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Evaluation of the Capability of Carbon Dioxide Greenhouse Gas Absorption Using Nano Bio-Activated Carbon of Crataegus Sanguinea Core

P. Farhadi (MSc)[1], H. Ahmadpour kacho (MSc)[1], H.A. Asgharnia (PhD)*[2], M. Masomi (PhD)[1]

1.Department of Chemical Engineering, Faculty of Engineering, Islamic Azad University, Ayatollah Amoli Branch, Amol, I.R.Iran
2.Environmental Health Research Center, Health Research Institute, Babol University of Medical Sciences, Babol, I.R.Iran

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ABSTRACT

BACKGROUND AND OBJECTIVE: Considerable increase in carbon dioxide gas in the Earth's atmosphere has caused several problems such as increasing the temperature of the earth, droughts and sudden changes in the climate. The purpose of this study was to evaluate the capability of carbon dioxide as greenhouse gas absorption using activated nanobiocarbon from the Crataegus Sanguinea core.

METHODS: In this experimental study, the carbon dioxide gas penetration time in three subgroups with pressure (5,10,15 bars), flow (5,10,15 ml/min) and temperatures (20,30,60 °C) at concentrations of 0 to 1 gr / ml through a carbon dioxide gas capsule in a fixed bed column filled with 2 g of adsorbent synthesized by a carbon dioxide gas sensor. The synthesized nano-biocarbon adsorbent from the Crataegus Sanguinea Core was pyrolysed at a temperature of 300 ° C and activated at 600 °C. The research data were examined with pseudo -first-order and pseudo-second-order models.

FINDINGS: Significant increase in gas infiltration time was observed at 15 bars pressure (86.71±0.09 min, $p<0.001$), temperature of 20 ºC (67.68±0.13 min, $p\leq0.001$) and flow of 5 ml/min (75.78±0.11 min, $p\leq0.001$) was more than 5 bars (37.14±0.17 min) and 10 bars (60.33±0.27 min) and 30 °C (54.36±0.03 min) and 60 ºC (45.34±0.31 min) and 10 ml/min (53.8±0.13 min) and 15 ml/min (45.09±0.09 min) respectively. Both models fit well with a coefficient of $R^2>0.98$ on empirical data from absorption.

CONCLUSION: The results of the study showed that increasing pressure and decreasing temperature and flow increase the time of carbon dioxide penetration onto synthesized adsorbent.

KEY WORDS: *Adsorption, Nano-Biocarbon, Carbon Dioxide, Pollutant, Greenhouse Gas.*

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***Corresonding Author: H.A. Asgharnia (PhD)**
Address: Department of Environment Health, Faculty of Paramedical Sciences, Babol University of Medical Sciences, Babol, I.R.Iran
Tel: +98 11 32190101
E-mail: ehaamin2@gmail.com

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Introduction

The comprehensive development of industrial activities over the past few decades has led to an increase in the concentration of greenhouse gases, especially carbon dioxide, in the Earth's atmosphere (1-3). Therefore, the capture and storage of carbon dioxide from large point sources is essential (4-6). Three approaches to carbon dioxide capture are considered based on fossil fuel power plants (absorption after combustion, before combustion and oxygen combustion) (7, 8). However, these three methods are still not feasible for fossil fuel plants due to their non-scalability and cost-effectiveness (9, 10).

The use of solid adsorbents due to low energy recovery, high absorption capacity and high selectivity has better advantages than other methods and has attracted attention of scientific and industrial centers (11-13). The use of adsorbents, especially activated carbon, to absorb carbon dioxide as a greenhouse gas that has had many environmental effects has attracted researchers in recent years.

The Crataegus Sanguinea, known as Crataegus sanguinea, is abundant in the Iranian forest areas, especially in Mazandaran and Kurdistan, depending on the color of this fruit black Crataegus Sanguinea and red Crataegus Sanguinea exist in these areas. The core of this fruit is a very tense and lignin-rich tissue, which, given its abundance, low cost and availability, has high capacity to convert active bio carbons as adsorbent in commercial scale (11). Shahkararmi et al. investigated various activation methods on the activity of Co2 adsorption on activated carbon prepared from biological materials (14).

Hidayu et al. also prepared and identified activated carbon compounds prepared from coconut skin and palm kernel to absorb carbon dioxide (15). Himeno et al. also investigated the amount of carbon dioxide capture capacity on 5 types of industrial absorbents, which is the amount of carbon dioxide absorption capacity of an industrial sample manufactured by Osaka Corporation of Japan called Active Carbon A made of coconut oil at the pressure of 10 bar and the temperature of 298 K were 7 mmol/g (16). Since one of the main problems is the using activated carbon, is its high preparation cost. Therefore, the use of inexpensive raw materials from agricultural waste, such as the Crataegus Sanguinea core, that is an appropriate alternative to producing activated carbon at a low cost. In terms of economies are very affordable and have low recovery energy because of the abundance, availability and use of resources that are considered as waste.

The purpose of this study was to investigate the production of active nanobiocarbon adsorbent from Crataegus Sanguinea core and carbon dioxide gas adsorption capacity in 3 different operating conditions such as pressure, temperature and inlet gas flow rate of carbon dioxide.

Methods

In this study, Phosphoric acid made by Mercer Germany was used. To measure the intake of carbon dioxide and nitrogen gas the flow meter (Ukogawa the RGAN model) was used and to identify carbon dioxide gas, the TESTO 535 gas meter (made in Germany) was used . Also for the preparation of nanoparticle images, the FESEM electronic microscope model MIRA3TESCAN-XMU was used and to study the special adsorbent surface the BET device (Belsorp mini II model, made by the Japanese company BEL) was used. Preparation of activated Nanobiocarbon Absorber: A Crataegus Sanguinea core from the forests around Babol was prepared in the autumn and was pyrolysed at 400 ° C, then activated by phosphoric acid, saturation at 600 ° C. Carbon was prepared with the same and granular mesh 0.8 mm (17). Finally, to observe the particle size and shape of the nanobiocarbon surface porosity, a Field Emission Scanning Electron microscope (FESEM) was used, and to study the specific surface, the volume of microcavities and the size of the cavities BET machine was used.

Absorption and Emission Test Method: Dynamic absorption of carbon dioxide gas in the presence of nitrogen gas in a column filled with activated synthesized carbon with constant amounts of 2 g of adsorbent and a concentration of 20% carbon dioxide to 80% nitrogen, at pressures (15- 10-15), Flow (50-10-15 ml/min) and temperatures (20-30-60 ° C) were investigated (Fig. 1).

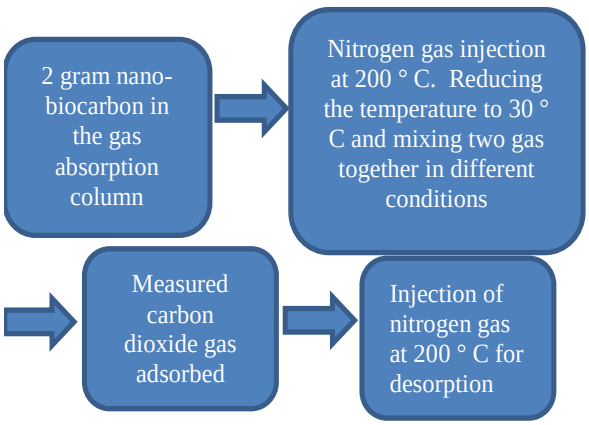

Figure1. Diagram of absorption and emission processes

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Calculating the Absorption Rate in the System: In this study, according to equation (1), adsorbent absorption capacity as the studied variable and the concentration of carbon dioxide gas at different times and adsorbent mass as constant variables and gas inlet flow, various temperature and various pressures of absorbing and determined as impressing operation conditions.

$$\bar{q}_{(t)} = \frac{QC_0}{W}\int_0^t \left(1 - \frac{c}{c_0}\right) dt \quad (1)$$

The synthetic study: the synthetic study of carbon dioxide absorbance on nanobiocarbon with two first-order and quasi-quadratic models was investigated. The parameters of nonlinear regression adsorption of synthetic models on empirical data were obtained from MATLAB software.

Nanobiocarbon Specifications: To determine the shape of the outer surface of the cavities and the relative surface cavities size of the activated carbon, a field emission scanning electron microscope (FESEM) was used and the BET method was used to measure the surface area, volume and distribution of adsorbent pores. The BET system operates on the basis of measuring the amount of nitrogen gas absorbed and emitted by the material at a constant liquid nitrogen temperature (77 °K). In order to determine the structural properties of cross-sectional analyzer, at Sharif University of Technology Materials Analysis Laboratory was used.

Statistical analysis: The experiment with three replications was performed using the results of infiltration time in these three subgroups at concentrations of 0.2 / 0.4 / 0.6 / 0.8 and 0.05 g/ml by SPSS software 21 and analyzed using ANOVA test and

Results

Impact of effective factors on dynamic absorption

Pressure effect: At the highest pressure, 15 Bar with increasing pressure, compared to two other pressures the penetration time increased from 58±0.06 minutes to 86.71±0.90 minutes (p≤0.001) (Table 1) and The time for the invasion was 126 to 158 minutes. The emission curve for each of the three input pressure was reduced by closing the carbon dioxide gas input, reducing its concentration from one to zero. The emission process in other conditions was also measured and then drawn in the same way (Fig. 2).

Effect of adsorption temperature: The effect of temperature on the dynamic absorption capacity of carbon dioxide gas was carried out at temperatures of 20-30 °C and 60 ° C. The highest adsorption rate was at 20 °C (32.65±0.3 to 67.68±13.03 min) (p≤0.001) and the time of penetration was zero to 32 minutes (Fig. 2).

Intake Effect: The highest absorption rate in ml/min 5 was from 32.94±10.10 to 75.8±0.19 (p=0.001) (Table 1). In this case, the time of penetration flow was 0 to 33 minutes (Fig. 2).

Kinetic study: A quasi-first and second-order model approximates almost all experimental empirical data on synthesized nanobiocarbons in all operating conditions, which both in quasi-first and quasi-second degrees have the highest compliance and minimum error in pressure 15 Bar in 2 g of adsorbent, flow 10 ml/min and 30ºC (Table 2, 3).

Table1. Comparison of gas infiltration time in subgroups of each parameter as well as comparison between each subgroup related to a parameter in different concentrations of carbon dioxide gas

Parameters / Concentration		0 mg/ml	0.2 mg/ml	0.4 mg/ml	0.6 mg/ml	0.8 mg/ml	1 mg/ml
Pressure (bar)	5	14.28±0.37^a	23.57±04^a	26.66±0.28^a	28.86±0.35^a	30.55±0.13^a	37.14±0.17^a
	10	37.85±0.13^b	42.1±0.07^b	46.04±0.05^b	48.82±0.01^b	52.19±0.05^b	60.33±0.27^b
	15	58±0.06^c	64±0.16^c	69±0.09^c	71±0.01^c	75±0.17^c	86.71±0.09^c
	P-value	0.001	0.001	0.001	0.001	0.001	0.001
Temperature (ºC)	20	32.65±0.3^a	43.87±0.1^a	47.41±0.26^a	51.14±0.08^a	57.27±0.17^a	67.68±0.23^a
	30	28.39±0.05^a	33.56±0.12^b	39.63±0.11^b	40.33±0.1^b	44.77±0.23^b	54.36±0.03^b
	60	11±0.26^b	28.56±0.27^c	30.54±0.29^c	34.61±0.24^c	36.65±0.09^c	45.34±0.31^c
	P-value	0.001	0.001	0.001	0.001	0.001	0.001
Flow (ml/min)	5	32.94±0.1^a	51.26±0.11^a	57.15±0.13^a	61.57±0.12^a	63.25±0.11^a	75.78±0.11^a
	10	17.36±0.11^b	32.23±0.03^b	35.79±0.11^b	39.48±0.13^b	42.05±0.18^b	53.8±0.13^b
	15	13.52±0.12^c	26.55±0.22^c	28.7±0.23^c	30.1±0.22^c	34.27±0.13^c	45.09±0.2^c
	P-value	0.001	0.001	0.001	0.001	0.001	0.001

a, b, c: Common lower semantic letters in each cell indicate no significant difference at different times.

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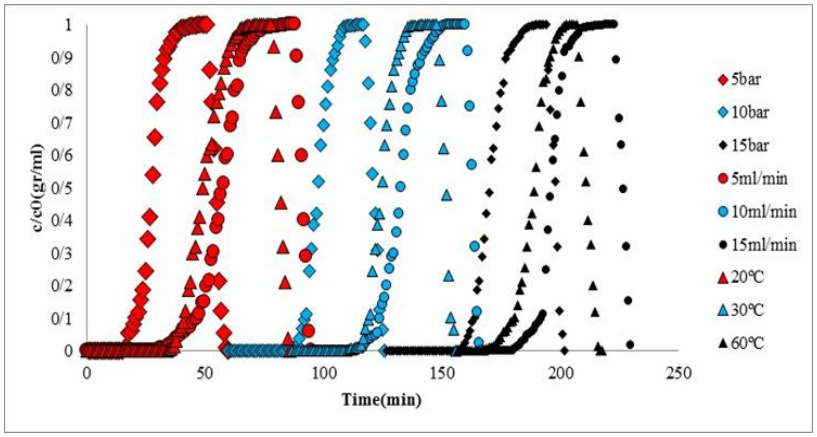

Figure2. Absorption and emission curves of carbon dioxide gas under different operating conditions

Analysis (FeSem): The surface properties of active nanobiocarbon before and after absorption of carbon dioxide by a Field-emission scanning electron microscopy in keV 5 are shown in Fig. 3. Figure A shows the porosity of active nanobiocarbons at different sizes in a diameter of about 5 nanometers and a uniform distribution. But in Fig. B, carbon dioxide molecules cover the absorbent surface and fill the holes in the canals and changed the diameter of the channels from an average of 5 nm to 3 nm.

BET analysis: Activated nanobiocarbon made from Crataegus Sanguinea core have a total specific surface area of 1100 m^2/gr, a volume of microcavities of 0.48m^2/gr and a pore size of 0.25m^2/gr, and the BET absorption and emission charts were drawn (Fig. 4). $p \leq 0.001$ was considered significant.

Table 2. Constant values of the quasi-first-order synthetic model

Operational conditions	qe (mg/gr) Equilibrium Capacity	K2(ml/mg min) constant rate	R2 The correlation
15 bar	1.253	0.064	0.996
10 ml/min	0.721	0.026	0.9578
30 ºC	0.884	0.042	0.988

Table3. Constant values of quasi quadratic synthetic model

Operational conditions	qe (mg/gr) Equilibrium Capacity	K2(ml/m g min) constant rate	R2 The correlation
15 bar	1.588	0.04	0.993
10 ml/min	1.136	0.014	0.9563
30 oC	1.23	0.028	0.982

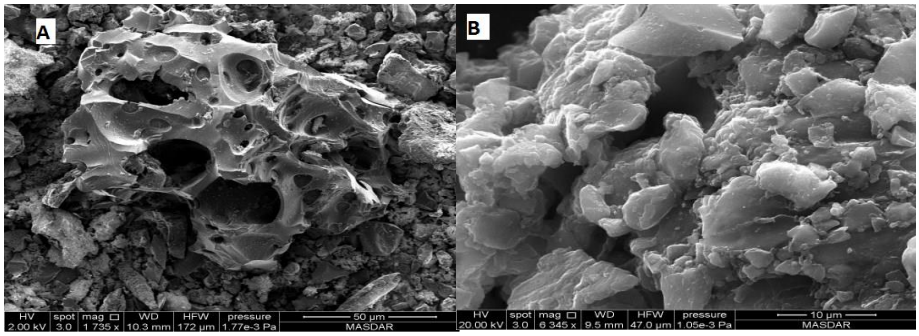

Figure 3. FE-SEM image of Synthetic nanobiocarbon A: before the absorption process. B: After the absorption process

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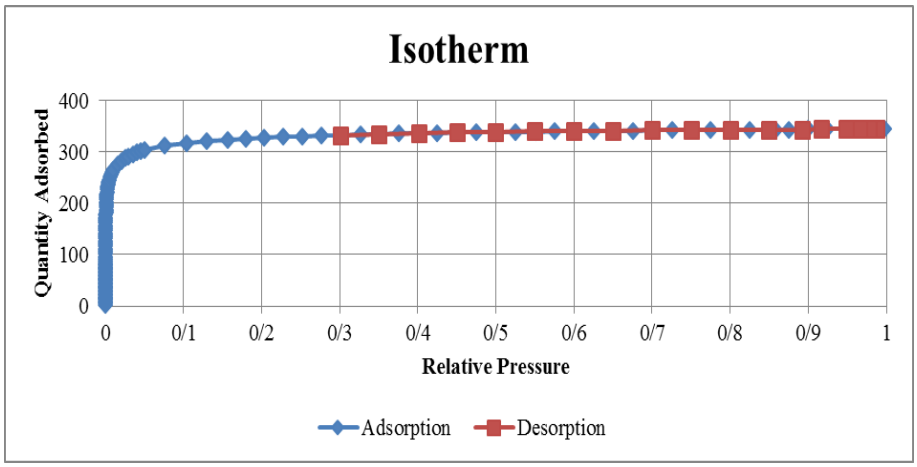

Figure4. Absorption and Emission Graph of NanobioCarbon Equilibrium Isotherm with BET Test

Discussion

In this study, a pressure of 15 Bar the carbon dioxide gas penetration into a sorbent produced with a penetration time of 86 minutes played an effective role for absorption, which, with increasing inlet pressure, the penetration time due to the entry of gas to high pressure and the channel filled by Carbon oxide. In this study, with increasing temperature, it causes more carbon dioxide emissions, as well as an appropriate opportunity to escape from the bed of activated nanobiocarbons without appropriate absorption.

The amount of 5 ml/min had a longer penetration time than other input flow. The reason is that due to the volume and speed of the gas entering the column before absorption of nanobiocarbon exit, which reduces the absorption capacity and penetration curve, it decreases the penetration time. Activated nanobiotic isotoms are type (I), which means absorbents are of microporous material (less than 2 nm).

In the first stage of absorption, the volume of N2 is rapidly increased due to absorption in the micropores, and then the amount of adsorption is slowly increased with relative pressure without any noticeable hysteresis, which indicates the denser filling of large macroscopes and mesoporous.

The equilibrium capacity data obtained in empirical absorption experiments with equilibrium capacity obtained from quasi-first-degree and second-order models were closer and more consistent. In a study by Fiuza et al., Carbon dioxide absorption at 25 °C was better than 70 ° C, which suggests that this study is consistent with their results, because at lower temperatures the time to increase contact with adsorbent gas and to absorb better the face (18). Also, in the study of Goel et al., the highest amount of carbon dioxide was adsorbed at 30 °C and 5 ml/min (19), which is consistent with the present study. In the study of Sivadas et al., the highest level of carbon dioxide gas penetration was observed in the adsorption process at a pressure of 1 bar and a temperature of 0 ° C, which, according to the present study, decreases the flow rate and increases the rate of absorption. According to Figure 6, all of them can be seen.

At a pressure load of 15 bar, the experimental data obtained from the model showed better compatibility and less error, it can be concluded that the nature of the priority of adsorption of carbon dioxide molecules under the pressure of carbon is faster. Also, in investigating the effect of pressure and emission on the absorption efficiency, a high rate of carbon dioxide absorption occurred in the early minutes, and in the next minutes until the time of equilibrium, Only the remaining adsorption takes place and the two-stage absorption process is confirmed by the second degree adsorption kinetics and is completely consistent with various studies (21-23).

According to the results, active nanobiocarbon adsorbent of Crataegus Sanguinea core can be used as effective and inexpensive absorbers for greenhouse gas

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elimination, including carbon dioxide, from industrial pollutants. The results showed that the removal of carbon dioxide gas by activated nanobiocarbon in the howthorn core was studied under different conditions, pressure 15 bar, 5 ml/min flow and temperature of 20°C.

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