Adsorption Performance Indicator for Power Plant CO₂ Capture on Graphene Oxide/TiO₂ Nanocomposite

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ABSTRACT: This study presents the adsorption performance indicator for the evaluation of thermal power plant CO₂ capture on mesoporous graphene oxide/TiO₂ nanocomposite. To begin, this adsorbent was synthesized and characterized using N₂ adsorption-desorption measurements (BET and BJH methods), X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM) and FT-IR spectroscopy. Subsequently, the pure single-component adsorption isotherms measured at 298 K and the Ideal Adsorbed Solution Theory (IAST) solved with direct search minimisation were applied to estimate the selectivity of the synthesized mesoporous graphene oxide/TiO₂ nanocomposite for CO₂ over N₂ and predict CO₂ adsorption capacity in the CO₂:N₂ binary gas mixtures, including the molar ratio of 5:95, 10:90 and 15:85. Finally, the results validated by the breakthrough experiments at a fixed-bed column were applied to estimate the Adsorption Performance Indicator (API) for the evaluation of CO₂ separation from N₂ in the Pressure Swing Adsorption (PSA) process with respect to different types of thermal power plants.

KEYWORDS CO₂ capture; Thermal power plants; Adsorption performance indicator; Graphene oxide/TiO₂ nanocomposite; Ideal adsorbed solution theory; Breakthrough experiments.

INTRODUCTION
The increase in the use of conventional fossil fuels such as coal, oil, and natural gas as a result of rapid economic growth has the serious damage on our environment and this trend has been led to increasing the emission of carbon dioxide as the main anthropogenic greenhouse gas [1]. The atmospheric carbon dioxide concentration has increased from 280 ppm before industrial revolution to 400 ppm in 2013 [1]. Without greenhouse gas mitigation policies, the atmospheric CO₂-equivalent concentration will reach to 600-1500 ppm [1]. According to scientific literature, there are different approaches to control greenhouse gas emissions. Improving energy efficiency, increasing the consumption of the low carbon fuels (including hydrogen and natural gas), utilizing renewable energy (such as wind, solar, hydropower and bio-energy), using geoengineering techniques and applying CO₂ Capture and Storage (CCS) technologies are the major approaches to mitigate global climate change [1]. Efficient CO₂ capture from the large point sources such as power plants, cement industries,
refineries, metal industries and other anthropogenic sources are some of the most important priorities to reduce the global warming effect [2]. In this regard, several technologies with various degrees of maturity have been developed for pre-combustion and post-combustion CO₂ capture processes. The main technologies include absorption, adsorption, membrane separation, chemical looping, hydrate-based separation and cryogenic distillation [1,2,3]). Absorption technology requires significant amounts of heat, which leads to the energy penalty for absorbent regeneration [4]. Furthermore, this technology has environmental impacts related to the sorbent degradation [1,2,3]). On the other hand, membrane gas separation technology is in the infancy stage and more studies are required to develop this technology [1,2,3]). The chemical looping process is under development and there is not any large plant operation experience. In addition, this technology has serious technical problems such as low fluxes and fouling [1]. Hydrate-based separation as a new technology that uses chilled water requires more research and development [1]. Cryogenic distillation as an energy intensive technology conducted at very low temperature and this technology is feasible for very high carbon dioxide concentrations (approximately above 90% v/v) [1]. Therefore, adsorption technology which needs fewer energy requirements and has several competitive advantages too, including lower capital cost, simplicity of operation and applicability in the wide range of temperature and pressure conditions has been introduced as an attractive technology to control CO₂ emissions [2,5]. Solid adsorbents which are the main important part of this technology allow the selective separation of CO₂ from the flue gas mixture as a result of different interaction forces between CO₂ molecules and the solid surface [6]. Recently, a group of solid adsorbents developed based on graphene and graphene oxide has been studied by scholars [2,6]. These adsorbents have some advantages as a result of the unique combination of graphene’s chemical, mechanical, structural and thermal properties [2,6] such as high specific surface area and lowered production cost [2,6]. These properties make them more attractive in comparison with other conventional adsorbents including carbon fiber, metal organic frameworks, porous silica, porous polymers, zeolites, alumina, activated carbon and metal oxides [2]. The above mentioned features introduce graphene and graphene oxide-based adsorbents as the next generation of CO₂ adsorbents [2,6]. Therefore, great efforts have been made to explore CO₂ capture on these adsorbents since 2012 [6]. The determination of pure CO₂ uptake on several graphene/graphene oxide based adsorbents has been the main aim of these studies [2, 6-12]. Therefore, there is a literature gap to calculate CO₂ adsorption performance on these adsorbents in the mixed-gas system especially in the binary mixed-gas system which has different CO₂ partial pressures similar to CO₂ concentration in the flue gas of thermal power plants. Determination of CO₂ adsorption capacity in the multicomponent gas system on graphene and graphene oxide-based adsorbents has been recommended for future research on these adsorbents [2]. On the other hand, determination of CO₂ selectivity over other gases such as N₂ on different adsorbents to evaluate the performance of these adsorbents is one of the most important challenges for development of them [2,6]. CO₂ concentration is commonly in the range of 5%-15% depending on the fuel type fired in the combustion process, and the type of thermal power plants [13,14]. In this study, the selectivity of CO₂ over N₂ and CO₂ adsorption capacity in the binary mixed-gas system on the synthesized mesoporous graphene oxide/TiO₂ nanocomposite are theoretically and experimentally determined by the ideal adsorbed solution theory solved with direct search minimisation and the breakthrough experiments at a fixed bed column. The prediction of multi-component gas adsorption isotherms which is used to design the adsorption separation units has been studied by scholars with different models. One of the most famous models is the ideal adsorbed solution theory [15]. This model has the appropriate ability to anticipate multi-component adsorption isotherm data [15]. The applicability of the Ideal Adsorbed Solution Theory (IAST) to predict CO₂ selectivity over N₂ from the single component adsorption isotherm has been reported by some scholars [15-21]. Scholars apply this model to predict CO₂ adsorption uptake in the gaseous mixtures of CO₂/N₂ (or CO₂/CH₄) and determine selectivity of CO₂ over N₂ (or CH₄) on MCM-41, MOF-14, different porous carbon adsorbents and biomass-based activated carbons ([16-21]. Recently, some scholars have proposed the new indicator entitled the adsorption performance indicator to compare the promising adsorbents such as metal-organic frameworks
and biomass-based activated carbons for separation CO₂ from CH₄ in the pressure swing adsorption process. This indicator merges three important parameters, including working capacity, selectivity and the heat of adsorption to screen the novel adsorbents for the gas separation [21,22]. For the first time in this study, the adsorption performance indicator is applied to compare the potential of the synthesized mesoporous graphene oxide/TiO₂ nanocomposite as the promising and energy-efficient carbon dioxide adsorbent [12] with other reported adsorbents for thermal power plant CO₂ capture.

In sum, the main objectives of this study are illustrated as follows:

-Determination of CO₂ adsorption capacity and CO₂ selectivity over N₂ on the synthesized mesoporous graphene oxide/TiO₂ nanocomposite in the binary mixed-gas system using the ideal adsorbed solution theory solved with direct search minimisation with respect to different CO₂ concentrations in the flue gas of thermal power plants.

-Validation of CO₂ adsorption capacity in the binary mixtures by the breakthrough experiments at a fixed bed column and estimation of the uncertainty of it using a combined uncertainty calculation method.

-Evaluation using the synthesized mesoporous graphene oxide/TiO₂ nanocomposite in comparison with other reported adsorbents for thermal power plant CO₂ capture by calculating the Adsorption Performance Indicator (API).

EXPERIMENTAL SECTION

Synthesis of mesoporous graphene oxide/TiO₂ nanocomposite

Graphene oxide was prepared from graphite powder (LOBA Chemie) based on the improved Hummer’s procedure [12]. A one-step colloidal blending procedure was applied to prepare graphene oxide/TiO₂ nanocomposite (GO to TiO₂ mass ratio=0.1). According to this procedure, 0.2 g of graphene oxide was dispersed into the deionized water by ultrasonication for 0.5 h then 2 g of TiO₂ powder (Degussa) was added to the prepared graphene oxide suspension. After sonication of the final mixture for 1.5 h, graphene oxide/TiO₂ homogeneous mixture was prepared with a further stirring at room temperature for 12 h. After filtering and drying, mesoporous graphene oxide/TiO₂ nanocomposite was prepared at room temperature [12].

Characterization of graphene oxide/TiO₂ nanocomposite

The structure and surface morphology of the synthesized graphene oxide/TiO₂ nanocomposite were studied by field emission scanning electron microscopy (Hitachi S-4160, Japan), wide angle X-ray diffraction (PANalytical, Netherlands), N₂ adsorption-desorption measurements using BET and BJH methods (Microtrac Belsorp-mini II, Japan) and FT-IR spectra (400-400 cm⁻¹) (Perkin-Elmer Spectrum One FT-IR Spectrometer, U.S.A).

Pure gas adsorption measurements

The measurement of pure CO₂ and pure N₂ adsorption equilibrium isotherms on the synthesized graphene oxide/TiO₂ nanocomposite were volumetrically carried out by Microtrac Belsorp-max adsorption apparatus (Japan). Adsorption isotherms were measured at 298 K and pressurized up to 100 kPa. For desorption of any moisture and organic compounds, all of the samples were degassed under vacuum and at 393 K for 24 h. Ultra high purity grade CO₂ and N₂ gases (99.9%) were applied during the tests of this study.

Validation of CO₂ adsorption capacity in the binary mixed-gas system

Binary breakthrough adsorption tests of CO₂/N₂ system were conducted in a fixed-bed setup packed with the synthesized graphene oxide/TiO₂ nanocomposite (Fig. 1). LNI SONIMIX 2106 (programmable gas divider, Switzerland) was utilized to generate the simulated flue gas mixture, (including CO₂ and N₂) with CO₂ concentration of 5-15%. The multi-component gas analyzer (MRU DELTA 1600 S-IV, Germany) equipped with a CO₂ Non-Dispersive InfraRed (NDIR) detector was applied to analyze the CO₂ concentration at the outlet of the experimental setup. Before each experiment, for desorbing any moisture and organic compounds, the samples of the synthesized graphene oxide/TiO₂ nanocomposite (approximately 0.7 g) were degassed at 393 K under vacuum for 24 h. The simulated flue gas, including CO₂:N₂ mixtures of 5:95, 10:90 and 15:85 were fed to the adsorption fixed-bed column (glass, 10 cm in height and 1 cm in diameter) and CO₂ adsorption The dynamic CO₂ adsorption capacity (q) calculated as a function of the feed gas CO₂ concentration is illustrated as in the following [23-25]:
Fig. 1: Experimental setup for determination of CO\textsubscript{2} capture on graphene oxide/TiO\textsubscript{2} nanocomposite.

\[ q = \frac{Q_F c_0 t_q}{m_s} \]  

(1)

Where \( Q_F \) is the volumetric flow rate of the feed gas, \( c_0 \) is the inlet CO\textsubscript{2} concentration, \( m_s \) is the mass of adsorbent loaded in the bed and \( t_q \) is the stoichiometric time, which is calculated from the breakthrough profile as follows:

\[ t_q = \frac{C_{CO_2,in} t_s - \int_{t_s}^{t} C_{CO_2}(t) \, dt}{C_{CO_2,in}} \]  

(2)

Where, \( t_s \), \( t_b \) and \( C_{CO_2}(t) \) are saturation time (sec), breakthrough time (sec) and CO\textsubscript{2} concentration at time \( t \), respectively. Saturation and breakthrough times are defined as the times when outlet CO\textsubscript{2} concentration reaches to 5% and 95% of inlet CO\textsubscript{2} concentration respectively [23]. The relative error (RE) applied in this study to analyze the error between the experimental CO\textsubscript{2} adsorption capacity and the calculated CO\textsubscript{2} adsorption capacity is illustrated, below: [21].

\[ \text{RE}(\%) = \left| \frac{q_{\text{meas}} - q_{\text{calc}}}{q_{\text{meas}}} \right| \times 100 \]  

(3)

Where \( q_{\text{meas}} \) is the experimental CO\textsubscript{2} adsorption capacity and \( q_{\text{calc}} \) is the calculated CO\textsubscript{2} adsorption capacity predicted by the Ideal Adsorbed Solution Theory (IAST) solved with the direct search minimisation. Using the combined uncertainty calculation method, the uncertainty of CO\textsubscript{2} adsorption capacity is determined. According to this method, the absolute combined standard uncertainty of CO\textsubscript{2} adsorption capacity is illustrated as follows [26]:

\[ u_c(q) = q \times \sqrt{\left( \frac{u(Q_F)}{Q_F} \right)^2 + \left( \frac{u(c_0)}{c_0} \right)^2 + \left( \frac{u(t_q)}{t_q} \right)^2 + \left( \frac{u(m_s)}{m_s} \right)^2} \]  

(4)

Where, \( u_c(q) \) is the combined standard uncertainty of CO\textsubscript{2} adsorption and \( u(Q_F/Q_F) \), \( u(c_0/c_0) \) and \( u(m_s/m_s) \) and \( u(t_q/t_q) \) are the relative uncertainty of the volumetric flow rate of the feed gas, the inlet CO\textsubscript{2} concentration, the mass of adsorbent loaded in the column and the stoichiometric time respectively.

THEORETICAL SECTION

Estimation of CO\textsubscript{2} selectivity over N\textsubscript{2} and prediction of CO\textsubscript{2} adsorption capacity using the ideal adsorbed solution theory solved with the direct search minimisation

The ideal adsorbed solution theory assumes that the adsorbed phase and the ideal gas phase are in equilibrium...
and the adsorbed phase as an ideal phase follows equations should be solved to predict multicomponent gas adsorption on different adsorbents [27]:

\[ P_{tot}y_i = P_i^0x_i \quad i = 1, 2, 3...N \]

(5)

\[ \sum_{i}^N x_i = 1 \]

(6)

\[ n_i = f_i(P_i^0, T) \quad i = 1, 2, 3...N \]

(7)

\[ \frac{\pi_i}{RT} = \int_0^{P_i^0} n_i d\left[\ln(P_i^0)\right] \quad i = 1, 2, 3...N \]

(8)

Where \( P_{tot} \) (kPa) and \( y_i \) are the total pressure of gaseous mixture on the adsorbent surface and the molar fraction of component \( i \) of the non-adsorbed mixture respectively. The molar fraction of component \( i \) in the adsorbed phase, the total number of components and the adsorption amount of component \( i \) from the adsorption isotherm are defined by \( x_i \), \( N \) and \( n_i \) (mol/kg), respectively. The surface pressure of component \( i \), the equilibrium temperature, the specific spreading pressure of component \( i \) and the specific surface area covered by the adsorbed mixture are illustrated by the parameters, \( P_i^0 \) (kPa), \( T \) (K), \( \pi_i \) (kPa m) and \( A \) (m²/kg), respectively [27].

When the spreading pressure \( (\pi_i A/RT) \) of each component has the same value, the system achieves equilibrium.

Therefore, the equilibrium condition is shown as in the following equation [27]:

\[ \frac{\pi_i A}{RT} = \text{const} \quad t \quad i = 1, 2, 3...N \]

(9)

If the parameters, \( P_{tot} \), \( y_i \) and the single component adsorption equilibrium data are given, the problem can be solved. The substitution of variables causes the IAST equations to be reduced to a smaller system of iso-spreading pressure conditions. The spreading pressure is illustrated as the terms of molar fraction \( x_i \) by using an initial change of variable from \( P_i^0 \) to \( x_i \) replacing the Eq. (5)-(8). Spreading pressure acquired by this variable change is illustrated as [27]:

\[ d\ln\left(\frac{P_{tot}y_i}{x_i}\right) = -\frac{1}{x_i}dx_i \]

(10)

Raoult's law [27]. The following algebraic-integral

The following equation represents the analytically integrated form of the spreading pressure for the Toth adsorption isotherm [27]:

\[ \frac{\pi_i A}{RT} = \frac{y_iP_{tot}K_{T;i}q_{s,i}}{x_i} \]

(11)

\[ f_i\left(\frac{1}{t_i} - \sum_{i=1}^{N} \left(1 + \frac{1}{t_i} \right) \frac{y_iP_{tot}K_{T;i}q_{s,i}}{x_i}\right) \]

Where \( f_i \) illustrates the Gauss hypergeometric function. Using this spreading pressure, the iso-spreading pressure condition is set as a minimisation problem. Eq. (6) is used to calculate the objective function of the minimisation problem for the binary system. Therefore, the following function is obtained as [27]:

\[ f_{binary}(x_1) = \left| \frac{\pi_1(x_1)A}{RT} - \frac{\pi_2(x_2)A}{RT} \right| \]

(12)

The selectivity for CO₂ over N₂ is estimated by the following equation [12]:

Selectivity = \[ \frac{x_{CO_2}}{x_{N_2}} \]

(13)

Selectivity is defined by the mole fraction of components CO₂ and N₂ adsorbed on the adsorbent and \( y_{CO_2} \) and \( y_{N2} \) show the mole fraction components of CO₂ and N₂ component in the gaseous mixture, respectively.

In this study, the fitting parameters related to the Toth model have been obtained by Levenberg- Marquardt algorithms using LAB Fit curve fitting software (V 7.2.48).

**Determination of the adsorption performance indicator**

Comparing different adsorbents with various natures for a specific separation process has the most important implication on developing them. For the gas separation by the adsorption process, the high uptake capacity and selectivity, as well as the low isosteric heat of adsorption, are the most important factors to evaluate an adsorbent.

On the other hand, the results reported by some scholars show that these parameters solely are not appropriate to screen the adsorbents for the gas mixture separation [21,22]. Therefore, it is essential to introduce an indicator that combines these parameters for primary selection of the...
adsorbents. To this end, the Adsorption Performance Indicator (API) for the bulk removal and the gas purification processes based on the balances among the three aforementioned parameters have been developed by the scholars as in the following [21,22]:

$$API = \frac{(S_{1/2} - 1)^A \times WC_1^B}{Q_{ST,1}^C}$$  \hspace{1cm} (14)

Where, $S_{1/2}$, $WC_1$ and $Q_{ST,1}$ are the selectivity of component 1 over component 2, the working capacity of component 1 and the isosteric heat of adsorption of component 1, respectively. In this study, the adsorption performance indicator is applied to compare the potential adsorbents for separating CO$_2$ molecules from N$_2$ molecules. In this regard, the exponent of working capacity (B) which has considerable importance has been established to 2 and the rest of exponents (A and C) have been considered to 1 [21]

RESULTS AND DISCUSSION

Mesoporous graphene oxide/TiO$_2$ nanocomposite characterization

Fourier Transform InfraRed (FT-IR) spectroscopy

The FT-IR spectra of graphene oxide, TiO$_2$ and graphene oxide/TiO$_2$ nanocomposite are illustrated in Fig. 2. The broad peak at 3398.09 cm$^{-1}$, 3337.22 cm$^{-1}$ and 3345 cm$^{-1}$ indicate the presence of surface O-H stretching vibrations (Figs. 2a, 2b and 2c) [28,29]. The C-OH stretching vibration peak at 3345 cm$^{-1}$ in graphene oxide (Fig. 2c) has shifted to the higher wavenumber in graphene oxide/TiO$_2$ nanocomposite (3398.09 cm$^{-1}$) as a result of the Ti-O-C bond formation (Fig. 2a) [28,29]. The peaks at 1427.76 cm$^{-1}$ and 1261.44 cm$^{-1}$ are attributed to tertiary C-OH and epoxy C=O groups, respectively (Fig. 2a). The absorption peak at around 1626.78 cm$^{-1}$ is related to the skeletal vibration of the graphene oxide sheets (Fig. 2a) [28,29]. For graphene oxide/TiO$_2$ nanocomposite, the C-O stretching vibration peak at 1040 cm$^{-1}$ and the C=O stretching vibration of –COOH group peak at 1721 cm$^{-1}$ of graphene oxide have been completely disappeared (Figs. 2a and 2c) [28,29]. The strong absorption band at 672.26 cm$^{-1}$ (in the synthesis of graphene oxide/TiO$_2$ nanocomposite) is probably related to the vibration modes of Ti-O-Ti and Ti-O-C bonds (Fig. 2a) [28,29]. This vibration mode is similar to the FT-IR spectrum of pure TiO$_2$ (Fig. 2b). These vibration modes

Fig. 2: FT-IR spectra of graphene oxide/TiO$_2$ nanocomposite (a), TiO$_2$ nanoparticles (b) and graphene oxide (c).
indicate that the TiO$_2$ nanoparticles strongly bond to the graphene oxide sheets [28, 29].

**Nitrogen adsorption–desorption isotherms**

The identification of pore and textural structures of an adsorbent has the most significant implication on designing the related adsorption process [30]. This identification is performed by the adsorption/desorption measurements of Nitrogen at 77 K and subsequently using BET and BJH methods to calculate specific surface area and pore size distribution on the synthesized graphene oxide/TiO$_2$ nanocomposite and its major component (TiO$_2$ nanoparticles). Fig.3a and 3b shows a Type IV isotherm which is typical of the mesoporous compounds [31]. The specific surface area and total pore volume of the synthesized graphene oxide/TiO$_2$ nanocomposite as a result of incorporation TiO$_2$ nanoparticles between 2D graphene oxide sheets in comparison with TiO$_2$ powder have been increased from 47.420 m$^2$/g to 96.367 m$^2$/g and 0.2864 cm$^3$/g to 0.4834 cm$^3$/g, respectively [6]. Furthermore, the average pore diameter has been increased from 24.319 nm to 37.051 nm. Fig.3 (c and d) obtained by applying BJH method shows that the pore size distribution in graphene oxide/TiO$_2$ nanocomposite is principally in the mesoporous range (6.946 nm to 46.13 nm). Moreover, the average pore size of this composite which has been estimated as 37.051 nm verifies the mesoporous textural structure of it. The synthesized graphene oxide/TiO$_2$ nanocomposite does not show any limiting adsorption
at high $P/P_0$ in adsorption/desorption isotherm. Therefore, it indicates that typical of a Type H3 hysteresis loop has been involved with the presence of non-rigid aggregates of plate-like particles forming slit-shaped pores [12,31]. This case is relevant to the presence of the graphene oxide nanosheets coated with TiO$_2$ nanoparticles and observed in the FE-SEM images (Fig. 4).

Field Emission Scanning Electron Microscopy (FE-SEM)

The microstructure of the synthesized mesoporous graphene oxide/TiO$_2$ nanocomposite has been characterized by FE-SEM image (Fig. 4). It has been clearly observed that the TiO$_2$ nanoparticles have been distributed on both sides of the graphene oxide nanosheets. The reciprocal electrostatic interaction between positively charged Ti$^{4+}$ of TiO$_2$ and negatively charged oxygen atoms of graphene oxide has been led to the heterostructure of mesoporous graphene oxide/TiO$_2$ nanocomposite [32].

X-ray diffraction pattern (XRD)

The XRD patterns, the synthesized graphene oxide, pure graphite as its precursor and the synthesis mesoporous graphene oxide/TiO$_2$ nanocomposite are illustrated in Figs. 5 a and 5b, respectively. The XRD pattern of graphene oxide and graphite show the characteristic peak from (002) diffraction at $2\theta=10.77^\circ$ correlated to a d-spacing of 8.1 Å and a major peak from (002) at $2\theta=26.52^\circ$ correlated to a d-spacing of 3.3 Å, respectively (Fig. 5a). The intercalation of oxygen functional groups and water molecules during Hummer’s process might lead to the large interlayer spacing of graphene oxide [12]. The XRD pattern of graphene oxide/TiO$_2$ nanocomposite has been mainly composed of the anatase and rutile TiO$_2$ phases (Fig. 5b). The major peaks at $2\theta=25.34^\circ$, 37.90$^\circ$, 48.15$^\circ$, 54.07$^\circ$, 55.17$^\circ$ and 62.78$^\circ$ belong to the diffractions of the (101), (004), (200), (105), (211) and (002) crystal planes of the anatase phase in TiO$_2$ (Joint Committee on Powder Diffraction Standards card No.21-1272) [12]. On the other hand, the major peaks shown at $2\theta=27.53^\circ$ and 36.16$^\circ$ may be attributed to the (110) and (101) crystal planes of rutile phase in TiO$_2$ (Joint Committee on Powder Diffraction Standards card No. 21-1276) [12]. Because of the stacking disorder caused by the intercalation of TiO$_2$ particles into stacked graphene oxide layers, the characteristic diffraction peak of graphene oxide has been absent in graphene oxide/TiO$_2$ nanocomposite pattern [12].

Estimation of CO$_2$ selectivity over N$_2$, prediction, and validation of CO$_2$ adsorption capacity

The Toth isotherm parameters of the pure components used to calculate the reduced spreading pressure and estimate CO$_2$ selectivity over N$_2$ in the CO$_2$:N$_2$ binary gas mixtures are illustrated in Table. 1. The parameter $K_T$ defined as the adsorption affinity has been assessed to be 0.308×10$^{-2}$ 1/kPa and 0.156×10$^{-2}$ 1/kPa for CO$_2$ and N$_2$ molecules, respectively. The Toth parameter $t$ which represents the system heterogeneity and the interaction and mobility of the gas molecules adsorbed (adsorption affinity) on the adsorbent has been assessed to be 0.302 and 1.683 for pure CO$_2$ and pure N$_2$ adsorption isotherms, respectively. The value of this parameter (if $t<1$) indicates that the system, including CO$_2$ molecules and synthesized mesoporous graphene oxide/TiO$_2$ nanocomposite, is heterogeneous. On the other hand, the $t$ value greater than unity for N$_2$ adsorption indicates that the adsorptive potential of N$_2$ molecules on synthesized graphene oxide/TiO$_2$ nanocomposite is heterogeneous. The greater affinity for CO$_2$ molecules over N$_2$ molecules on the synthesized graphene oxide/TiO$_2$ nanocomposite concluded by the difference between physical properties of CO$_2$ molecules and N$_2$ molecules is led to the higher selectivity of CO$_2$ molecules versus N$_2$ molecules on the synthesized graphene oxide/TiO$_2$ nanocomposite. The most important of these properties

![Graphene oxide TiO2 nanocomposite](image-url)
Table 1: Toth isotherm parameters for pure CO$_2$ - pure N$_2$ adsorption at 298 K.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>$q_s$(mmol/g)</th>
<th>$K_T$(1/kPa)</th>
<th>$t$</th>
<th>$r^2$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure CO$_2$</td>
<td>35.806</td>
<td>0.308x10$^{-2}$</td>
<td>0.302</td>
<td>0.9995</td>
<td>This study</td>
</tr>
<tr>
<td>Pure N$_2$</td>
<td>1.433</td>
<td>0.156x10$^{-2}$</td>
<td>1.683</td>
<td>0.9999</td>
<td>This study</td>
</tr>
</tbody>
</table>

Fig. 5: XRD patterns of graphite and graphene oxide (a) and graphene oxide/TiO$_2$ nanocomposite (b).

are polarizability and quadrupole moment. The ratios of polarizability and quadrupole moment of CO$_2$ molecule over N$_2$ molecule are 1.672 and 2.851, respectively [12]. In addition, CO$_2$ molecules are more condensable than N$_2$ molecules because CO$_2$ has a higher critical temperature (304.1 K) in comparison with that of N$_2$ (126.2 K) (Li et al., 2015). Fig. 6a, 6b, and 6c show the curve of the reduced spreading pressure versus the molar fraction of CO$_2$ in the synthesized graphene oxide/TiO$_2$ nanocomposite at different total pressures and 298 K for different CO$_2$ concentrations. As shown in this figure, the equilibrium molar fraction (iso-spreading pressure condition) at 1 bar has been predicted to be 0.780, 0.700 and 0.570 for the binary mixtures, including CO$_2$:N$_2$=15:85, 10:95 and 5:95, respectively. In this study, these curves have been calculated for 14 total pressures to predict the equilibrium molar fraction of CO$_2$ with respect to the different CO$_2$ concentrations in the adsorbed mixture. Subsequently, the selectivity of CO$_2$ molecules over N$_2$ molecules on the synthesized graphene oxide/TiO$_2$ nanocomposite has been estimated. The values of selectivity (Fig.6d) decrease when the pressure increases. This behavior is explained by the fact that, the CO$_2$ molecules (as the stronger adsorbate component) prefer the high energy sites in comparison with the N$_2$ molecules (as the weaker adsorbate component) which prefer the weaker adsorption sites. Therefore, the greater amount of CO$_2$ molecules is adsorbed at lower pressures [33]. Furthermore, when the pressure increases and the high energy sites are filled, the CO$_2$ molecules begin to compete with the N$_2$ molecules for the weaker sites which have the lower local values of selectivity [33]. For the case of $y_{CO2}$=0.15, which is a typical composition of coal-fired steam power plant [13,14], the selectivity is in the range of 20.09-60.187. For the case of $y_{CO2}$=0.1, which is the typical composition of oil-fired steam power plant [13,14], the selectivity is in the range of 21-44.886. For the case of $y_{CO2}$=0.05, which is the typical composition of gas turbine and combined cycle power plant [13, 14], the selectivity is in the range of 25.185-49.476. For these conditions, the selectivity of CO$_2$ molecules over N$_2$ molecules (at 1 bar and around 298 K) on the synthesized graphene oxide/TiO$_2$ nanocomposite in these binary mixture systems is higher than the parameter on other adsorbents, including MOF-508b (selectivity=6, CO$_2$:N$_2$=50:50), zeolite NaY (selectivity=14.5, CO$_2$:N$_2$=50:50), molecular sieve 5A (selectivity=4.7, CO$_2$:N$_2$=50:50), activated carbon (selectivity=6.1, CO$_2$:N$_2$=50:50), MIL-53 (Al) (selectivity=10.1, CO$_2$:N$_2$=50:50), zeolite beta
Fig. 6: Reduced spreading pressure as a function of the molar fraction of adsorbed CO$_2$ for CO$_2$:N$_2$=5:95 (a), 10:90 (b), 15:85 (c) and selectivity of CO$_2$ over N$_2$ on graphene oxide/TiO$_2$ nanocomposite (d).

(selectivity=12.5, CO$_2$:N$_2$=50:50), Na-SAPO-34
(selectivity=11.66, CO$_2$:N$_2$=50:50), SAPO-43
(selectivity=15.28, CO$_2$:N$_2$=50:50), NaETS-4
(selectivity=18.35, CO$_2$:N$_2$=50:50) [34-38].

Fig.7a illustrates CO$_2$ adsorption isotherms calculated by the ideal adsorbed solution theory solved with the direct search minimisation. According to this figure, the maximum CO$_2$ adsorption capacity for CO$_2$/N$_2$ binary gas mixture, including CO$_2$:N$_2$=15:85, 10:90 and 5:95 were predicted to be 0.954 mmol/g, 0.771 mmol/g and 0.553 mmol/g at 298 K, respectively. To evaluate the reliability of CO$_2$ adsorption prediction by this method, the breakthrough experiments with the aforementioned simulated flue gas composition were conducted at 1 bar and 298 K (Fig. 7b). According to Fig. 7b, the stoichiometric time for CO$_2$ =15%, 10% and 5% was calculated to be 138.1 sec, 144.5 sec, and 169.5 sec, respectively. The CO$_2$ adsorption capacity for CO$_2$ =15%, 10% and 5%, was measured to be 0.987±0.052 mmol/g, 0.837±0.045 mmol/g and 0.508±0.032 mmol/g respectively. The relative errors between the measured and predicted data were calculated to be 3.343%, 7.885%, and 8.858% respectively. As a result, the ideal adsorbed solution theory solved with the direct search minimisation predicted the experimental data with an appropriate degree of accuracy and uncertainty with respect to different CO$_2$ concentrations.

These measured CO$_2$ adsorption capacities are higher than (or comparable with) those reported by Chowdhury et al.[39,40] for other adsorbents, such as acid treated bentonitic clay (0.58 mmol/g for pure CO$_2$), Cu-MOF (0.65 mmol/g for pure CO$_2$), γ-Alumina (0.68 mmol/g
for pure CO₂, ZIF-8 (0.11 mmol/g for coal-fired power plant and 0.07 mmol/g for gas turbine and combined cycle power plant), amino-MIL-53(Al) (0.92 mmol/g for coal-fired power plant and 0.22 mmol/g for gas turbine and combined cycle power plant), Chabazite (0.37 mmol/g for coal-fired power plant and 0.13 mmol/g for gas turbine and combined cycle power plant).

**Screening thermal power plant CO₂ capture using the adsorption performance indicator**

According to the calculation performed in this study, the order of the Adsorption Performance Indicator (API) for CO₂ capture on the synthesized graphene oxide/TiO₂ nanocomposite is a coal-fired power plant (1.363) > oil-fired power plant (0.949) > combined cycle & gas turbine power plant (0.388). This indicator for coal-fired power plant (Fig. 8a) and combined cycle & gas turbine power plant (Fig. 8b) has the highest value in comparison with other adsorbents, including Ni₂(dobdc) (pip)₃,5, K-BEA, activated carbon from cellulose fibers, holey graphene frameworks, Chabazite, ZIF-8 and Amino-MIL-53(Al). As can be seen in Tables 2 and 3, the sequence order of working capacity, the isosteric heat of adsorption of CO₂ and the selectivity of CO₂ over N₂ on these adsorbents are not matched with the order of the adsorption performance indicator values. This observation indicates
the importance of the API parameter for screening the adsorbents for thermal power plant CO₂ capture in the PSA process.

**CONCLUSIONS**

The binary CO₂/N₂ selectivity of synthesized mesoporous graphene oxide/TiO₂ nanocomposite using the ideal adsorbed solution theory solved with the direct search minimisation and CO₂ adsorption uptake in the gaseous mixtures of CO₂/N₂ (with respect to CO₂ concentrations in the flue gas of thermal power plants) based on the breakthrough experiment as well as the reported heat of CO₂ adsorption was used in this study to calculate the adsorption performance indicator. The order of the adsorption performance indicator for thermal power plant CO₂ capture on the synthesized mesoporous graphene oxide/TiO₂ nanocomposite is higher than that of other CO₂ adsorbents such as Ni₃(dobdc) (pip)₀.₅, K-BEA, activated carbon from cellulose fibers, holey graphene frameworks, Chabazite, ZIF-8 and Amino-MIL-53(Al).

This finding indicates that the aforementioned adsorbent has the appropriate performance in comparison with the common and novel adsorbents for the separation of CO₂ from a CO₂/N₂ mixture similar to the flue gas composition of thermal power plants in the PSA units. The order of the Adsorption Performance Indicator (API) for CO₂ capture on the synthesized graphene oxide/TiO₂ nanocomposite indicates that the coal-fired power plant in comparison with other thermal power plant type (including oil-fired and gas turbine & combined cycle power plants) is the preferred type for the CO₂ separation by the mentioned adsorbent.

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**REFERENCES**


