Investigations on the adsorption of acidic gases using activated dolomite

A. Duffy, G.M. Walker [*], S.J. Allen

School of Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, Northern Ireland, UK

Received 11 March 2005; received in revised form 12 October 2005; accepted 9 November 2005

Abstract

In this work activated dolomite adsorption was investigated for removal of acidic gaseous pollutants. Charring was found to be an effective method for the activation of dolomite. This thermal processing resulted in partial decomposition, yielding a calcite and magnesium oxide structure. Adsorbents were produced over a range of char temperatures (750, 800 and 850 °C) and char times (1–8 h). The surface properties and the adsorption capability of raw and thermally treated dolomite sorbents were investigated using porosimetry, SEM and XRD. The sorbates individually investigated were CO_2 and NO_2. Volumetric equilibrium isotherm determinations were produced in order to quantify sorbate capacity on the various sorbents. The equilibrium data were successfully described using the Freundlich isotherm model. Despite relatively low surface area characteristics of the activated dolomite, there was a high capacity for the acidic gas sorbates investigated, showing a maximum of 12.6 mmol/g (554 mg/g) for CO_2 adsorption and 9.93 mmol/g (457 mg/g) for NO_2 adsorption. Potentially the most cost effective result from the work concerns the adsorptive capacity for the naturally occurring material, which gave a capacity of 9.71 mmol/g (427 mg/g) for CO_2 adsorption and 4.18 mmol/g (193 mg/g) for NO_2 adsorption. These results indicate that dolomitic sorbents are potentially cost effective materials for acidic gases adsorption.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Dolomite; Adsorption; Adsorbent characterisation; Carbon dioxide; Nitrogen dioxide; Freundlich isotherm

1. Introduction

1.1. Dolomitic materials

Dolomite is a low cost adsorbent which consists of a calcium and magnesium carbonate compound. Its properties are similar to that of limestone and it is known as magnesium limestone in industry. The dolomite group is composed of minerals with an unusual trigonal bar 3 symmetry. The general formula of this group is $AB(CO_3)^2$, where A can be either calcium, barium and/or strontium and the B can be either iron, magnesium, zinc and/or manganese. The structure of the dolomite group is taken from the calcite group structure. The calcite group structure is layered with alternating carbonate layers and metal ion layers. The amount of calcium and magnesium in most specimens is equal, but occasionally one element may have a slightly greater presence than the other [1]. Small amounts of iron and manganese are sometimes also present. It is the alkali qualities found in dolomite that has lead to research into gaseous pollutants; characterised as acidic [2].

1.2. Thermal processing of dolomite

The thermal processing, or "calcining" process, uses the fact that the magnesium carbonate component of the dolomite decomposes at temperatures around 800 °C. The decomposition of dolomite at 800 °C leads to changes in the chemical composition of the surface and the porosity of the mineral [3,4]. Generally, the product of partial decomposition of dolomite contains calcium carbonate (calcite) and magnesium oxide and shows a significant increase in specific surface area and pore volume [5,6].

1.3. Gaseous pollutants investigated

The pressure on industry to decrease the emission of gaseous pollutants has increased in recent years due to the strict regulations brought in to force, coinciding with the Kyoto Protocol. It is generally accepted that the cost associated with the separation of CO_2 from flue gases introduces the largest economic penalty to the industries involved [7].

The major sources of carbon dioxide are from fossil fuel power stations, natural gas treatment, purification of hydrocarbons, production of hydrogen gas and the aerospace industry. Therefore a broad spectrum of cost effective gas separation pro-

* Corresponding author. Tel.: +44 2890 974172; fax: +44 2890 974627.
E-mail address: g.walker@qub.ac.uk (G.M. Walker).

cesses have been developed. In relation to price/performance, physical adsorption is one of the most important techniques to control air pollution [8].

A mixture of nitrogen dioxide (NO_2) and nitric oxide (NO) are emitted during combustion processes. This mixture of oxides of nitrogen is termed NO_X. NO produced is subsequently oxidised to NO_2 in the atmosphere. NO_2 is thought to have both acute and chronic effects on airway and lung function, particularly in people with asthma.

Total UK emissions of NO_X have declined by 39% between 1990 and 2001. The total NO_X emissions in 2001 were 1,680,000 tonnes. By 2010, the UK has agreed to cut the emissions of NO_X to below 1,181,000 tonnes [9].

2. Experimental

2.1. Adsorbent characterisation

The dolomite used in this study was mined from a deposit in Co. Fermanagh, Northern Ireland. The typical chemical composition of the dolomite in the deposit was 44% $MgCO_3$ and 53% $CaCO_3$ (determined by XRD analysis). The particle size distribution of the various charred samples was constant as a size fraction between 1.00 and 1.20 mm sieves. The raw dolomite was charred in a furnace at 750, 800 and 850 °C for a period of 1–8 h with an air atmosphere. Charring dolomite at these temperatures produces a porous calcite–magnesium oxide structure. Samples of dolomite and charred dolomite were analysed for specific surface area using BET nitrogen adsorption employing a Nova 4200e, surface area and pore size analyser (Quantachrome Instruments).

The presence of air/N_2 affects the charring process in that decomposition of the magnesium carbonate will start at a lower temperature than would be the case for a CO_2 atmosphere. Also the effect of an air atmosphere results in a continuous decomposition of dolomite rather than a two-stage decomposition found using a CO_2 atmosphere [10].

2.2. Adsorbate characterisation

Both carbon dioxide and nitrogen dioxide (CP grade) were supplied by BOC Gases, Guildford, Surrey.

2.3. Experimental method

Equilibrium adsorption isotherms were determined for single component gaseous systems using a volumetric technique. All isotherms were conducted at ambient temperature (20 °C). The experimental set-up comprised of a glass reactor vessel with ports to monitor temperature and pressure, a sample injection port and a vacuum port. A constant mass of sorbent, of defined particle size, was suspended in the vessel and the vessel was sealed. The vessel was then set to the required isotherm temperature and evacuated to achieve a maximum vacuum.

An adsorbate sample, of known volume, was injected into the vessel by use of a gas tight syringe. The pressure change, caused by the charge of adsorbate to the vessel, was recorded and

the pressure was constantly monitored. The equilibrium pressure, i.e. the point at which no further change in pressure was observed, was recorded and a further charge of adsorbate was injected. This procedure was repeated until a relative pressure of unity was reached or until no further pressure change was observed with successive charges of adsorbate.

3. Results and discussion

3.1. Adsorbent characterisation

A typical observed isotherm of the nitrogen adsorption analysis on dolomite and charred dolomite is shown in Fig. 1 (1 h at 800 °C); displaying a type II isotherm. This indicates a meso-macroporous material or a material which contains inter-spacial voids between crystalline structures [11].

Results of the nitrogen adsorption analysis on dolomite and charred dolomite are shown in Table 1 as surface area determined by BET analysis. These results indicate that there is a significant rise in specific surface area on charring of the dolomite due to the partial calcining process according to equation [8,9]

$$CaCO_3 \cdot MgCO_3 \rightarrow MgO + CO_2 + CaCO_3 [\approx 800\,°C]$$
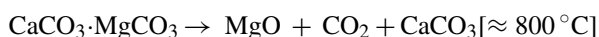
Charring effectively creates a porous structure of calcium carbonate and magnesium oxide which has an increased specific surface area to that of the untreated dolomite. It is clear from these analyses that charred dolomite has the potential to act as an adsorbent, albeit with a relatively low surface area compared to commercial adsorbents.

The data indicate that the specific surface area increases with increasing char time and char temperature to a maximum of 7.1 $m^2 g^{-1}$ for 8 h at 850 °C. These surface area data are significantly lower than previous studies using the same raw material with a lower particle size [12]. Dolomite with a mean particle size of 100 μm produced a surface area of 19.5 $m^2 g^{-1}$ when thermally treated (charring conditions 6 h at 800 °C) [12]. This indicates that the particle size of the dolomite has a significant effect on the activation process, with the probability of an un-reacted core of dolomite surrounded by a layer of calcium carbonate/magnesium oxide when processing larger sized material (1.10 mm), as in this case. These results correlate well

Table 1

BET nitrogen adsorption analysis using Nova 4200e, surface area and pore size analyser (Quantachrome Instruments), particle size 1.0–1.2 mm

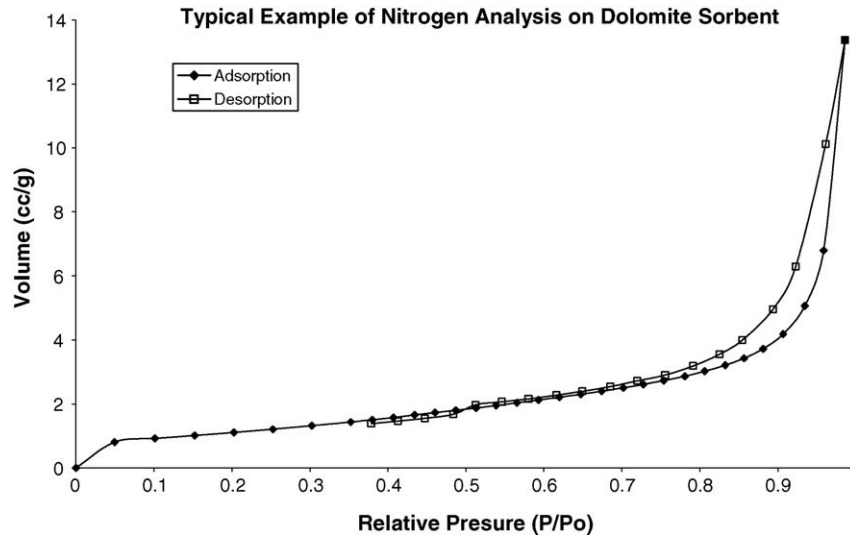| Sample		Surface area ($m^2 g^{-1}$)
Char temperature (°C)	Char time (h)	
750	1	2.91
	8	5.19
800	1	4.44
	8	6.12
850	1	5.05
	8	7.10
Untreated dolomite		1.36

Fig. 1. A representative nitrogen isotherm for the charred dolomite sorbents investigated (1 h at 800 °C).

to those of other researchers mechanistic studies who shown that the thermal dissociation of dolomite begins at the solid surface. An initial latent phase is produced, followed by a "surface germination" which extends over time until the interior of the particle is reached [13].

The activation energies for surface and bulk dissociation have been measured by previous researchers and have been found to vary [13,14]. This dissociation is endothermic, which means that heat exchanges must take place at the surface and inside the particles. Given that the solid has a low thermal conductivity, it is possible that thermal gradients will be created, adding to the heterogeneity of the reaction media. In addition, the CO_2 that is produced concentrates inside the bed and may lead to the reverse reaction: lime carbonation [14].

SEM analysis was performed on the charred dolomite sorbents and a typical example is shown in Fig. 2 (un-charred) and Fig. 3 (1 h at 800 °C). From the images illustrated it can observed that the dolomite structure consists of a crystalline structure with inter-spacial voids (Fig. 2). However, as the char
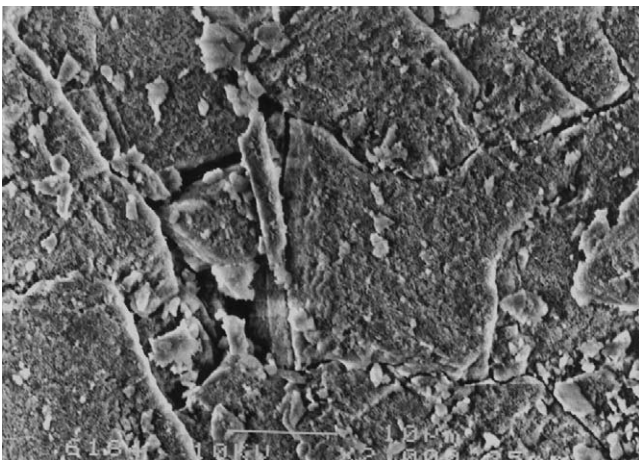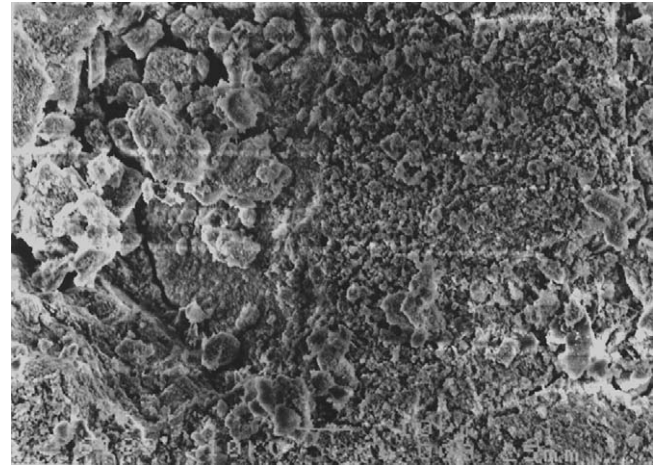

Fig. 3. SEM of surface of charred dolomite (1 h at 800 °C) at a magnitude of 2000 mm × 25 mm.

time increases, the crystalline structure degrades and this results in a more porous structure (Fig. 3) with evidence of a meso- and macro-pore structure being formed. Fig. 4 shows an XRD trace for dolomite particles charred for 1 h at 800 °C. The plot indicates two main peaks, the $2\theta = 29$ peak is produced from crystalline calcite and the $2\theta = 31$ peak is produced by crys-
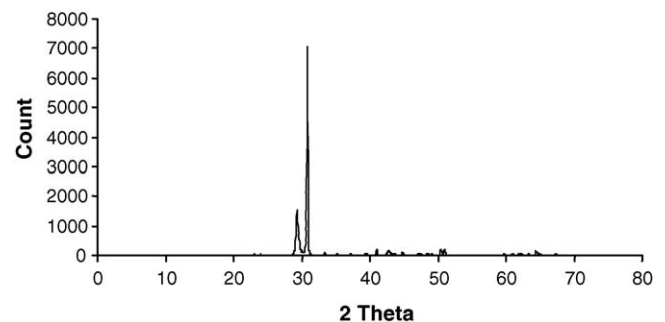

Fig. 2. SEM of surface of un-charred dolomite sample at a magnitude of 2000 mm × 25 mm.

Fig. 4. XRD trace for dolomite (1.1 mm diameter) charred for 1 h at 800 °C ($2\theta = 29$, calcite; $2\theta = 31$, dolomite).

Carbon Dioxide Isotherms of Dolomite Sorbents at Different Char Temperatures and Char Times
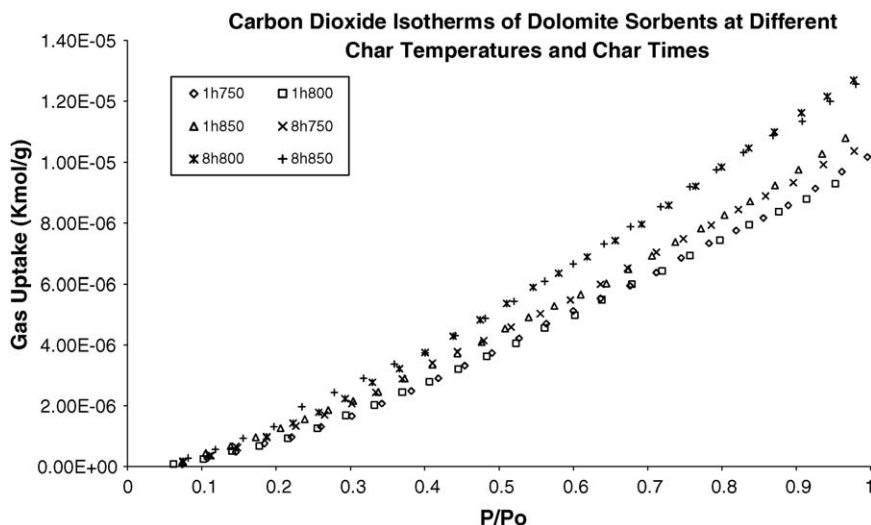
Fig. 5. Experimental adsorption isotherm data for carbon dioxide adsorption onto the dolomite sorbents synthesised in this study.

talline dolomite. The data indicate that there are still significant amounts of un-calcined dolomite still within the particles. This data correlates with the specific surface area data discussed above and is further evidence if an un-reacted core of dolomite.

3.2. Adsorption of carbon dioxide using the volumetric technique

The isotherms observed from the adsorbents charred at 750, 800 and 850 °C (Fig. 5) follow the same trend, with many of the data points initially coincident. The adsorbent with the highest surface area was the 8 h 850 °C, which with the 8 h 800 °C sample, obtained the highest gas sorption of the dolomite samples investigated. It was also noted that the untreated dolomite sample followed the same isotherm trend (Fig. 6) as thermally processed dolomite samples. The gas uptake of this adsorbent was significantly lower than other materials for carbon dioxide adsorption. The data from the gas adsorption using the volumetric technique shows good correlation with the surface area

analysis, in that there is a direct relationship between surface area determined by nitrogen adsorption (BET) and quantity of gas adsorbed in the volumetric technique (Tables 1 and 2).

The results in Table 2 indicate the maximum gas uptake of the different thermally processed materials for carbon dioxide adsorption. These results illustrate that a longer char time correlates to a higher carbon dioxide sorptive capacity. It also indicates that dolomite has a physico-chemical affinity to carbon dioxide as the untreated dolomite has a relatively high gas sorptive capacity.

3.3. Adsorption of nitrogen dioxide using the volumetric technique

Equilibrium isotherms for nitrogen dioxide adsorption onto the dolomitic sorbents are illustrated in Fig. 7 for material charred at 750, 800 and 850 °C. The data indicate that the isotherms follow the same general trend as the carbon dioxide results. However unlike the carbon dioxide isotherms, certain

Untreated Dolomite Isotherms for both Carbon Dioxide and Nitrogen Dioxide
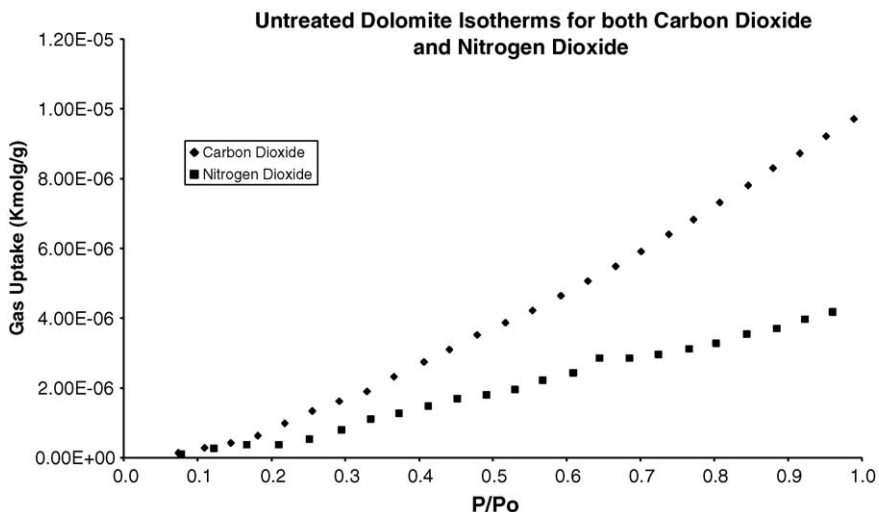
Fig. 6. Experimental adsorption isotherm data for carbon dioxide and nitrogen dioxide adsorption onto un-charred dolomite.

Table 2
The maximum gas uptake for the different dolomite sorbents for both gases investigated

Sample		Carbon dioxide	Nitrogen dioxide
Char temperature (°C)	Char time (h)	Maximum gas uptake ($\times 10^{-5}$) (kmol/g)	Maximum gas uptake ($\times 10^{-5}$) (kmol/g)
750	1	1.017	0.507
	8	1.040	0.706
800	1	0.928	0.633
	8	1.270	0.683
850	1	1.131	0.627
	8	1.260	0.993
Untreated dolomite		0.971	0.418

isothermal data for particular sorbents coincide, e.g., the 1 h 850 °C char and the 8 h 800 °C. A comparison of adsorbent surface area with equilibrium capacity shows a good correlation, with the adsorbent with the highest surface area from the BET analysis (8 h at 850 °C) having the highest equilibrium capacity.

The untreated dolomite isotherm for nitrogen dioxide analysis (Fig. 6) observed the same shape as the other isotherms. The data for maximum gas uptake in Table 2 shows that the 8 h 850 °C had a significantly higher nitrogen dioxide affinity than the other chars investigated. Despite relatively low surface area characteristics of the activated dolomite, Table 2 indicates that there was a high capacity for the acidic gas sorbates investigated, showing a maximum of 12.6 mmol/g (554 mg/g) for CO_2 adsorption and 9.93 mmol/g (457 mg/g) for NO_2 adsorption (8 h 850 °C). Potentially the most cost effective result from the work concerns the adsorptive capacity for the naturally occurring, which gave a capacity of 9.71 mmol/g (427 mg/g) for CO_2 adsorption and 4.18 mmol/g (193 mg/g) for NO_2 adsorption.

3.4. Freundlich isotherm modelling

In isothermal adsorption systems the equilibrium relationship between the adsorbent and adsorbate can be characterised by single curve or isotherm, where the solid phase solute concentration, q_e, is a function of the gaseous phase solute concentration characterised by the partial pressure of the gas, P/P_0. Positive adsorption in solid gaseous systems results in the removal of the solute from the gaseous phase onto the surface of the solid, until the solute remaining in gas is at dynamic equilibrium with that at the surface, i.e. the rate of adsorption equals the rate of desorption. At equilibrium there is a defined distribution between the solid and gaseous phases which can be expressed mathematically using model relationships.

The Freundlich isotherm equation is used to describe adsorption where the adsorbate has a heterogeneous surface with adsorption sites that have different energies of adsorption and which are not always available. The energy of adsorption varies as a function of the surface coverage (q_e) with the energy term represented by the Freundlich constant (K_F)

$$q_e = K_F \left(\frac{P}{P_0} \right)^{n_F} \tag{1}$$

n_F is a heterogeneity factor which has a lower value for more heterogeneous surfaces. When considering the Freundlich equilibrium isotherm model, higher values of Freundlich heterogeneity factor (n_F) and Freundlich constant (K_F), indicate greater affinity between the adsorbate and the adsorbent. The closer the n_F to zero, the greater the heterogeneity of the adsorbent. It can be
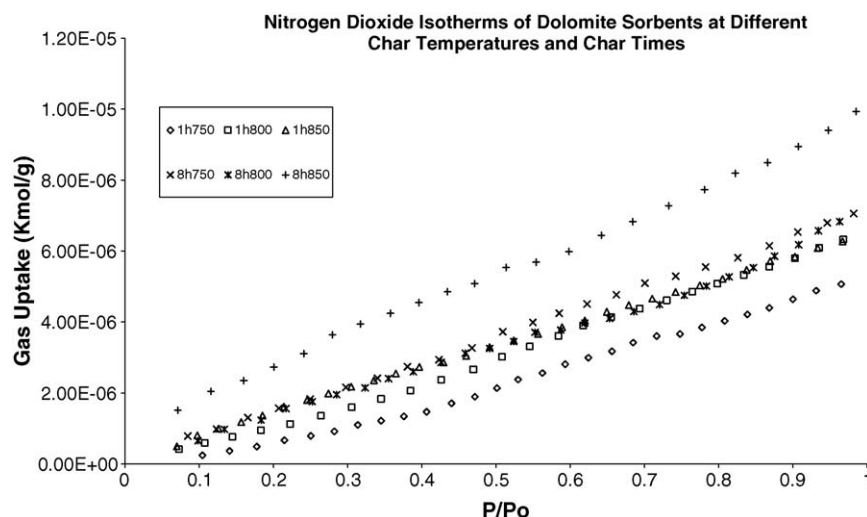

Fig. 7. Experimental adsorption isotherm data for nitrogen dioxide adsorption onto the dolomite sorbents synthesised in this study.

Table 3
The adsorption constants determined for the Freundlich isotherm model and the r^2 value of the analysis for both gases investigated

Sample		Carbon dioxide			Nitrogen dioxide		
Char temperature (°C)	Char time (h)	n_F	K_F (N^{-1} m^{-2})	r^2	n_F	K_F (N^{-1} m^{-2})	r^2
750	8	1.5758	0.01837	0.995	0.9331	0.00207	0.998
800	8	1.6385	0.01901	0.997	0.9754	0.00288	0.998
850	8	1.4773	0.01287	0.997	0.7275	0.00025	0.996
Untreated dolomite		1.6234	0.02247	0.998	1.4749	0.02548	0.994

seen from Table 3 that for all adsorbents studied, with carbon dioxide, n_F values were all within the range of 1.4–1.7. This indicated that all the adsorbents studied were heterogeneous in nature. When the value of the correlation coefficient, r^2, determined from the linear regression of the Freundlich model was considered, it could be seen that the values were greater than 0.99, which indicated that the regression technique appropriate and that the experimental data were described accurately by the Freundlich isotherm model.

The Freundlich isotherm constants for the adsorption of nitrogen dioxide also indicated that all the adsorbents studied were heterogeneous in nature, with n_F values in the range 0.7–1.4. The values of r^2, determined from the linear regression of the Freundlich model, gave values greater than 0.99, which indicated the experimental data were described accurately by the Freundlich isotherm model.

3.5. Comparison of the gaseous pollutant adsorption

It is evident from the experimental data that the dolomitic sorbents have an affinity to both carbon dioxide and nitrogen dioxide. From the equilibrium isotherms illustrated (Figs. 5–7) there is a difference in isothermal shape between gases. This disparity is in relation to the degree of adsorption rather than alternative isotherm type.

The maximum gas uptake results in Table 2 indicate that dolomitic sorbents have a higher capacity for carbon dioxide than nitrogen dioxide. Results with respect to the untreated dolomite, show the capacity for carbon dioxide is twice that of nitrogen dioxide. The constants determined from the Freundlich isotherm model for both gases in Table 3, also observe this trend. The numerical values of the Freundlich constants, n_F and K_F are higher for carbon dioxide adsorption compared to those obtained from nitrogen dioxide. The Freundlich constants for the untreated dolomite (Table 3) are more comparable between carbon dioxide and nitrogen dioxide.

4. Conclusion

The surface area of the dolomite was significantly increased by thermal treatment which resulted in sorbent properties that are particularly suited to the adsorption of gaseous pollutants. Generally the capacity for gaseous adsorption increased with the greater char time and char temperature. For the adsorbents investigated, the capacity for nitrogen dioxide is less than that of carbon dioxide. Untreated dolomite exhibited a significant adsorption capacity for both gases considering it is a naturally occurring material. The data obtained from the Freundlich isotherm model suggests that for both carbon dioxide and nitrogen dioxide, the adsorbents studied were heterogeneous in nature. Also the linearisation technique employed was accurate and indicated that the Freundlich model described the data well under the experimental conditions investigated. The work indicates that dolomitic materials have the potential to act as adsorbents for acidic gases, albeit with a relatively low surface area compared to commercial adsorbents.

References

[1] R.S. Boynton, Chemistry and Technology of Lime and Limestone, Interscience Publishers, New York, 1967.
[2] G. Kiely, Air pollution – Environmental Engineering, McGraw-Hill, London, 1997, pp. 334–389.
[3] P. Staszczuk, E. Stefaniak, R. Dobrowolski, Characterisation of thermally treated dolomite, Powder Technol. 92 (1997) 257.
[4] P.V. Brady, H.W. Papenguth, J.W. Kelly, Metal sorption to dolomite surfaces 1, Appl. Geochem. 14 (5) (1999) 569–579.
[5] H. Roques, Phosphorous removal from wastewater by half burnt dolomite, Water Res. 25 (8) (1991) 959–965.
[6] G.M. Walker, L. Hansen, J.-A. Hanna, S.J. Allen, Kinetics of reactive dye adsorption onto dolomitic sorbents, Water Res. 37 (2003) 2081–2089.
[7] J.C. Abanades, The maximum capture efficiency of CO$_2$ using a carbonation/calcinations cycle of CaO/CaCO$_3$, Chem. Eng. J. 90 (2002) 303–306.
[8] Z. Youg, V. Mata, A.E. Rodrigues, Adsorption of carbon dioxide at high temperatures – a review, Sep. Purif. Technol. 26 (2001) 195–205.
[9] Department of Environment, Foods and Rural Affairs (Defra), UK Government, Air Quality Legislation, 1998.
[10] A. Aanani, Applications of dolomite, Ind. Miner. (1984) 45–55.
[11] F. Rouquerol, J. Rouquerol, K. Sing, Adsorption by Powders and Porous Solids: Principles, Methodology and Application, 1st ed., Academic Press, London, 1999.
[12] G.M. Walker, G. Connor, S.J. Allen, Copper II removal onto activated dolomite, Chem. Eng. Res. Design 82 (A8) (2004) 961–966.
[13] M. Hartman, O. Trnka, V. Vesely, K. Svoboda, Predicting the rate of thermal decomposition of dolomite, Chem. Eng. Sci. 51 (23) (1996) 5229–5232.
[14] R. Otsuka, Recent studies on the decomposition of the dolomite group by thermal analysis, Thermochim. Acta 100 (1986) 183–189.