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RESEARCH PAPER

Environmental Performance of Alternative Schiff Bases Synthesis Routes: A Proposal for CO_2 Storages

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ABSTRACT

The increased consumption of fossil fuels provokes high levels of carbon dioxide (CO_2) emissions, which give rise to serious environmental issues. Accordingly, designing and utilizing new classes of materials, such as Schiff bases, to capture CO_2 gained significant attention from researchers worldwide. In the present work, two Schiff bases were synthesized and examined as storage materials for carbon dioxide gas. The prepared compounds were obtained by reacting trimethoprim with two aldehydes severally (benzaldehyde and parabromobenzaldehyde) in boiling methanol. The surface morphology of the compounds was investigated via field emission scanning electron microscopy (FESEM). The Brunauer-Emmett-Teller (BET) test showed that Schiff bases 1 and 2 have surface areas of 17.993 and 2.732 m^2/g, pore volumes of 0.008 and 0.005 cm^3/g, and pore diameters of 17.02 and 74.89 nm, respectively. Reasonable uptake values of CO_2 (31.36 cm^3/g, 6.2 wt%) and (25.30 cm^3/g, 5.0 wt%) were achieved by the prepared Schiff bases 1 and 2, respectively, at 313 K temperature and 40 bars pressure.

Keywords: Schiff bases; gas storage; environmental pollution; carbon dioxide uptake; CO_2 capturing; adsorption.

INTRODUCTION

The accelerated rates of fossil fuels combustion, due to worldwide energy demand, led to an increase in the carbon dioxide emissions to the environment to unacceptable levels (Owusu, 2016). As a result, this increment in the atmosphere is potentially affecting human and animal health, and disturb the natural balance of aquatic ecosystems with global weather discrepancy (Qazi et al., 2019). Therefore, reducing CO_2 emissions became a task for many research groups due to its direct relation with the recent climate changes and global warming issues (Ludin et al., 2018). Thereby, different approaches have been pursued to mitigate the problems associated with high carbon emissions (Owusu, 2016). These strategies involved the

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problems associated with high carbon emissions (Owusu, 2016). These strategies involved the implementation of renewable energy sources, mainly solar, wind, and biomass, which could reduce CO_2 emissions dramatically to zero (Qazi et al., 2019; Ludin et al., 2018). Yet, even these energy resources are widely invested in many regions across the globe, they are barely capable to provide the required energy to meet the global and industrial demands, in addition to their high cost of installation. Since the usage of fossil fuel is inevitable, a raised technological trend has been provoked to reduce CO_2 emission by storing the gas within designed porous materials (Correia de Carvalho et al., 2020; Busu, 2019; Borhan et al., 2019; Razavian et al., 2014). Hence, several chemical adsorbent materials have been utilized and investigated as media for capturing CO_2 gas, such as activated carbons, silica, zeolites, ionic liquids supported matrix, metal oxides, and cross-linked polymers (Lu et al., 2016). In particular, metal organic frameworks (MOFs) compounds (Mohammed et al., 2020; Hadi et al., 2019), porous organic polymers (POPs) (Ahmed et al. 2018; Satar et al., 2020), and poly (ionic liquid)-based nanocomposites have been widely used in the past two decades for CO_2 storage (Kaya et al., 2009). In the quest for new adsorbents for CO_2 capture, we turned our attention to heterocyclic compounds containing a 2,4-diaminopyrimidine moiety, because they are useful as biologically active compounds (Ouyang et al.2017).

Trapping the gas is mainly achieved via physical or chemical adsorption-interaction processes between the adsorbents' surfaces and CO_2 gas (Liu et al., 2017). The physical processes involve taking up the gas within the adsorbent's internal pores; while the chemical adsorption is represented by the chemical bonds between the adsorbent's surface and the gas molecules due to polarity. Therefore, chemical adsorption relies on the presence of polar groups or heteroatoms, like oxygen, sulfur, nitrogen, boron, and phosphorus, within the structure of the adsorbents (Lysova et al., 2020; Chiang et al., 2019; Al-Ghurabi et al. 2018; Staciwa et al., 2019). Interestingly, the incorporation of polar functional moieties on the adsorbents' surfaces would increase and facilitate the adsorption of CO_2 (Dawson et al., 2012). In this regard, nitrogen-rich Schiff bases compounds have been recently suggested as promising alternatives for CO_2 storage (Satar et al., 2019; Mohammed et al., 2020). In this research, the objective was to synthesize two Schiff bases by reacting trimethoprim (an antibiotic medical compound that contains nitrogen and oxygen heteroatoms) with benzaldehyde and one of its derivatives. The prepared compounds are highly aromatic and retain porous merits that make them suitable media for CO_2 capture.

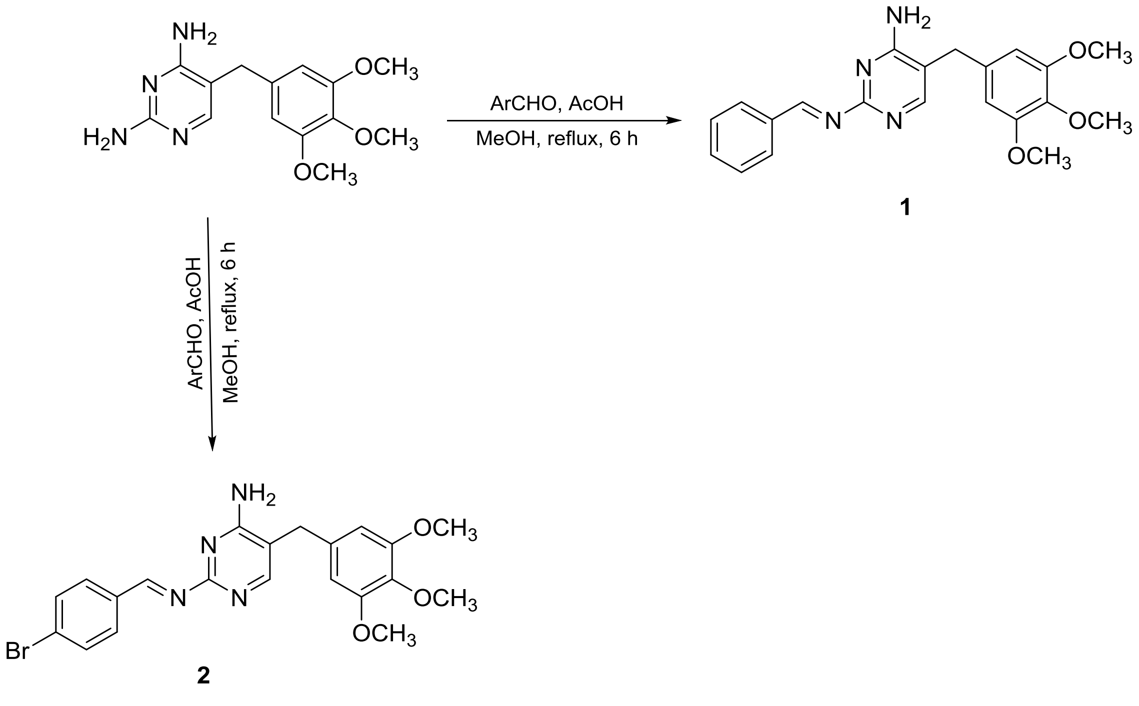
MATERIAL AND METHODS

Trimethoprim (99%), Aldehydes (benzaldehyde and parabromobenzaldehyde) (99.5%), and solvents were supplied from Merck company (Schnelldorf, Germany). The chemicals were used as obtained without further purification. A Fourier transform infrared (FTIR) device (FT-IR 8300, Shimadzu Corporation, Tokyo, Japan) was used to detect the reflected spectra and identify the structural groups. Field emission scanning electron microscopy (FESEM) images were captured using a Tescan MIRA3 LMU device from Tescan Orsay Holding (Brno-Kohoutovice, Czech Republic). While a Varian INOVA spectrophotometer operated at 400 MHz was used to detect the spectra of proton and carbon nuclear magnetic resonance (^{1}H-^{13}C-NMR). All compounds were dissolved in deuterated dimethyl sulfoxide (DMSO-d^6) solvent.

The Schiff bases were prepared following the general protocol of condensing 1 mole of trimethoprim and 1 mole equivalents of the suitable aldehyde (benzaldehyde and 4-bromobenzaldehyde). The reaction was conducted in boiling methanol and catalyzed by acetic acid; it continued for 6 h under reflux. The specimens were dried for 4 h at 60 °C using a vacuum oven prior to the measurements. The Brunauer-Emmett-Teller (BET) method was applied to estimate the surface area (SA) and identify the nitrogen (N_2) adsorption isotherms at 77K. The pores’ size and volume were analyzed via the Barrett-Joyner-Halenda (BJH) method (Sing, 2001). The Schiff bases capacity for gas uptake was verified using a high-pressure volumetric adsorption device (Hsorb 2600). Before the test, 1 g of each Schiff base was weighted and degassed in a vacuum oven for 1 h at 60 °C to terminate any trace of moisture or trapped solvent within the pores. The gas uptake analysis was repeated at least thrice under identical conditions for both samples to obtain the optimum pressure. The apparatus diagram and fully described measurement method were previously reported (Kacem et al., 2015; Hauchhum and Mahanta, 2014).

RESULTS AND DISCUSSION

The reaction of selected aldehydes, benzaldehyde and 4-bromobenzaldehyde, and trimethoprim (one equivalent mole) was carried on in boiling methanol to produce Schiff bases 1 and 2, respectively. The reaction afforded the Schiff bases in good yield ratios, and its mechanism was illustrated in Scheme 1. The yield ratios, colors, melting points (m.p.), and spectroscopic data from the ^{1}H-NMR, ^{13}C-NMR, and FT-IR analyses are reported below.



Scheme 1. Synthesis of the Schiff bases.

For Schiff base 1, the reaction gave white powder, a yield of 83% and m.p. of 187–190 ºC. The FTIR (KBr, 1/cm) spectra show: NH_2 (3446) 1/cm, HC=N (1656) 1/cm, C=N Ar (1589) 1/cm, C=C (1543) 1/cm, and O-CH_3 (1128) 1/cm. The ^{1}HNMR (400 MHz, DMSO-d^6) displayed the following peaks: 8.76 (s, H, 1-CH=N), 6.48-7.49 (m, 7H Ar), 3.43-3.95 (s, 9H, 3O-CH_3, 2H, 1NH_2), 1.87 (s, 2H, 1CH_2). Whereas, the ^{13}CNMR (DMSO-d^6) attained the peaks at: 173.58 (HC=N), 162 (C-NH_2), 161-162 (2C=N), 21.9 (CH_2), 105.9-106.3 (4C Ar), 152 (3C-O), 135 (4C Ar), 55.9-60 (O-CH_3).

The product of Schiff base 2 was yellow powder with a yield of 79% and m.p. of 193-194 °C. The FTIR (KBr, 1/cm) spectra show: NH_2 (3446) 1/cm, HC=N (1654) 1/cm, C=N Ar (1591) 1/cm, C=C (1529) 1/cm, and O-CH_3 (1120) 1/cm. The ^{1}HNMR (400 MHz, DMSO-d^6) displayed the following peaks: 7.45 (m, H, 1-CH=N), 5.81-6.61 (m, 8H Ar), 3.45-3.77 (s, 9H, 3O-CH_3, 2H, 1NH_2), 1.91(m, 2H,1CH_2). The ^{13}CNMR (DMSO-d^6) gave the peaks at: 169.7 (HC=N), 161.1 (C-NH_2), 155 (2C=N), 25.2 (CH_2), 99.1-101, 6-104.9 (5C Ar), 151.2 (3C-O), 146 (4C Ar), 68.2-74.8 (O-CH_3).

The surface morphology of the prepared Schiff bases 1 and 2 was examed by the FESEM and presented in Figures 1 and 2, respectively. The figures indicate that the Schiff bases have a heterogeneous and porous structure. Furthermore, they showed a minor agglomeration of various shapes and sizes particles. The particles size of Schiff bases 1 and 2 was noted to range from 24.85 - 53.66 nm and 42.29 - 47.16 nm, respectively. It is obvious that the particle size of Schiff base 2 had a smaller variety than that of Schiff base 1. In addition, Schiff base 1 has larger particle dimensions and different shapes compared to Schiff base 2, which could be attributed to the presence of the bromide group. Such a group motivates prominent irregularity in particle size and shape; subsequently, it attains a highly porous structure. The high porosity could improve the surface area and gases uptake capacity (Omer et al., 2020). However, the pore size of the prepared Schiff bases is considered average, where it is larger than some complexes and smaller than other Schiff bases and POPs (Ahmed et al., 2018; Satar at al., 2019; Mohammed et al., 2020; Hadi et al., 2019; Omer et al., 2020)

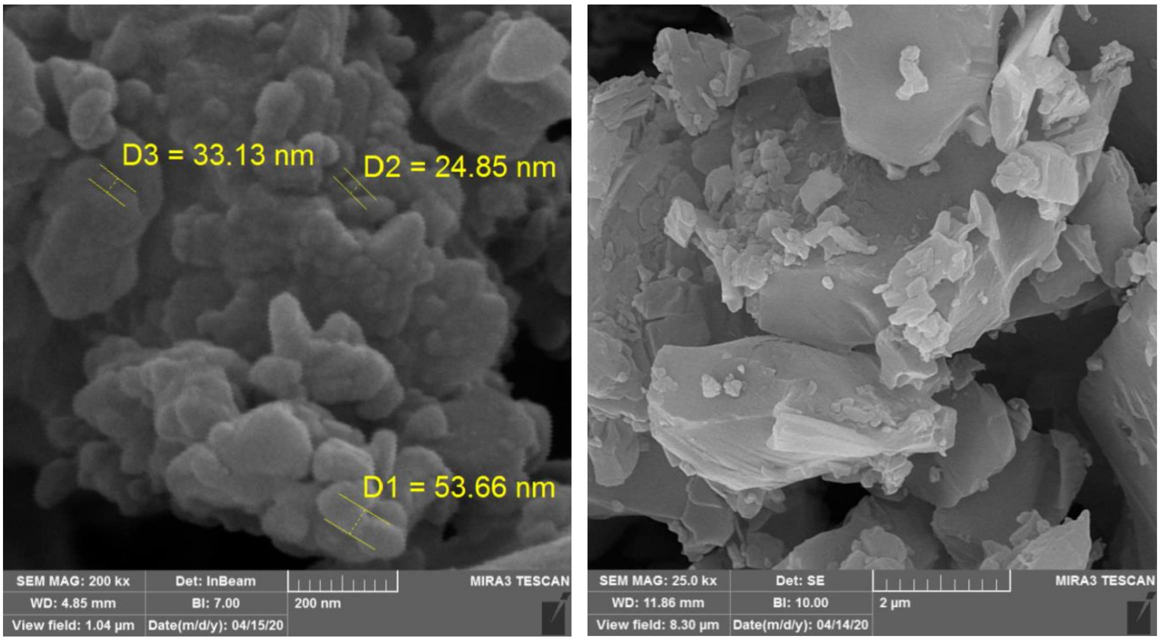


Fig. 1. Field emission scanning electron microscopy images of Schiff base 1.

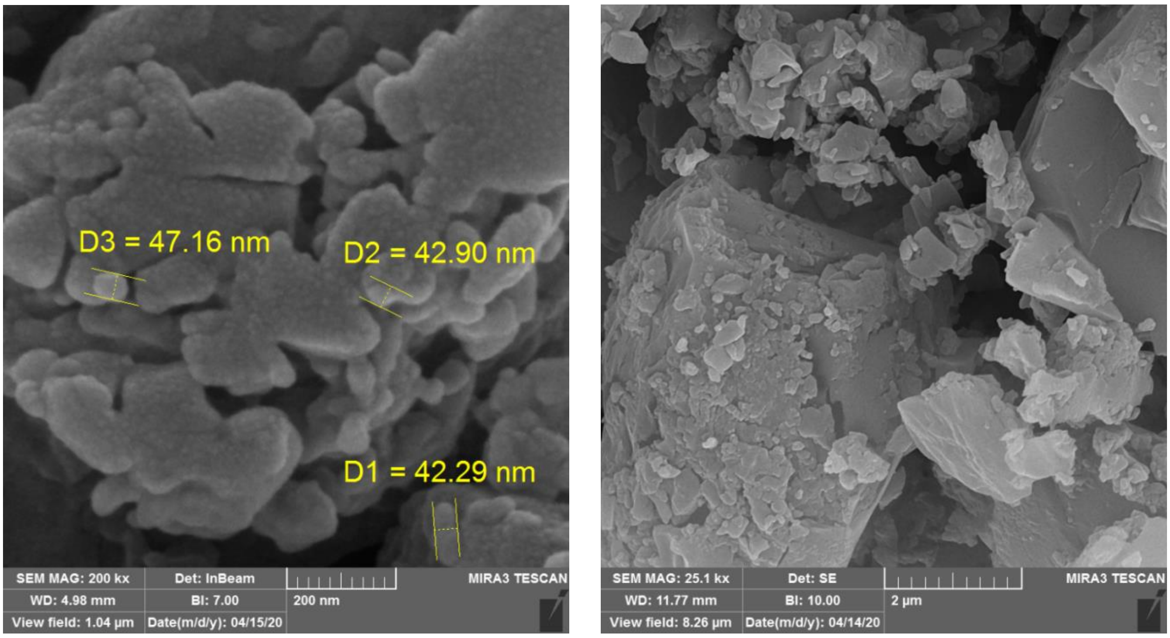


Fig. 2. Field emission scanning electron microscopy images of Schiff base 2.

The surface area is considered a crucial factor in determining the adsorption capacity of adsorbents, which could be detected via different methods, including the BET. In the mentioned method, the SA is calculated by filling nitrogen within the materials' pores and monitoring the adsorption/desorption isotherms (Awad et al., 2019). The adsorbent's porosity is a parameter that could help to predict the physical and/or chemical interactions of the adsorbate. In this regard, the nitrogen adsorption/desorption isotherms and pore size distributions of the prepared Schiff bases were estimated and illustrated in Figs. 3 and 4. Based on these isotherms, the adsorbate-adsorbent interactions could be considered weak since the Schiff base 2 (bearing Bromo group) has a type IV isotherm. The structure of the Schiff bases is mesoporous with no clear formation of a monolayer (Alias et al., 2013; Mahmood et al., 2021; Hamdani et al. 2019). The observed hysteresis loops are common for H2 type mesoporous materials with slit-shaped pores. However, Schiff base1 has type III isotherm, which shows a gradual increase along with the x-axis, then a huge increase occurred at the end. The isotherm information also indicates the formation of unrestricted multilayer (Mahmood et al. 2021; Hamdani, and Amane, 2019). This structure may arise due to the lateral strong interactions among adsorbed molecules comparing with the interactions between the adsorbent's surface and adsorbate.

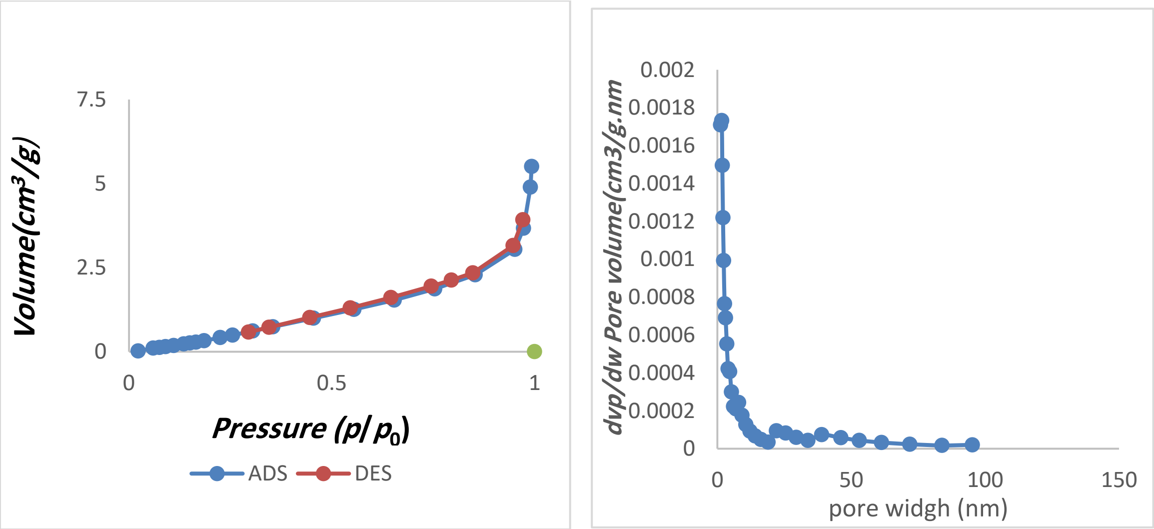


Fig. 3. N_2 adsorption/desorption isotherms and pore size distribution of Schiff base 1.

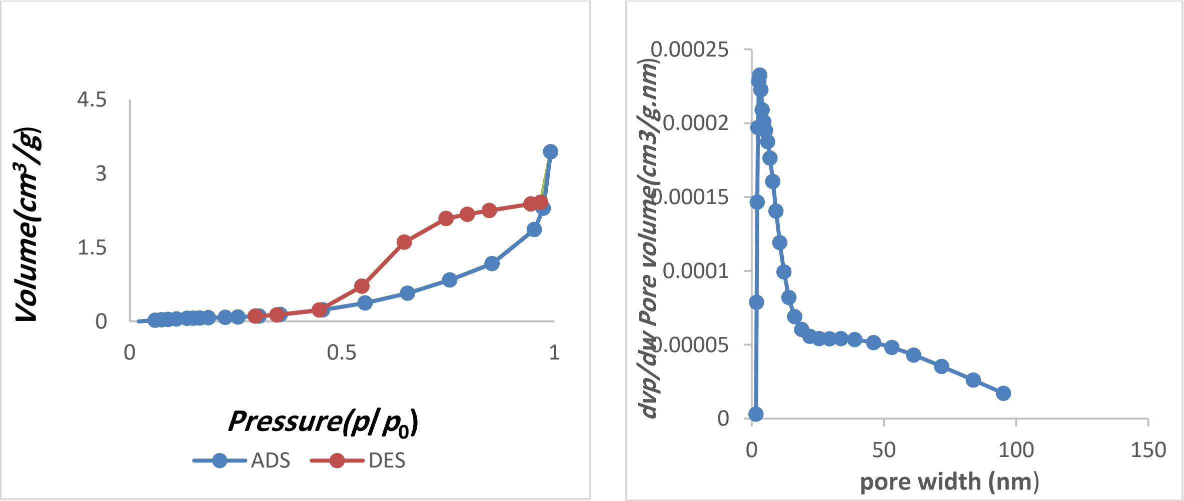


Fig. 4. N_2 adsorption/desorption isotherms and pore size distribution of Schiff base 2.

The pore volume and surface area were computed from nitrogen adsorption data at P/Po=0.9 using the BET procedure, and the average pore size was evaluated from the desorption isotherm using the BJH method. The parameters values were listed in Table 1. The surface areas, pore volumes, and pore diameters of Schiff bases 1 and 2 were 17.9 and 2.73 m^2/g, 0.008 and 0.005 cm^3/g, and 17.02 and 74.8 nm, respectively. The Schiff base1 had a higher surface area and pore volume than the other Schiff base, while it had a lower pore diameter.

Table 1. Surface area and pore size distributions of Schiff bases obtained via N_2 adsorption

Schiff bases	**S_{BET}(m^2/g)**	**Pore volume(cm^3/g)**	**Average pore diameter (nm)**
Schiff base 1	**17.99**	**0.0083**	**17.02**
Schiff base 2	**2.73**	**0.0052**	**74.8**

The gas adsorption mainly depends on three basic factors, namely: the pore size, the existence of heteroatoms, and the interaction forces among the adsorbent and adsorbate molecules (Dodoff et al., 2006). Hence, high levels of supplied energy are needed for gas adsorption when the aperture size is lower than the adsorbate's molecular size (Hamdani and Amane, 2019). The pore volume has an important effect in estimating the gas uptake capacity of adsorbents (Dodoff et al., 2006; Hamdani and Amane, 2019). Multiple conditions were applied where the operational pressure ranged from 1-40 bars to find out the uptake optimization. However, the CO_2 uptake of the synthesized Schiff bases 1 and 2 relations with pressure was studied at 313 K and shown in Figures 5 and 6, respectively. From the figures, it can be observed that the gas uptake increases as the applied pressure increases.

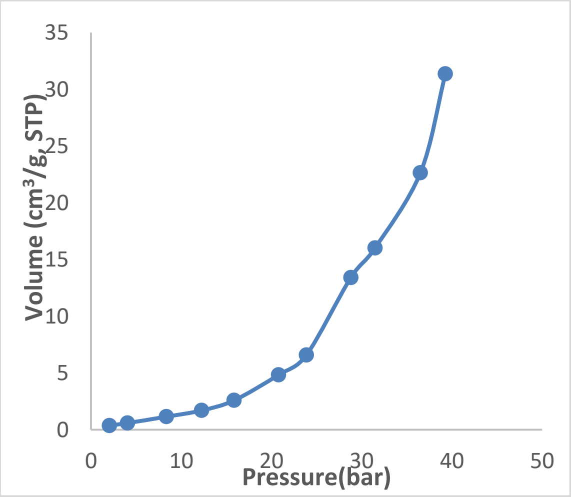


Fig. 5. Gas adsorption isotherms for 1.

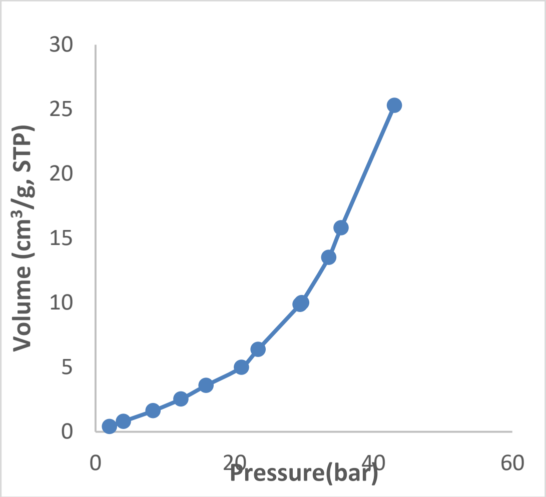


Fig. 6. Gas adsorption isotherms for 2.

CO_2 is known for its high quadrupole moment and diffusivity, which result in obtaining high adsorption capacity. The high attraction forces, including the electrostatic and van der Waals forces between the Schiff bases and CO_2 molecules, may increase the gas uptake (Omer, 2020). In general, the adsorption process takes place via the combination of various interactions. Here, Schiff base 1 had a higher gas uptake (6.2 wt%) than Schiff base 2 (5 wt%) as shown in Figures 5 and 6, which could be attributed to the larger surface area and pore volume of Schiff base 1. For more illustration, the results were listed in Table 2, in which the measured CO_2 uptake values were 31.36cm^3/gm STP and 25.30cm^3/gm STP for Schiff base1 and Schiff base 2, respectively. Table 3 shows a performance comparison for this work's bases and other components.

Table 2. CO_2 adsorption capacity of Schiff bases at 313 K and 40 bar.

Schiff bases	**cm^3.g^{-1}**	**mmol**	**Wt.%**
Schiff base1	**31.36**	**1.399**	**6.2**
Schiff base2	**25.30**	**1.128**	**5.0**

Table 3. A comparison of CO_2 uptake of this works' components and other publications

Adsorbent	**CO_2 Uptake wt%**	**Reference**
Schiff base1	6.2	Current work
Schiff base2	5.0	Current work
Polyphosphates containing 1,4-diaminobenzene	6.0	Ahmed et al. 2018
Valsartan-metal complexes	6.8	Mohammed et al.,2020
Telmisartan-tin complexes	7.1	Hadi et al.,2019
Porous aromatic melamine Schiff bases	10.0	Omer et al.,2020

CONCLUSIONS

In this work, two Schiff bases include benzaldehyde and parabromobenzaldehyde were prepared and their chemical formulas were reported. The Schiff bases particles have different shapes, sizes, and pores' volume and diameter. It was found that Schiff base 1 had a higher surface area (4.1 m^2/g) compared to Schiff base 2 (0.69 m^2/g), so as the pore volume. The prepared Schiff bases 1 and 2 had CO_2 storage ratios of 6.2 and 5 wt%, respectively. The higher value of storage ratio of Schiff base 1 was attributed to the larger surface area. From the present work, Schiff bases could be good candidates for gas storing, where many could be synthesized and tested for this purpose.

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The present research did not receive any financial support.

CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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