Gas adsorption capacity of Municipal Solid Waste Incineration Bottom Ashes based materials

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Abstract

In order to deepen the knowledge on MSWI BA (Municipal Solid Waste Incineration Bottom Ashes) properties, a study has been focused on gas adsorption capacities of MSWI BA. Tests have been carried out on two materials based mostly on MSWI BA: physico-chemical characterisation (based on the elemental and chemical compositions, scanning electron microscopy coupled to energy dispersive X-ray spectrometry, porosity determination and surface pH), gas adsorption isotherms and kinetics performed in a static reactor, and gas breakthrough test in fixed bed reactor.

The first stage of physico-chemical characterisation showed similar results for both materials in terms of average porosity properties, chemical composition and surface pH. The results of this first characterisation highlight the adsorption possibilities towards acid gas for the studied materials. Thus the reactor studies will focus on one acid gas: H_2S. The adsorption isotherms and kinetics in static reactors allow determining removal performances of H_2S under the influence of various parameters: air humidity, gas composition, sample moisture. They show 1) a great influence of the global moisture (air humidity but mostly sample moisture) on H_2S adsorption for both samples; 2) adsorption capacity similar to the one of some activated carbons but with necessary contact time much longer; 3) and confirm that there is no competition between CH_4 and H_2S adsorption. The breakthrough test shows: 1) a very high purification efficiency from the beginning and all along the test; 2) but some residual H_2S concentration still existing at the outlet of the gas treatment process indicating that the fixed bed thickness must be increased.

Thus this study highlights the good performances of MSWI BA-based materials to adsorb acid gas (especially H_2S) considering long enough contact time and in presence of humidity in the material to allow chemisorptions.

1. Introduction

According the literature, Municipal Solid Waste Incineration Bottom Ashes (MSWI BA) may have good gas adsorption capacities (Tirnoveanu, 2004; Rendek et al, 2006). Among the potentially adsorbed gas, there is the hydrogen sulphide (H_2S). This gas has several negative effects, from odour to high toxicity for human health, corrosion of most equipment, to harmful environmental effects producing sulphur dioxide emissions when combusted. In order to have a better knowledge of MSWI BA gas adsorption capacities, a study between the CRPE and GEPEA has been carried out. The case of two Municipal Solid Waste Incineration Bottom Ashes (MSWI BA)-based materials is described in this paper. These materials are mainly composed of MSWI BA with addition of other wastes.

The adsorption properties are assessed according the following methodology:

- physico-chemical characterisation based on the elemental and chemical compositions, scanning electron microscopy coupled to energy dispersive X-ray spectrometry, porosity determination (density, BET specific surface, porosity volume, porosity distribution) and surface pH ;
- gas adsorption isotherms and kinetics performed in a static reactor for controlled gas initial concentration in air, temperature and relative humidity ;
- gas breakthrough test in fixed bed reactor to evaluate breakthrough time and capacities, for controlled inlet concentrations of gas and water vapour and for a fixed air flow rate. For this test in dynamic reactor, MSWI BA-based material has been compacted following Proctor test standards.

2. Physico-chemical properties of MSWI BA-based material

The first stage of physico-chemical characterisation shows in Table 1 similar results for both materials in terms of average porosity properties, chemical composition and surface pH if compared with commercial adsorbents such as activated carbon commonly used for gas treatment (which highlights the differences between the two sets of materials). The basic surface pH at around 11, can favour H_2S solubility with water and then adsorption/reaction with surface functional groups of tested materials. Indeed, water plays an important role for hydrogen sulphide oxidation on material surface because H_2S requires a film of water for dissociation to HS^- in basic environment (Bagreev and Bandosz, 2005).

Semi-quantitative elemental analysis of MSWI-BA materials is performed using scanning electron microscopy coupled to energy dispersive X-ray spectrometry. MSWI-BA-A sample is mainly composed of approximately $30\%_{wt}$ C, $20\%_{wt}$ Ca, $30\%_{wt}$ O and other compounds such as $1\%_{wt}$ Mg. Moreover, chemical composition of MSWI BA-based material shows available sites containing CaO or MgO. Those surface sites can be converted to their corresponding hydroxide chemical compounds in the presence of water and as a consequence participate in hydrogen sulphide oxidation. This oxidation mechanism can be in competition with CO_2, which deactivates surface basic sites by forming carbonates. On the other hand, the samples porosity indicates that no CH_4 or COV should be adsorbed by the studied materials as these two gases are trapped by physisorption in micropore volumes. Table 1 shows that MSWI BA-based material has almost no microporosity. The results of this first characterisation highlight the adsorption possibilities towards acid gas for the studied materials. The reactor studies will then focus on one acid gas: H_2S.

Table 1. Structural and chemical properties of MSWI-BA materials

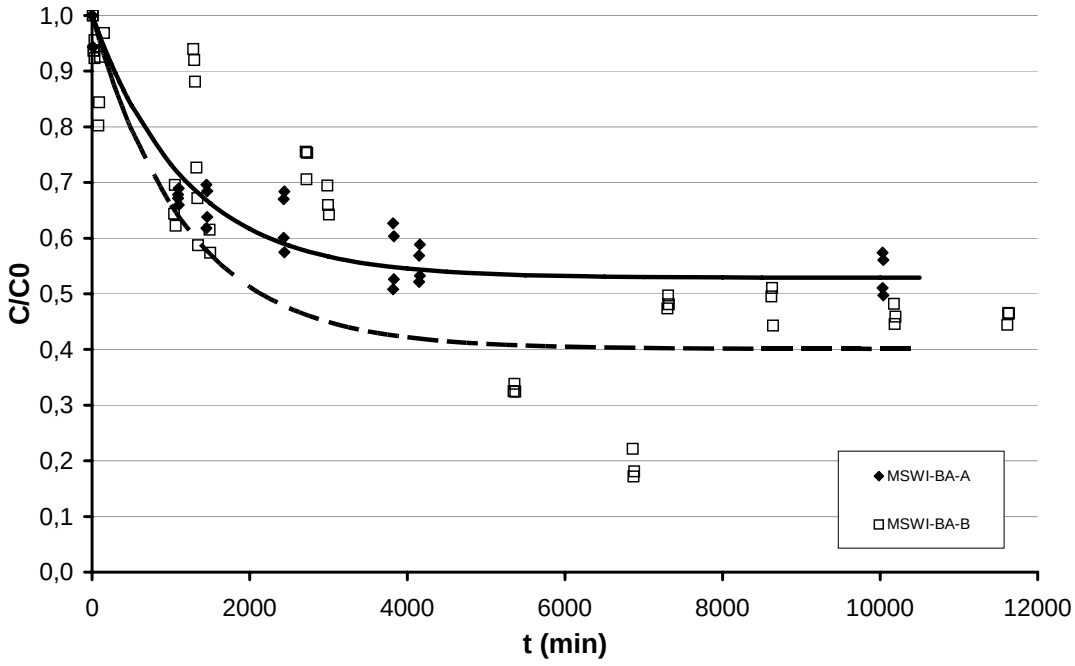
	S_{BET} m^2/g	V_{macro} cm^3/g	V_{meso} cm^3/g	V_{micro} cm^3/g	ash content %wt	Surface pH
MSWI-BA-A	7	0.19	0.016	0.002	97	11.3
MSWI-BA-B	19	0.13	0.038	0.005	90	11.3
Commercial GAC	1090	/	0.097	0.312	6	8

3. H_2S adsorption capacity and contact time

The adsorption isotherms and kinetics in static reactors allow determining removal performances of H_2S under the influence of various parameters: air humidity, gas composition, sample moisture. MSWI-BA-B materials exhibits slightly better performances regarding H_2S separation from gas. Indeed for sample B, adsorption capacity at equilibrium reaches 155 mg/g compared to 129 mg/g for sample A (Table 2), but for similar contact time of approximately 19 hours as can be shown in Figure 1. Considering structural and chemical characterisations of these materials, the better adsorption performances of sample B can be explained by the higher mesoporous volume rather than by chemical properties.

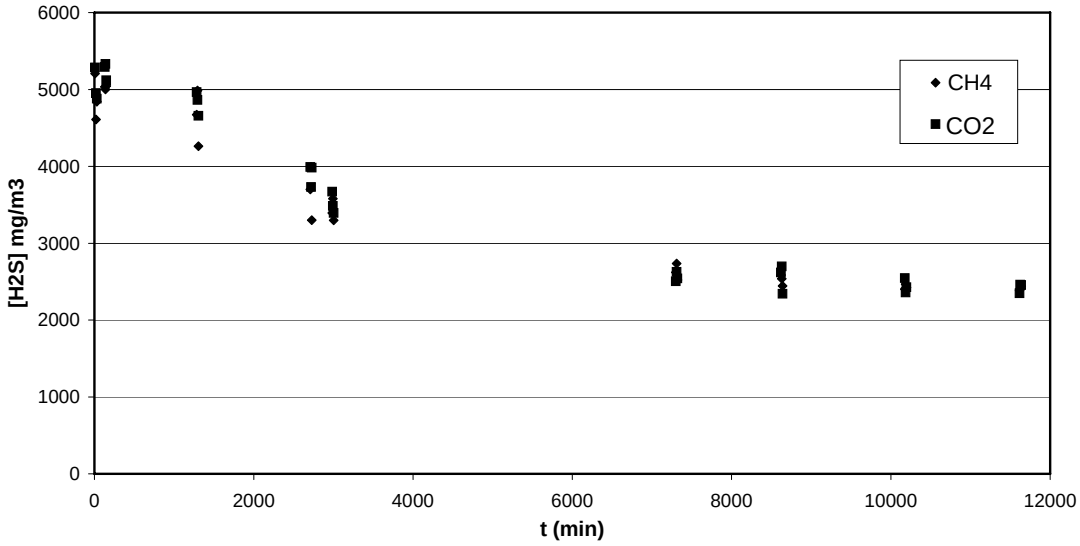
Results of kinetic study presented in Figure 2 and Table 2 highlight the following conclusions:

- a great influence of the global moisture: air humidity but mostly sample moisture, on H_2S adsorption for both samples ;
- adsorption capacity similar to the one of some activated carbons but with necessary contact time much longer ;
- and confirmation that there is no competition between CH_4 and H_2S adsorption.



Gas composition: 45% CO_2 + 55% N_2, C_0=5000 mg/m^3, 60%HR, 35°C ; sample moisture: MSWI-BA-A = 18%wt, MSWI-BA-B = 26%wt

Figure 1. H_2S adsorption kinetic on studied MSWI-BA materials



Gas composition: 45% CO_2 or CH_4+ 55% N_2, C_0=5000 mg/m^3, 60%HR, 35°C ;

Figure 2. H_2S adsorption kinetic on MSWI-BA-B material containing 26%wt water

Table 2. H_2S adsorption performances of for MSWI-BA materials regarding gazeous conditions

	moisture % wt	gazeous conditions	C0 mg/m3	Ce mg/m3	qe mg/g	Ce/C0	τ hours
MSWI-BA-A	18	45% CO2 + 55% N2, 60%HR, 35°C	5905	3124	129	0.53	19.3
MSWI-BA-B	26	45% CO2 + 55% N2, 60%HR, 35°C	5310	2130	155	0.40	19.2
MSWI-BA-B	26	**45% CO2 + 55%CH4**, 60%HR, 35°C	5100	2050	153	0.40	19.3
MSWI-BA-B	50	Air, **100%HR**, 20°C	4850	0	/	/	> 2
MSWI-BA-B	50	Air, **50%HR**, 20°C	1978	400	52	0.20	1.5

C_0: initial concentration; C_e: concentration at equilibrium; q_e: adsorption capacity at equilibrium, τ: contact time, HR: relative humidity

4. H_2S removal in packed bed reactor of MSWI BA-based material

The breakthrough test is performed in fixed bed reactor for MSWI BA-A material packed to obtain a porous bed of permeability 6.2 10^{-10} m². An initial concentration of 165 mg/m^3 of H_2S in an air flow of 25°C and 60% relative humidity is provided through the materials containing 18%wt moisture in order to ensure good mechanical properties of the packed porous bed (moisture content of the Optimal Proctor). H_2S concentration at the outlet of the column is measured during 30 hours, results are shown in Figure 3 in terms of dimensionless concentration C/C_0.

The obtained breakthrough curve indicates very high purification efficiency from the beginning and all along the 30 hours of the test. Nevertheless, residual H_2S concentration still exists at the outlet of the gas treatment process since the very beginning of the test. This means that MSWI-BA-A bed thickness is lower than the critical thickness of adsorbent necessary to ensure enough contact time to avoid any breakthrough at the beginning of the test. Considering the low H_2S concentration along the 30 hours of test (C/C0 < 3%), this MSWI-BA material exhibits very promising performances regarding H_2S removal from humid gas (higher than 50% HR for 25-30°C) if considering an increase of fixed bed thickness.

The importance of gas humidity for H_2S removal performances on MSWI-BA materials can be explained by chemisorption mechanisms with calcium (or magnesium) carbonate

and metallic oxides for basic pH conditions. The reaction mechanisms can be summarized as follow (Met = Metal) :

$$H_2S_g + H_2O \leftrightarrows 2\,H^+ + S_{aq}^{2-} + H_2O \quad (1)$$

$$S_{aq}^{2-} + Met^{2+} \leftrightarrows MetS \quad (2)$$

$$CO_{2g} + H_2O \leftrightarrows CO_3^{2-} + H^+ \quad (3)$$

$$CO_3^{2-} + Ca^{2+} \leftrightarrows CaCO_3 \quad (4)$$

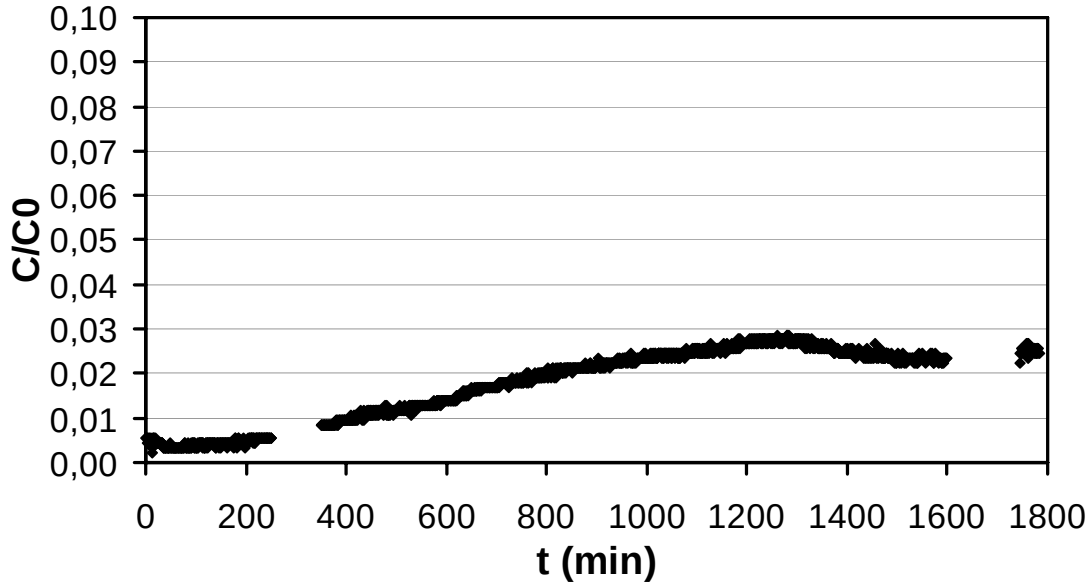


Figure 3. H_2S adsorption breakthrough curve on MSWI-BA-A material containing 18%wt moisture and packed in fixed bed

(air flow: 0.017 m/s, C_0=165 mg/m^3, 60%HR, 25°C)

5. Conclusions

This study highlights the good performances of MSWI BA-based materials to adsorb H_2S considering long enough contact time and in presence of humidity in the material to allow chemisorptions. Some additional experiments could be performed with gas containing CO_2 to study the influence of CO_2 as competitor in involved chemical reactions.

References

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