Govindan, S.J. Chung, H.-H. Moon, J.W. Jang, I.-S. Moon, Moon, Development of a Biphasic Electroreactor with a Wet Scrubbing System for the Removal of Gaseous Benzene, ACS Combi. Sci. 15 (2013) 439-446.

[31] M. Govindan, I.-S. Moon, A single catalyst of aqueous Co^{III} for deodorization of mixture odor gases: A development and reaction pathway study at electro-scrubbing process, J. Hazard. Mater. 260 (2013) 1064-1072.

[32] G. Muthuraman, I.S. Moon, Sustainable Generation of a Homogeneous Ni(I) Catalyst in the Cathodic Compartment of a Divided Flow Electrolytic Cell for the Degradation of Gaseous Carbon Tetrachloride by Electroscrubbing, ACS Sustainable Chem. Eng. 4 (2016) 1364-1372.

[33] G. Muthuraman, A.G. Ramu, Y.H. Cho, E.J. McAdam, I.S. Moon, Sustainable degradation of carbon tetrafluoride to non-corrosive useful products by incorporating reduced electron mediator within electro-scrubbing, J. Ind. Eng. Chem. 63 (2018) 275-280.

[34] C.M. Klug, W.G. Dougherty, W.S. Kassel, E.S. Wiedner, Electrocatalytic Hydrogen Production by a Nickel Complex Containing a Tetradentate Phosphine Ligand, Organometallics 38 (2019) 1269-1279.

[35] G. Azadi, Z. Zand, Y. Mousazade, R. Bagheri, J. Cui, Z. Song, R. Bikas, K. Wozniak, S.I. Allakhverdiev, M.M. Najafpour, A tetranuclear nickel(II) complex for water oxidation: Meeting new challenges, Int. J. Hydrogen Energy 44 (2019) 2857-2867.

[36] E.T. Martin, A.L. Goodson, C.M. McGuire, J.A. Rose, A. Ourari, M.S. Mubarak, D.G. Peters, Catalytic reduction of 1-bromodecane and 1-iododecane by electrogenerated, structurally modified nickel(I) salen, J. Electroanal. Chem. 815 (2018) 225-230.

[37] E. Dunach, M.J. Medeiros, S. Olivero, Electrochemical cyclizations of organic halides catalyzed by electrogenerated nickel(I) complexes: towards environmentally friendly methodologies, Electrochim. Acta 242 (2017) 373-381.

[38] T. Mizuta, H. Samejima, T. Kwan, Hydrogenation, Hydrogenolysis, or Isomerization of Dienes and Monoenes Catalyzed by the Nickel Cyanide Complex, B. Chem. Soc. Jpn. 41 (1968) 727-729.

[39] O.V. Zhalko-Titarenko, O.A. Lazurskii, V.D. Pokhodenko, Electrocatalytic reduction of carbon dioxide on electrodes modified by polypyrrole with an immobilized complex of nickel with 1,4,8,11-tetraazacyclotetradecane, Theor. Exp. Chem. 26 (1990) 40-44.

[40] L.A.M. Baxter, A. Bobrowski, A.M. Bond, G.A. Heath, R.L. Paul, R. Mrzljak, J. Zarebski, Electrochemical and spectroscopic investigation of the reduction of dimethylglyoxime at mercury electrodes in the presence of cobalt and nickel, Anal. Chem. 70 (1998) 1312-1323.

[41] O. Pantani, E. Anxolabehere-Mallart, A. Aukauloo, P. Millet, Electroactivity of cobalt and nickel glyoximes with regard to the electro-reduction of protons into molecular hydrogen in acidic media, Electrochem. Commun. 9 (2007) 54-58.

[42] M.K. Kadirov, I.R. Knyazeva, I.R. Nizameev, R.A. Safiullin, V.I. Matveeva, K.V. Kholin, V.V. Khrizanforova, T.I. Ismaev, A.R. Burilov, Y.H. Budnikova, O.G. Sinyashin, Oxygen reduction reaction catalyzed by nickel complexes based on thiophosphorylated calix[4]resorcinols and immobilized in the membrane electrode assembly of fuel cells, Dalton T. 45 (2016) 16157-16161.

[43] M. Orlik, Z. Galus, Electrochemistry of the nickel-cyanide system at mercury electrodes. Part III. The role of intermediate products in the mechanism of tetracyanonickelate(2+) electroreduction at mercury electrodes, J. Electroanal. Chem. Interfacial Electrochem. 248 (1988) 139-158.

[44] P.L. McCarty, J. Bae, J. Kim, Domestic wastewater treatment as a net energy producer–can this be achieved?, Environ. Sci. Technol. 45 (2011) 7100-7106.

[45] W. Verstreate, Microbial single cell protein revisited. 3rd iwa specialized international conference on ecotechnologies for wastewater treatment (ecoSTP16), 27-30 Jun 2016, Cambridge, UK

[46] W.C. Fernelius, J.J. Burbage, N.E. Ballou, Potassium Tetracyanonickelate(II), in: Inorganic Syntheses, John Wiley & Sons, Inc., New York, 2007, p. 227.

[47] M. Govindan, R. A.Gopal, I.S. Moon, Gaseous trichloroethylene removal using an

electrochemically generated homogeneous low-valent ligand-free Co(I) electrocatalyst by electro-scrubbing, J. Hazard. Mater. 311 (2016) 210-217.

[48] M. Govindan, R.A. Gopal, H.G. Ahn, I.S. Moon, Synergistic effect of mediated electrochemical reduction and mediated electrochemical oxidation on no removal by electro-scrubbing, J. Electrochem. Soc. 163 (2016) E390-E396.

[49] S. Gondal, Carbon dioxide absorption into hydroxide and carbonate systems, PhD Thesis, NTNU, Norway, October 2014.

[50] J. Zhang, Y.-H. Tse, A.B.P. Lever, W.J. Pietro, Electrochemical reduction of nitrous oxide (N_2O) catalysed by tetraaminophthalocyanatocobalt(II) adsorbed on a graphite electrode in aqueous solution, J. Porphyr. Phthalocya. 1 (1997) 323-331.

[51] K. Nozomi, H. Kohjiro, K. Akihiko, S. Tadayoshi, Electrochemical reduction of N_2O on gas-diffusion electrodes, B. Chem. Soc. Jpn. 69 (1996) 2159-2162.

[52] M. Zabilskiy, P. Djinovic, B. Erjavec, G. Drazic, A. Pintar, Small CuO clusters on CeO_2 nanospheres as active species for catalytic N_2O decomposition, Appl. Catal., B 163 (2015) 113-122.

[53] Q.-H. Trinh, S.H. Kim, Y.S. Mok, Removal of dilute nitrous oxide from gas streams using a cyclic zeolite adsorption-plasma decomposition process, Chem. Eng. J. 302 (2016) 12-22.

[54] M. Tsuji, N. Kamo, M. Senda, M. Kawahara, T. Kawahara, N. Hishinuma, Photochemical removal of N_2O in N_2 or air using 172 nm excimer lamps, Jpn. J. Appl. Phys. 48 (2009) 046002/046001-046002/046008.

[55] W.-H. Yang, M.H. Kim, Catalytic reduction of N_2O by H_2 over well-characterized Pt surfaces, Korean J. Chem. Eng. 23 (2006) 908-918.

[56] E.S. Gaddis, Mass transfer in gas–liquid contactors, Chem. Eng. Process.: Process Intensification 38 (1999) 503-510.

[57] P.-C. Chen, Absorption of carbon dioxide in a bubble-column scrubber. In: Greenhouse Gases – Capturing, utilization and reduction, Ed. G. Liu, Intech Open Ltd., London, UK, 2012.

Fig.1A

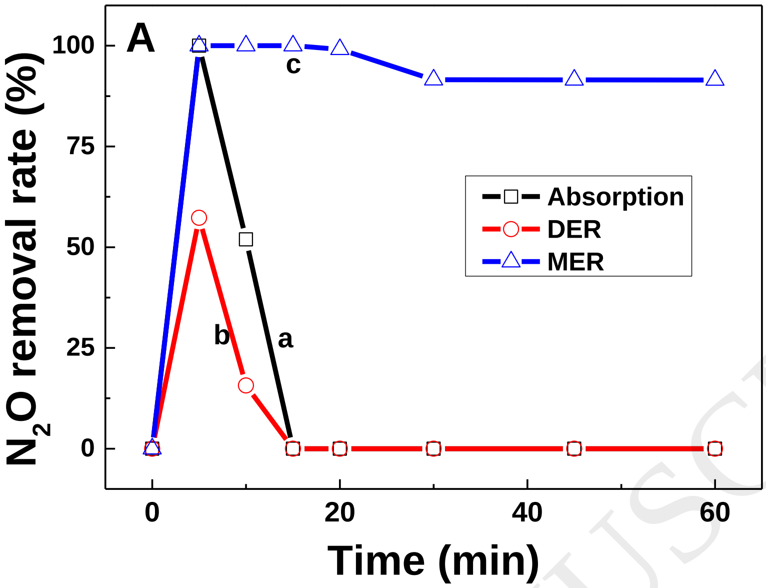
A
100
75
50
25
0
N_2O removal rate (%)
0
20
40
60
Time (min)
Absorption
DER
MER
a
b
c

Fig.1B

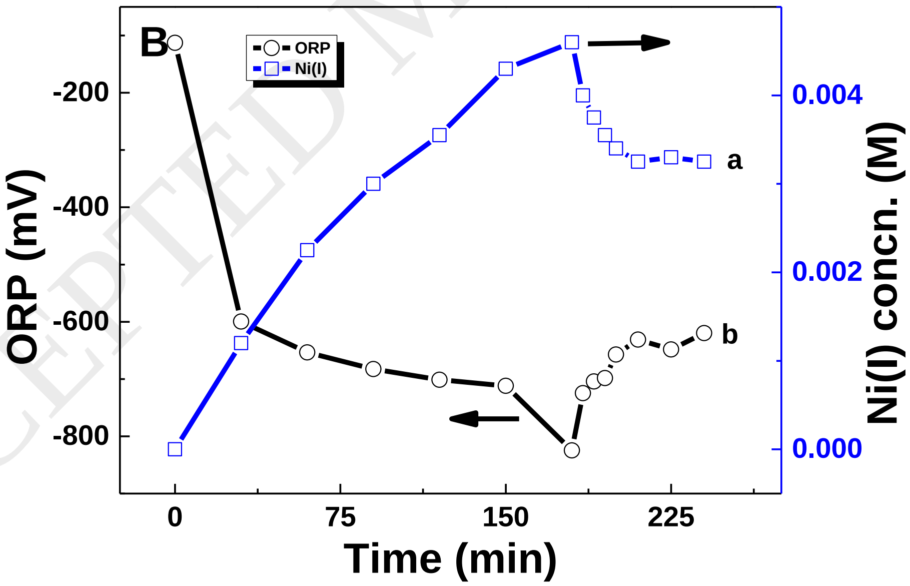
B
ORP
Ni(I)
-200
-400
-600
-800
ORP (mV)
0.004
0.002
0.000
Ni(I) concn. (M)
0
75
150
225
Time (min)
a
b

Fig.1 **A** Removal efficiency of N_2O with time during (a) only absorption by 9 M KOH, (b) during electrolysis of 9 M KOH, (c) during electrolysis in the presence of 50 mM $[Ni(II)(CN)_4]^{2-}$ in 9 M KOH at the wet scrubber. Conditions: Electrolyte volume = 600 ml; electrodes = Pt coated Ti anode (50 cm^2) and Cu cathode (50 cm^2); Current density = 25 mA cm^{-2}; Solution flow rate to cell = 2 L min^{-1}; Solution flow rate to scrubber = 3 L min^{-1}; Gas flow rate = 0.2 L min^{-1} with 10 ppm of N_2O.

B ORP and $[Ni(I)(CN)_4]^{3-}$ concentration change during the removal of N_2O at the electroscrubber. The electrolysis and electroscrubbing experimental conditions were the same as those detailed in the legend of **Fig.1A**.

Fig.2

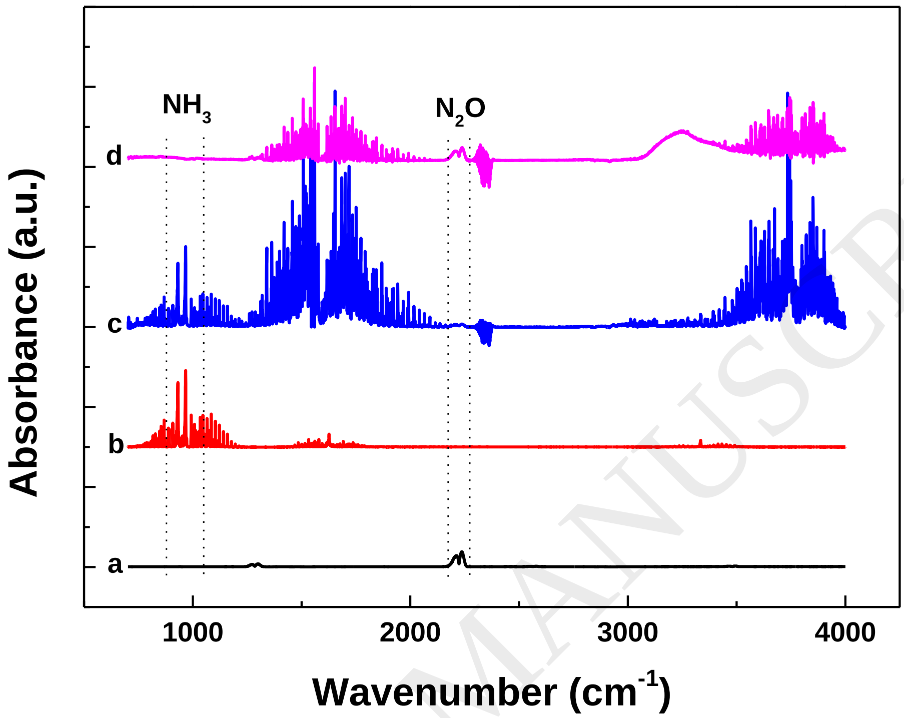

Fig.2 Online FTIR output results (a) standard spectrum for N_2O, (b) standard spectrum for NH_3, (c) NH_3 formation during N_2O removal, (d) direct feed of N_2O into scrubber at electroscrubbing process. The electrolysis and electroscrubbing experimental conditions were the same as those detailed in the legend of **Fig.1A**.

Fig.3

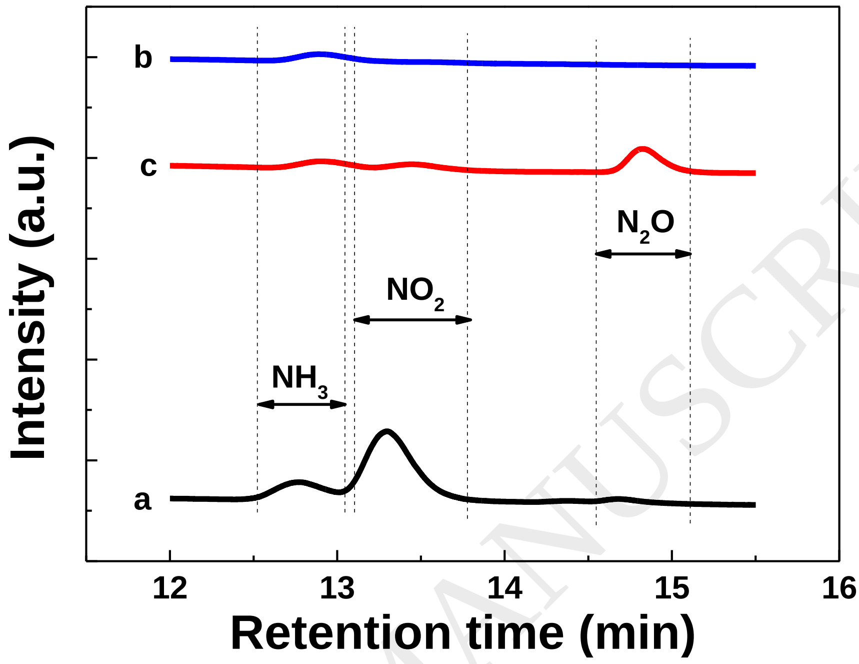

Fig.3 Online GC output results during 10 ppm N_2O removal under different conditions: (a) Removal by MER with a GC column temperature at 280 °C; (b) Direct feed of 10 ppm N_2O into GC with a column temperature at 100 °C; (c) Direct feed of 10 ppm N_2O with an Ar carrier gas at GC column temperature of 280 °C. Experimental conditions for MER by electroscrubbing and gas flow rate were the same as those detailed in the legend of **Fig.1A**.

Fig.4

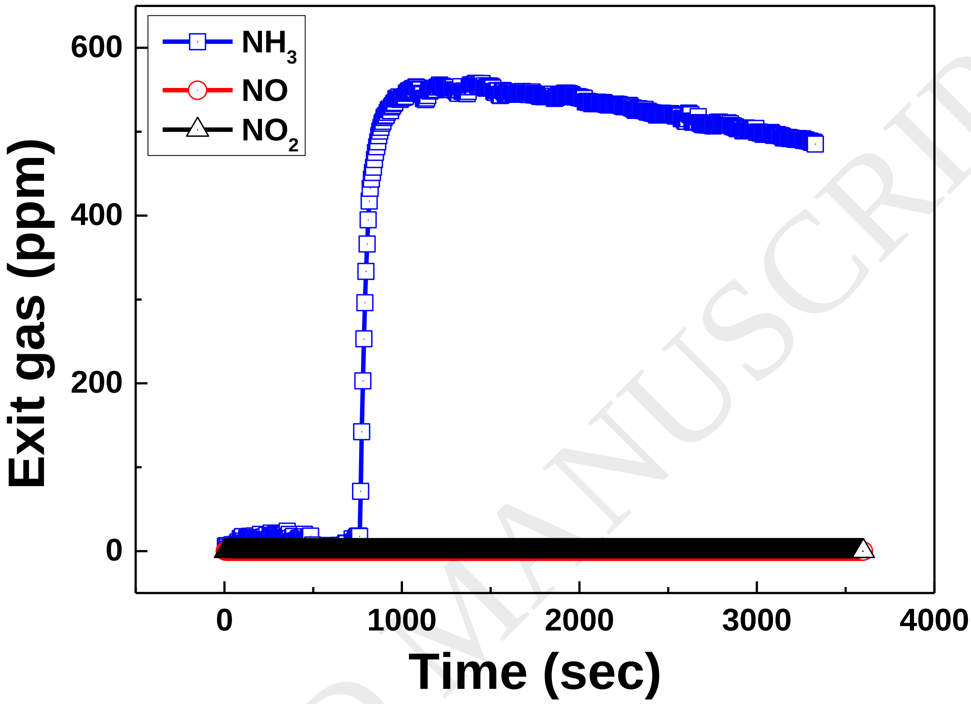

Fig.4 Exit gas concentration variation at the electroscrubber during the removal of N_2O by MER measured by online FTIR spectroscopy. The electrolysis and electroscrubbing experimental conditions were the same as those in the legend of **Fig.1A**.

Fig.5

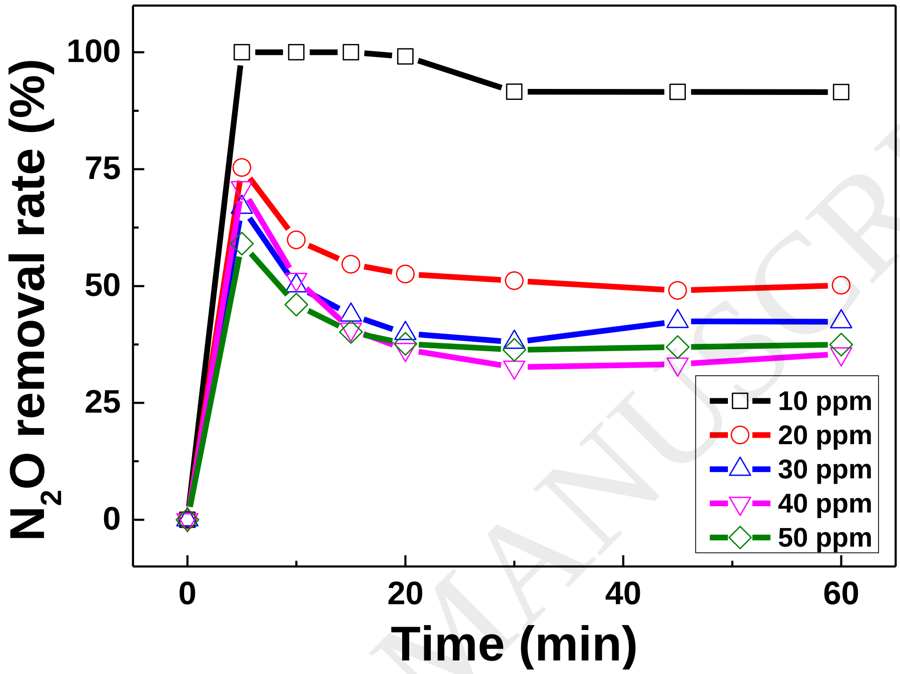

Fig.5 Removal efficiency variation of N_2O with different feed N_2O concentrations (mentioned in the figure) during MER by electrogenerated $[Ni(I)(CN)_4]^{3-}$ in 9 M KOH at the electroscrubber. The electrolysis and electroscrubbing experimental conditions were the same as those in the legend of **Fig.1A**.

Fig.6

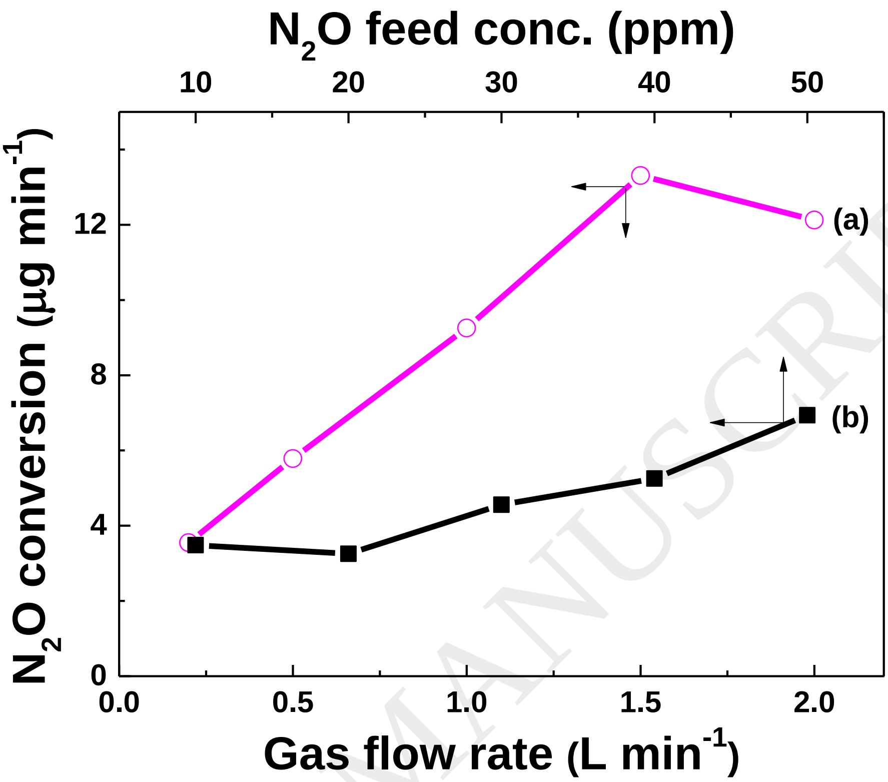

Fig.6 Mass conversion rate during N_2O removal by the gas flow rate (a) and N_2O feed concentration (b) at electro-scrubbing by electrogenerated $[Ni(I)(CN)_4]^{3-}$ in 9 M KOH solution. The electrolysis and electroscrubbing experimental conditions were the same as those in the legend of **Fig.1A.**

Fig.7

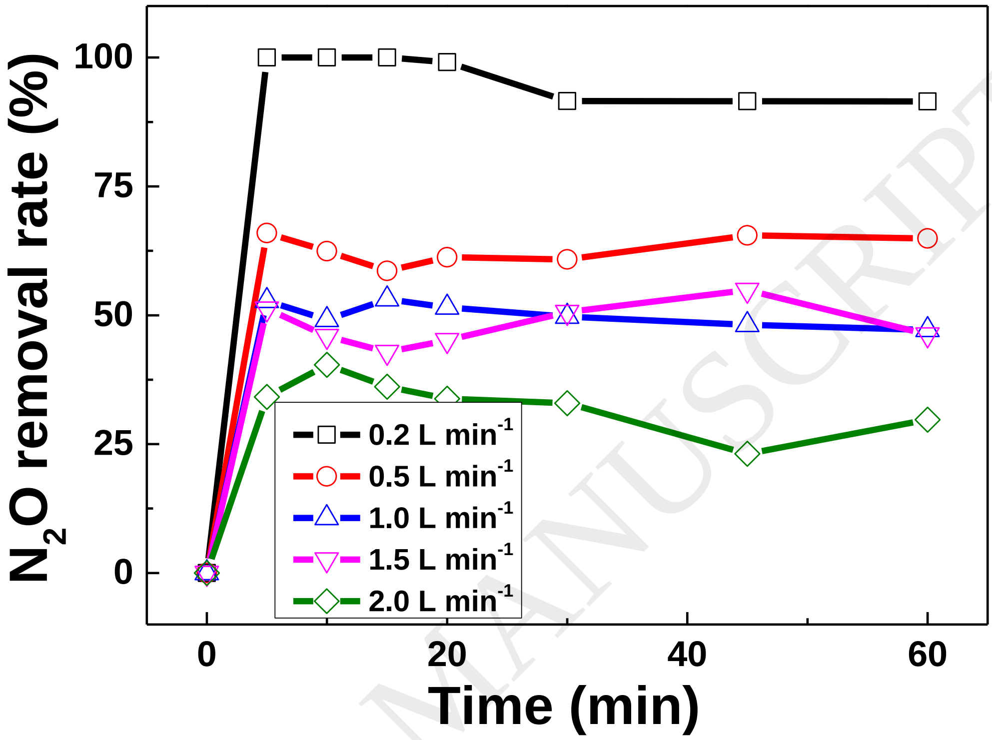

Fig.7 Removal efficiency of N_2O with different gas flow rates (mentioned in the figure) during MER by electrogenerated $[Ni(I)(CN)_4]^{3-}$ in 9 M KOH at the electroscrubber. The electrolysis and electroscrubbing experimental conditions were the same as those in the legend of **Fig.1A.**

Fig.8

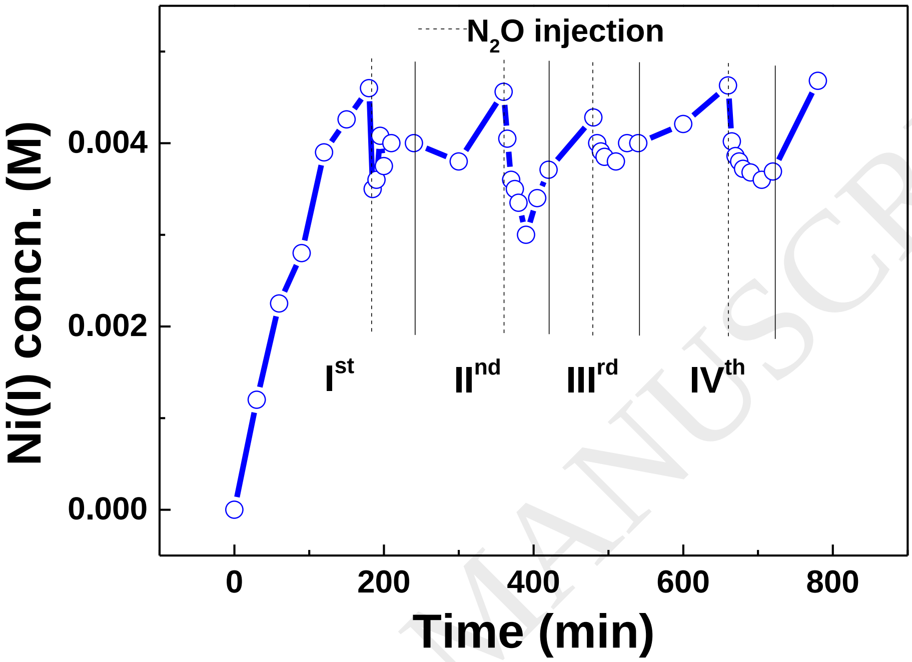

Fig.8 Variation of $[Ni(I)(CN)_4]^{3-}$ concentration with electrolysis time and N_2O removal time by electro-scrubbing for the four consecutive experimental batches towards sustainability. The experimental conditions were the same as those detailed in the legend of **Fig.1A**.