

Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/he

HCl removal from biogas for feeding MCFCs: Adsorption on microporous materials

Luca Micoli*, Giovanni Bagnasco, Maria Turco

Dipartimento di Ingegneria Chimica, Università di Napoli Federico II, P.le Tecchio, 80125 Napoli, Italy

ARTICLE INFO

Article history:

Received 15 March 2012

Received in revised form

9 August 2012

Accepted 17 September 2012

Available online 16 October 2012

Keywords:

HCl removal

Biogas

13X zeolite

Active carbon

Adsorption

MCFC

ABSTRACT

Modified 13X zeolites and active carbons were studied for HCl adsorption from biogas employed as fuel of MCFCs. 13X zeolite was modified by addition of Cu or Zn by ion exchange or impregnation: commercial active carbon was modified by impregnation with KOH, NaOH or Na₂CO₃ solutions. The materials were tested for HCl adsorption in a laboratory apparatus designed to the scope. The tests were carried out under flow conditions with a 100 ppm HCl/N₂ mixture at T = 40 °C and atmospheric pressure. Breakthrough curves were obtained from potentiometric analysis of HCl in the stream effluent from the adsorption cell. The zeolites modified by ion exchange were more effective for HCl adsorption than those modified by impregnation. The active carbon modified with Na₂CO₃ solution showed the highest adsorption capacity of 3.3 × 10⁻⁴ mol HCl g⁻¹ at breakthrough concentration of 1 ppm.

Copyright © 2012, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Molten carbonate fuel cells (MCFCs) are gaining great interest for power production due to their high efficiency and the possibility of using biomass derived fuels, with obvious environmental advantages. Since MCFCs work at high temperatures (600–700 °C), catalysts based on Ni instead of noble metals can be used at the electrodes [1,2]. Although MCFCs appear more attractive than other fuel cells due to relatively low costs, some problems still have to be solved. Those issues are named: degradation and short lifetime of cells due to some poisonous compounds contained in the raw biogas feed [3,4]. Therefore, a clean-up step is necessary by adsorption on suitable materials that must guarantee low residual concentration, high selectivity and easy regenerability [5]. The research activity on purification of biogas for

feeding MCFCs is mainly addressed to the elimination of sulphur compounds, that can poison Ni catalysts. Several materials have been studied for this purpose, among which zeolites and active carbons appear the most promising [5,6]. Zeolites show some advantages as adsorbent materials having a high adsorption capacity and selectivity, moreover they are more stable at high temperatures than other materials such as active carbons. However active carbons are widely proposed due to the high surface area and porosity [7]. Adsorption properties of zeolites and active carbon can be properly modified by treatments aimed to introduce specific adsorption functions [8]. It was found that the addition of metal ions or metal oxides increases the adsorption capacity of zeolites: Cu and Zn are largely proposed in literature and can be easily introduced in the zeolite structure [9,10]. On the other hand, the adsorption

* Corresponding author. Tel.: +39 0817682259; fax: +39 0815936936.

E-mail address: luca.micoli@unina.it (L. Micoli).

properties of active carbon can be improved by treatments with basic solutions [7,11].

While the issue of sulphur content in biogas has been studied in several works, no attention has been paid to the presence of acid contaminants, such as HCl and HF, that can impair the performances of MCFCs [3,4]. In particular, HCl is often present in biogas coming from landfill or biomass burned gases in amount varying from few tens to 1500–2000 ppm depending on the composition of the burned material [12–14] and, in smaller content, in biogas produced from sewage sludge and organic waste [15,16]. Hydrated lime or limestone are used for removal of HCl from biomass burned gases or incinerator flue gases [17,18]. However, this method, due to low conversion efficiencies, does not allow to achieve the high purification levels required for MCFC applications [19]. The MCFCs tolerance limit for HCl is <1 ppm [3] so an adequate cleaning process is required to obtain the purification of the feed.

In this work, Cu and Zn modified 13X zeolites and active carbons treated with alkaline solutions are studied for HCl removal from biogases. Similar materials gave promising results for the adsorption of sulphur compounds [6,20], so it is expected that they could be effective also for HCl removal. The use of these materials would allow the elimination of sulphur and acid contaminants from raw biogases in a single-step process, with obvious advantages for the economics and simplicity of the process. Active carbons and zeolites also remove HCl in fume hood systems [21]. The materials were obtained by ion exchange and impregnation methods: 13X zeolite was exchanged with Cu^{2+} or Zn^{2+} ions and impregnated with precursor salts of CuO or ZnO; the active carbon was impregnated with alkaline solutions of NaOH, KOH or Na_2CO_3 . These materials were tested in a properly made laboratory plant under diluted flow conditions.

2. Experimental

Commercial 13X zeolite (Si/Al ratio = 1.5, spherical, $d = 1.6$ mm) was supplied by Union Carbide; active carbon (RGM3) by Norit® (cylindrical, $d = 3$ mm, $l = 7$ mm).

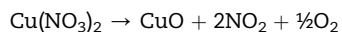
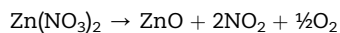
2.1. Modified zeolites preparation

Modified zeolites were prepared by ion exchange or impregnation methods.

The ion exchange was performed by treating 3 g zeolite with 250 mL of 0.1 M solution of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ or $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ under stirring at 80 °C for 2 h. Afterwards the sample was separated from the solution and dried at 120 °C for 2 h, then thermally treated in air flow at 250 °C for 2 h.

The impregnation of the zeolite was carried out under vacuum conditions obtained with a Venturi tube to enhance the penetration of the solution into the material pores. The sample (3 g) was impregnated to incipient wetness with 3 mL of 0.1 M solution of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ or $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 40 °C under stirring conditions. The sample was dried at 120 °C for 2 h and thermally treated in air flow at 250 °C for 2 h. The

thermal treatment leads to the decomposition of the nitrates and the formation of zinc or copper oxide, as follows:



2.2. Modified active carbons preparation

Active carbons (AC) were modified by impregnation under vacuum as suggested by previous papers regarding biogas purification [22,23]. The sample (3 g) was impregnated with 3 mL of 10% w/w alkaline solutions of NaOH, KOH or Na_2CO_3 at 40 °C and under stirring conditions. The sample was dried at 120 °C for 2 h and treated in air flow at 250 °C for 2 h.

The materials were characterised by scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) for the elemental analysis using a Philips XL 30 apparatus. Surface area measurements were carried out by N_2 adsorption at –196 °C using a Micromeritics ASAP 2020 instrument. The samples were pretreated at 250 °C under vacuum for 2 h.

2.3. Apparatus for HCl adsorption tests

HCl adsorption tests were carried out in a new experimental apparatus designed for the purpose (Fig. 1). The apparatus operates under flow conditions and at atmospheric pressure. It consists of three main sections: the feeding system, the adsorption cell containing the material under test and the analysis system. The gaseous feed containing 100 ppm HCl was obtained by bubbling pure N_2 ($100 \text{ cm}^3 \text{ min}^{-1}$) through a 22% w/w HCl/ H_2O solution at constant temperature of 0 °C. Water vapour was removed from the gaseous stream by a P_2O_5 trap (Sicapent, Merck). The saturation of the gaseous mixture was ascertained by titration after HCl dissolution in a Na_2CO_3 solution. The adsorption cell containing the material under test (200 mg) consisted in a U glass tube (i.d. = 0.4 cm) maintained at 40 °C by a water bath equipped with a PID controller. The samples were treated at 250 °C for 2 h in air flow ($100 \text{ cm}^3 \text{ min}^{-1}$) before the tests. HCl effluent from the adsorption cell was analysed using an original procedure based on potentiometric measurement. The stream effluent from the cell was bubbled through a test tube containing distilled water (40 cm^3) in which HCl dissolved. The test tube was properly designed to guarantee the complete HCl dissolution in the water. Preliminary tests with different amounts of water and depth of the bubbling point allowed to optimise the operating conditions: the complete HCl dissolution was ascertained by analysing the outlet gas. A pH probe HI1131B connected to a Hanna HI3220 pH meter was immersed in the solution. The pH value measured at a given time allowed to determine the amount of HCl dissolved in water until that time, that corresponds to the amount not adsorbed by the material: from these data, by a derivative procedure, the HCl concentration in the effluent from the cell was obtained as a function of time. In this way the breakthrough curve was obtained. Preliminary blank tests with the cell filled with an

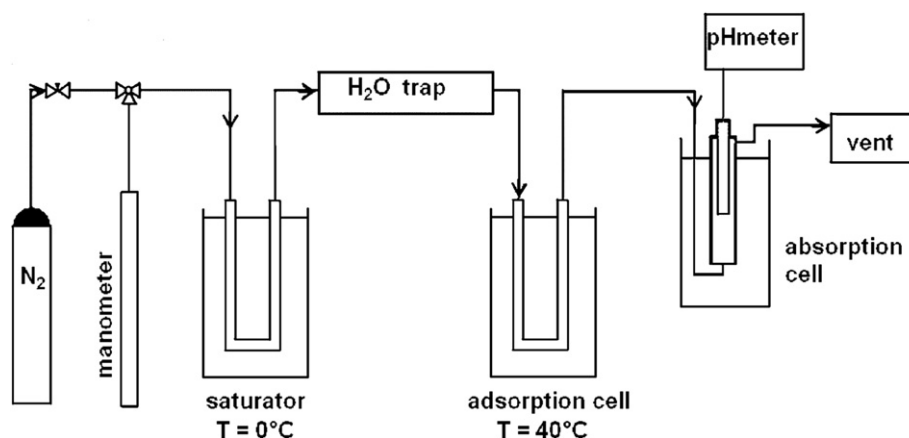


Fig. 1 – Experimental apparatus for tests of HCl adsorption.

inert material were carried out to check the accuracy of the method. The accuracy in HCl concentration in the gaseous phase was within ± 5 –10%, the highest error occurring at pH values close to neutrality. The sensitivity was as low as a fraction of 1 ppm HCl in the gaseous phase.

3. Results and discussion

The metal content and surface area of the modified zeolites and active carbons are reported in Table 1. It can be observed that 13X zeolites modified by ion exchange show higher metal contents compared to those modified by impregnation. This can be related to the large excess of solution employed in the exchange method. The metal content of exchanged samples is close to the amount corresponding to total exchange (5.8 meq g^{-1}). It must be noted that besides Na^+ other cations are exchanged (such as K^+ , Ca^{2+} and Mg^{2+}). Ion exchange, but not impregnation, causes a decrease of surface area, that however is still high. Such a reduction of surface area generally occurs when zeolites are modified with metal ions and is probably due to the formation of clusters of metal oxides that partially occlude micropores [24].

The modification of active carbon by the impregnation method causes negligible variation of surface area for the samples AC–NaOH and AC– Na_2CO_3 while an increase of surface area is observed for the sample AC–KOH. These results agree with previous data reported for similar modified ACs [22,23] and can be due to two opposite effects. The

chemical action of a strong base such as KOH and NaOH can lead to a textural modification of the active carbon causing an increase of surface area: on the other hand the presence of this additive can lead to the occlusion of some pores of the carbon causing a decrease of surface area. Probably the first effect prevails in the sample AC–KOH, that contains a lower amount of the additive, while the two effects balance in the other samples due to the higher content of the basic additive.

Breakthrough curves of the zeolitic samples are reported in Fig. 2.

The shapes of the breakthrough curves of the materials appear quite different from each other. This suggests different kinetics of HCl adsorption. Nevertheless, a detailed analysis of adsorption kinetics lies outside the aim of this work. The curve of not modified 13X (Fig. 2), after a very short delay time in which HCl concentration is below the detection limit ($\sim 0.1 \text{ ppm}$), shows a steady increase of HCl concentration with time up to about 120 min, then the slope reduces.

The breakthrough curves of Cu modified zeolites, 13X-Ex-Cu and 13X-Im-Cu, are quite similar, showing a delay time of about 40 min, after which HCl concentration increases steadily.

As regards the zeolites modified with Zn, a noticeable difference can be observed between the samples prepared by impregnation and by ion exchange. The former gives a breakthrough curve with a delay of about 40 min before the appearance of HCl, after which HCl concentration increases rapidly to values higher than 10 ppm. The latter shows a much longer delay of about 110 min before HCl detection, then HCl

Table 1 – Composition and surface area of the 13X zeolites modified.

Sample	Preparation method	Metal content (mmoleq g^{-1})				Surface area ($\text{m}^2 \text{g}^{-1}$)
		Cu^{2+}	Zn^{2+}	Na^+	Others (K^+ , Ca^{2+} , Mg^{2+})	
13X	–	–	–	3.65	1.92	582
13X-Ex-Cu	Ion exchange	4.66	–	0.22	1.48	370
13X-Ex-Zn	Ion exchange	–	5.46	0.16	1.10	356
13X-Im-Cu	Impregnation	1.80	–	3.44	1.90	575
13X-Im-Zn	Impregnation	–	0.50	3.60	1.89	585

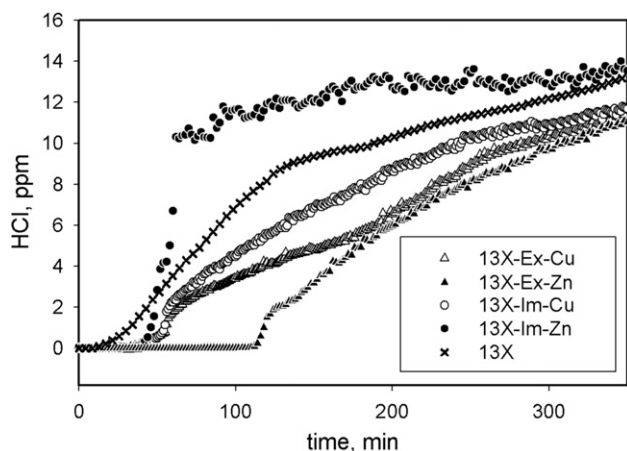


Fig. 2 – Breakthrough curves of modified 13X zeolites.

concentration increases steadily and approaches the values of the other samples at the end of the test.

The shape of the curves suggests that the rate of adsorption is gradually reduced with time: this behaviour is probably related to diffusive resistance in the narrow pores of the zeolite ($d \approx 8 \text{ \AA}$). Obviously this resistance increases with time due the increase of the amount of adsorbate in the pores.

At the end of the test, the zeolitic samples are not yet saturated with HCl. For the not modified zeolite it is assumed that HCl is chemisorbed according to Eq. (1)



where only Na^+ cation is considered for simplicity, but other ones, such as K^+ , Ca^{2+} , Mg^{2+} , can also be involved. On the basis of this assumption, the amount of HCl corresponding to saturation must equal the equivalent ion content of the zeolite, that is about $5.6 \text{ mmoleq g}^{-1}$. A similar value can be assumed for exchanged zeolites, where Na^+ is substituted by equivalent amount of Cu^{2+} or Zn^{2+} , while for the impregnated zeolites a higher value is expected due to the presence of the basic oxides CuO or ZnO . The total amount of HCl adsorbed during the tests varies between the minimum of 0.65 mmol g^{-1} for 13X-Im-Zn and the maximum of 0.70 mmol g^{-1} for 13X-Ex-Zn: therefore the HCl uptake is always far below the expected saturation value. However, for the purpose of employing these materials for biogas purification, more interesting than the adsorption capacity is the ability of the materials to maintain a low residual HCl concentration for a long time. To evaluate the performances of the materials in view of a practical application, we consider that the HCl tolerance limit for MCFCs is about 1 ppm. For this reason, the breakthrough times at 1 ppm and the corresponding amounts of adsorbed HCl are reported in Table 3 for each material.

These data show that the performance of modified zeolites is mainly related to the metal content. As said in the Introduction, the choice of Cu/Zn modified zeolites was not suggested by the adsorption properties towards HCl, but by the aim of using the same materials proposed for elimination of sulphur compounds [25,26]. In the case of impregnated

Table 2 – Composition and surface area of the active carbons (AC) modified.

Sample	Preparation method	Active phase (mmoleq g^{-1})	Surface area ($\text{m}^2 \text{g}^{-1}$)
AC	–	–	1110
AC–NaOH	Impregnation NaOH	7.98	1039
AC–KOH	Impregnation KOH	2.60	1322
AC– Na_2CO_3	Impregnation Na_2CO_3	5.01	1106

samples the metallic elements are present as the oxides CuO or ZnO [24]. The presence of these basic oxides can explain the higher HCl uptake compared to the not modified zeolite, considering also that there is no reduction of the surface area in the impregnated zeolites.

In the case of the exchanged zeolites, it is expected that the addition of Cu^{2+} or Zn^{2+} ions replacing Na^+ increases the acidity of the zeolite: this factor should not facilitate HCl adsorption. Moreover, this preparation method leads to a reduction of the surface area. In spite of these two negative factors, the exchanged samples give higher performances in terms of breakthrough time compared to the untreated zeolite, especially the 13X-Ex-Zn sample, that adsorbs about four times the amount adsorbed by the sample 13X at breakthrough conc. of 1 ppm. These results can be explained considering the high exchange degree obtained with Cu^{2+} or Zn^{2+} ions: the substitution of Na^+ with a divalent cation leads to halving the number of cations, thus leaving more free space in the zeolitic cages; moreover it increases the polarity of the material. These factors favour the adsorption of polar molecules, such as HCl. This effect is larger in the zeolite exchanged with Zn compared to that exchanged with Cu due to the higher degree of exchange of Na^+ and other ions present in the starting zeolite (Table 2): this explains the better performances of 13X-Ex-Zn, in terms of both delay time and breakthrough time for HCl concentration of 1 ppm.

The breakthrough curves of active carbons are reported in Fig. 3.

The curve of not modified AC shows a delay time of about 30 min, after which the HCl concentration rapidly increases with time. The sample AC–NaOH gives a worse performance, with a shorter delay of 20 min and a more rapid increase of HCl concentration. On the other hand AC–KOH shows better

Table 3 – Breakthrough times at 1 ppm for 13X zeolites and active carbons (AC) modified.

Sample	Time @ 1 ppm (min)	Adsorbed HCl (mmol g^{-1})
13X	28	0.06
13X-Im-Cu	54	0.11
13X-Im-Zn	46	0.10
13X-Ex-Cu	56	0.12
13X-Ex-Zn	110	0.23
AC	47	0.10
AC–NaOH	23	0.05
AC–KOH	85	0.18
AC– Na_2CO_3	158	0.33

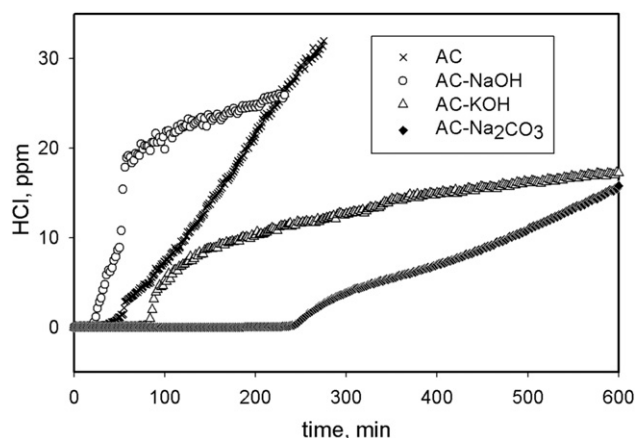


Fig. 3 – Breakthrough curves of modified active carbons.

performances compared to AC, with a longer delay time of about 90 min followed by a slower rise of HCl concentration. The best performances are exhibited by AC–Na₂CO₃ that gives a much longer delay time (≈ 250 min) and a slow rise of HCl concentration. Similarly to zeolites, it can be supposed that the rate of HCl adsorption decreases with time because it is affected by diffusive resistances that increase with the HCl uptake in the pores of the materials. Appreciable diffusive resistances are expected considering the texture of ACs with micropores of size ≈ 15 Å [27]. It is not easy to know the nature of the interaction of HCl with ACs: it can be of acid–base type involving basic sites that are generally present in these materials [28] and/or a dipole–dipole attraction with, for example, phenolic or chinonic groups. It is expected that the presence of an alkaline additive in the modified ACs, greatly enhances HCl adsorption. Although the adsorption capacity of HCl cannot be easily forecasted, it can be supposed, from observation of the breakthrough curves in Fig. 3, that the amount of HCl adsorbed is always much lower than the maximum capacity. Also for these materials, in view of practical applications, it is important to consider, more than the adsorption capacity, the ability of the materials to guarantee a low HCl concentration for a long time. For this reason the performances of the ACs can be evaluated considering the breakthrough times at HCl concentration of 1 ppm, reported in Table 3. These data confirm that the impregnation of ACs with KOH and Na₂CO₃ improves the HCl adsorption properties. This can be related to the increase of the amount of basic sites. The sample AC–Na₂CO₃ gives the longest breakthrough time at 1 ppm, that corresponds to an amount of adsorbed HCl about twice that adsorbed by the sample AC–KOH, probably due to the higher concentration of basic sites, as expected from the amounts of active phase (Table 2). On the other hand the sample AC–NaOH, that has the highest content of alkaline compound (Table 2), shows a very low HCl uptake, even lower than that of the not modified AC. This unexpected behaviour could be related to an excessive content of Na that leads to an occlusion of the micropores as suggested by the reduction of surface area (Table 2), and thus strongly reduces the amount of HCl adsorbed at breakthrough concentration of 1 ppm.

4. Conclusions

Modified 13X zeolites and active carbons have been studied for removal of HCl from diluted gaseous streams. For this purpose, a new experimental apparatus has been designed, that allows to obtain the HCl breakthrough curves with sensitivity as low as a fraction of 1 ppm.

The results have shown improved performances of modified 13X zeolites compared to the untreated zeolite: the best results have been obtained with the zeolite ion exchanged with Zn²⁺, that gives a breakthrough time of 110 min at 1 ppm compared to a breakthrough time of 28 min of the not treated zeolite. Among the modified active carbons, the best performance has been exhibited by the Na₂CO₃ impregnated sample, with a breakthrough time of 158 min at 1 ppm compared to a breakthrough time of 47 min for the not treated active carbon. It is found that a high NaOH content worsens the performance of AC probably due to pores occlusion.

HCl adsorption data on both types of modified materials appear encouraging in view of a practical application for biogas purification. Future work will regard the study HCl adsorption in the presence of water vapour and other contaminants poisonous for MCFCs, such as sulphur compounds, that are present in the biogas.

Acknowledgement

The authors thank ENEA (Italian national agency for new technologies, energy and sustainable economic development) for the financial support.

REFERENCES

- [1] Park K, Kim KY, Lu L, Lim TH, Hong SA, Lee H. Structural characteristics of (NiMgAl)O_x prepared from a layered double hydroxide precursor and its application in direct internal reforming molten carbonate fuel cells. *Fuel Cells* 2007;7:211–7.
- [2] Choi JS, Kwon HH, Lim TH, Hong SA, Lee HI. Development of nickel catalyst supported on MgO–TiO₂ composite oxide for DIR-MCFC. *Catal Today* 2004;93–95:553–60.
- [3] Cigolotti V, McPhail S, Moreno A. Molten carbonate fuel cells fed with biogas: combating H₂S. *J Fuel Cell Sci Tech* 2009;6: 3111–8.
- [4] Watanabe T, Izaki Y, Mugikura Y, Morita H, Yoshikawa M, Kawase M, et al. Applicability of molten carbonate fuel cells to various fuels. *J Power Sources* 2006;160:868–71.
- [5] Crespo D, Qi G, Wang Y, Yang FH, Yang RHT. Superior sorbent for natural gas desulfurization. *Ind Eng Chem Res* 2008;47:1238–44.
- [6] Hernandez S, Solarino L, Orsello G, Russo N, Fino D, Saracco G, et al. Desulfurization processes for fuel cells systems. *Int J Hydrogen Energy* 2008;33:3209–14.
- [7] Xiao Y, Wang S, Wu D, Yuan Q. Experimental and simulation study of hydrogen sulfide adsorption on impregnated activated carbon under anaerobic conditions. *J Hazard Mat* 2008;153:1193–200.
- [8] Martinez C, Corma A. Inorganic molecular sieves: preparation, modification and industrial application in catalytic processes. *Coord Chem Rev* 2011;255:1558–80.

- [9] Wang S, Peng Y. Natural zeolites as effective adsorbents in water and wastewater treatment. *Chem Eng J* 2010;156: 11–24.
- [10] Mohamed MM, Nohman AKH, Zaki M. Development of catalytic properties of mordenite zeolite via chemical modification. *Curr Top Cat* 2005;4:79–99.
- [11] Liang X, Wang Xuejiang. Technology of activated carbon modification and its application in wastewater treatment. *Shuichuli Jishu* 2011;37:1–6.
- [12] Jevic P, Hutla P, Malatak J, Sediva Z. Efficiency and gases emissions with incineration of composite and one-component biofuel briquettes in room heater. *Res Agric Eng* 2007;53:94–102.
- [13] Kameda T, Uchiyama N, Yoshioka T. Removal of HCl, SO₂, and NO by treatment of acid gas with Mg–Al oxide slurry. *Chemosphere* 2011;82:587–91.
- [14] Hedman B, Burvall J, Nilsson C, Marklund S. Emissions from small-scale energy production using co-combustion of biofuel and the dry fraction of household waste. *Waste Manag* 2005;25:311–21.
- [15] Allen Matthew R, Braithwaite A, Hills CC. Trace organic compounds in landfill gas at seven U.K. waste disposal sites. *Environ Sci Technol* 1997;31:1054–61.
- [16] Jaffrin A, Bentounes N, Joan AM, Makhlof S. Landfill biogas for heating greenhouses and providing carbon dioxide supplement for plant growth. *Biosystems Eng* 2003;86: 113–23.
- [17] Krebs T, Nathanson GM. Reactions of HCl and D₂O with molten alkali carbonates. *J Phys Chem A* 2011;115: 482–9.
- [18] Partanen J, Backman P, Backman R, Hupa M. Absorption of HCl by limestone in hot flue gases. Part I: the effects of temperature, gas atmosphere and absorbent quality. *Fuel* 2005;84:1664–73.
- [19] Yan R, Terence C, Tee Liang D, Laursen K, Yean Ong W, Yao K, et al. Kinetic study of hydrated lime reaction with HCl. *Environ Sci Technol* 2003;37:2556–62.
- [20] De Wild PJ, Nyqvist RG, De Bruijn FA, Stobbe ER. Removal of sulphur-containing odorants from fuel gases for fuel cell-based combined heat and power applications. *J Power Source* 2006;159:995–1004.
- [21] Cha CY, Wallace S, George AH, Rogers S. Microwave technology for treatment of fume hood exhaust. *J Environ Eng* 2004;130:338–48.
- [22] Jia G, Aik CL. Textural and chemical characterisations of activated carbon prepared from oil-palm stone with H₂SO₄ and KOH impregnation. *Microp Mes Mat* 1999;32:111–7.
- [23] Shima JW, Park SJ, Ryu SK. Effect of modification with HNO₃ and NaOH on metal adsorption by pitch-based activated carbon fibers. *Carbon* 2001;39:1635–42.
- [24] Ozaydin Z, Yasyerli S, Dogu G. Synthesis and activity comparison of copper-incorporated MCM-41-type 107 sorbents prepared by one-pot and impregnation procedures for H₂S removal. *Ind Eng Chem Res* 2008;47:1035–42.
- [25] Tomadakis MM, Heck HH, Jubran ME, Al-Harhi K. Pressure-swing adsorption separation of H₂S from CO₂ with molecular sieves 4A, 5A, and 13X. *Sep Sci Technol* 2011;46:428–33.
- [26] Pechler N, Hillmer G, Emig G. Experimental determination and model description of break-through curves in mixed adsorption of hydrogen sulfide and carbon disulfide. *Chem Ing Technik* 1990;62:734–5.
- [27] Herrera LF, Fan C, Nguyen V, Do DD, Horikawa T, Nicholson D. A self-consistent method to determine accessible volume, area and pore size distribution (APSD) of BPL, Norit and AX-21 activated carbon. *Carbon* 2012;50:500–9.
- [28] El-Sayed Y, Bandosz TJ. Adsorption of valeric acid from aqueous solution onto activated carbons. Role of surface basic sites. *J Colloid Interface Sci* 2004;273:64–72.