

Adsorption of Carbon Dioxide on Adsorbents Synthesized by Microwave Technique

Sailee Dhage S and Kavita Kulkarni S*

Department of Chemical Engineering, Bharati Vidyapeeth College of Engineering, Pune, India

Abstract

Batch adsorption studies were carried out for carbon dioxide adsorption on Tea Powder waste, microwave synthesized tea powder waste, microwave synthesized tea powder waste with 80 gram KOH solution, microwave synthesized tea powder waste with 300 gram KOH solution and a commercial activated carbon. Adsorption studies were carried out using these four adsorbents. The experiments were conducted in a batch reactor with various pressures i.e., 3, 4 and 5 kg/cm² and different weights of adsorbents i.e., 1, 2 and 3 grams. SEM results showed non porous channeled structure for untreated tea powder and highly porous compact structure for microwave synthesized tea powder. However, for microwave synthesized tea powder in 80 gram KOH solution and 300 KOH solution, the structures were less significant than simply microwave synthesized. Elemental analysis showed highest carbon weight percent for microwave synthesized tea powder of 62.08% while the microwave synthesized tea powder in 80 KOH solution had lowest carbon weight percent of 43.34%. Experiments showed highest adsorption capacity for 1 gram microwave synthesized tea powder waste followed by microwave synthesized tea powder waste in 300 gram KOH at 3 kg/cm². Kinetic studies were also performed.

Keywords: Adsorption; Carbon dioxide; Microwave synthesis; Organic waste; Tea powder waste

Abbreviations: SEM: Scanning Electron Microscope; BET: Brauner Emmett Teller; EDAX: Energy Dispersive X-ray Spectroscopy

Introduction

The pressure on environment due to global warming has been a prime attention for many environmentalists and researchers; the cause being population explosion and excessive use of energy. Global warming is the rise of surface temperature of earth due to the entrapment of green house gases like water vapor, carbon dioxide etc. Out of all the other greenhouse gases, carbon dioxide is the most significant gas and even slight increase in the level of carbon dioxide in the atmosphere will increase the surface temperature [1]. Some of adverse effects of greenhouse gases are changes in rainfall pattern, melting of glaciers followed by rise in sea level; the coral reefs are bleached since the water is warmer and acidification of water bodies and so on. Since the industrial revolution, there has been rise in carbon dioxide amount from 280 ppm (by volume) to 388 ppm (by volume) in 2010 [2]. Presently, carbon dioxide amount is increasing by 2 ppm every year and it is estimated that more than one-third of carbon dioxide which is emitted remains in the atmosphere [3]. There are various methods by which the carbon dioxide emission can be reduced; (i) By reducing energy intensity (ii) By using alternative fuels to fossil fuels (iii) By capturing carbon dioxide using carbon capture technologies [3]. The use of alternative fuels like solar energy, hydrogen, nuclear and many other sources of energy are not viable commercially since they do not meet the energy demands and also they are still in development stage. Therefore, using carbon dioxide capture technology is the best means for reducing carbon dioxide content in the atmosphere. It is clear that if the carbon dioxide capture technology is as innovative, it can lead to significant cost reduction [4]. There are few emerging trends in carbon capture technology which includes using carbonate based systems [5], aqueous ammonia [6], membranes [7], metal organic frameworks [8], ionic liquids [9] and so on. Adsorption is widely used for carbon dioxide capture since it can perform many separations which are impossible by many other separation processes. It has gained greater

importance since it concerns environmental factors and even fulfills the requirements of quality. There are developments related to adsorption in the type of adsorbent used, the way the adsorbents are synthesized and effective method of adsorption. Activated carbons and zeolite based molecular sieves are considered to have highest adsorption capacities [10]. Zeolites, however, do not have higher adsorption capacity at pressures greater than atmospheric pressure. Thus, activated carbon is most effectively and commercially used adsorbent for adsorption. Due to its large surface area and effective pore volume, it is always preferred for adsorption. Bingyun et al. found innovative carbon dioxide capture solid sorbents which are nano layered. It resulted in the formation of layers of desired thickness in such a way that adsorption capacity of treated carbon increased when compared to original carbon [11]. Activated carbon made from organic waste is one such adsorbent which can be used efficiently for adsorption [12]. The organic wastes have specific properties such as surface area, porosity and other advantages such as are inexpensive used with no or minimum processing, eco-friendly, low ash content etc. [12]. Anis and Ishak [13] produced microwave assisted activated carbon from rubber seed pericarp by using three different chemical activating agents like zinc chloride, potassium chloride and phosphoric acid. Adsorption studies were carried out and the adsorption capacity was found to be 297.24 mg/g for zinc chloride activation. Zhaung et al. [14] reviewed the modification of activated carbon by means of microwave heating and studied the effect on pore texture and surface chemistry. Here, two kinds of activated carbons i.e., coal based and coconut based were treated in nitrogen

***Corresponding author:** Kavita Kulkarni S, Associate Professor, Department of Chemical Engineering, Bharati Vidyapeeth College of Engineering, Pune-411 043, India, Tel: +91-9970814955; E-mail: kskulkarni@bvucceop.edu.in

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using microwave and different power input was supplied instead of conventional method. The coal based activated has BET surface area of $1090 \text{ m}^2/\text{g}$. But then, due to microwave treatments, it slightly decreases the surface area, pore volume and micro pore volume. Foo and Hameed [15] utilized rice husk as a precursor for activated carbon preparation using potassium hydroxide and potassium carbonate as activating agents. The dried rice husk was soaked in potassium hydroxide or potassium carbonate and this was followed by microwave synthesis with irradiation time of 7 minutes and nitrogen flow of $300 \text{ cm}^3/\text{min}$. Adsorption studies were carried out and the adsorption capacity was found to be 441.52 mg/g . Nabias [16] prepared and modified the activated carbon fibres by microwave heating. Three acrylic textile fibres along with three commercial activated carbon are used. These sub samples were synthesized in microwave for fifteen minutes. It showed that microwave heating is very effective means of modifying the porosity and surface chemistry of activated carbon. The main aim of our study is to study and develop new organic adsorbents for carbon dioxide capture and; find an efficient way for its synthesis which is energy efficient and requires less time to prepare.

Materials and Methods

Preparation of adsorbent

The raw material used for the batch adsorption experiment was Tea powder waste. Tea powder waste was collected from different households. This was then washed and boiled again to remove all the extract from the tea powder waste. The tea powder was then dried and powdered to pass through a sieve of 75 μm mesh size. This tea powder waste was then microwave synthesized in Department of Nanotechnology, Indian Institute of Science, Bengaluru. Two grams of tea powder waste was mixed in water- ethanol solution and sonicated for ten minutes. The mixture was then synthesized in microwave for four minutes. It was then centrifuged at 7660 rpm for ten minutes and then dried at 90°C . In a similar manner, two grams of tea powder waste was mixed in 80 gram KOH solution (80 gram KOH pellets dissolved in 10 mL distilled water) and 300 gram KOH solution (300 gram KOH pellets dissolved in 10 mL distilled water) and microwave synthesized. The untreated tea powder waste, microwave synthesized tea powder, microwave synthesized tea powder in 80 gram KOH solution and microwave synthesized tea powder in 300 gram KOH solution was then analyzed using SEM, EDAX and BET for surface morphology, elemental analysis and surface area respectively. Batch experiments were carried out using all the four adsorbents and commercial carbon for different pressures and different weights of adsorbents.

Batch experiments

Pure carbon dioxide was used for batch experiments. Height and diameter of the column was 9 cm and 1.44 cm respectively. 1 gram of untreated tea powder was filled in the column and pressure of 3 kg/cm^2 was introduced in the system. This pressure was analyzed by 8 Channel Universal Data Logger. Batch was started for eight hours and readings were obtained for equal interval of time with 8 Channel Universal Data Logger. Similarly, 4 and 5 kg/cm^2 was introduced in the system. The same procedure as repeated for 2 and 3 grams of untreated tea powder waste, microwave synthesized tea powder waste, microwave synthesized tea powder in 80 gram KOH solution, microwave synthesized tea powder in 300 gram KOH solution and commercial carbon at pressures of 3, 4 and 5 kg/cm^2 .

Results and Discussion

SEM, EDS and BET analysis

Scanning electron microscope was used to observe the surface morphology of untreated tea powder waste and microwave synthesized tea powder waste [17,18]. The untreated tea powder sample showed that the untreated tea powder waste has a rough surface and is non compact in nature (as shown in Figure 1) while the microwave synthesized tea powder showed a heterogeneous and sponge like porous texture with a bit of eroded surface after treatment (Figure 2). For the microwave synthesized tea powder in 80 gram KOH solution (Figure 3) and 300 gram KOH solution (Figure 4), a porous like structure is observed but the porosity seems to be not very significant for the later. The elemental analysis for adsorbent samples is shown in Table 1. Tea powder which

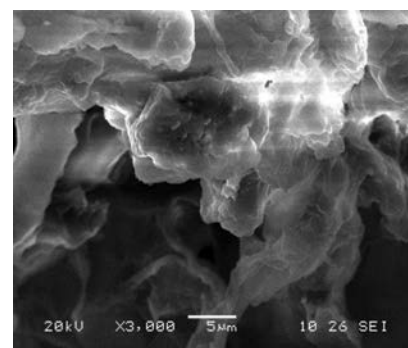


Figure 1: SEM image of untreated tea powder waste.

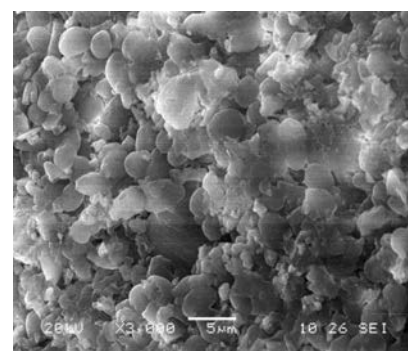


Figure 2: SEM image of Microwave synthesized tea powder waste.

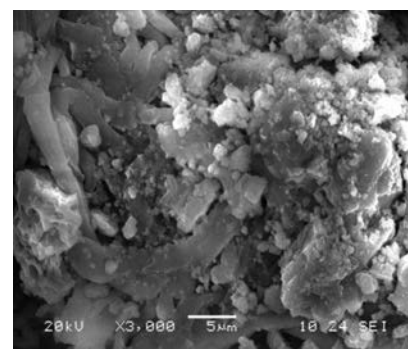


Figure 3: SEM image of microwave synthesized tea powder in 80 gram KOH solution.

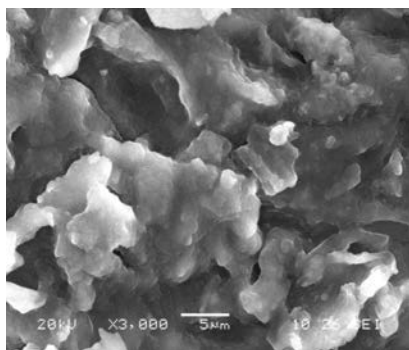


Figure 4: SEM image of microwave synthesized tea powder in 300 gram KOH solution.

was microwave synthesized showed highest carbon content of 62.08% while the untreated tea powder waste had carbon content of 56.93%. However the calcium weight percent for untreated tea powder was more than microwave synthesized tea powder. The lowest carbon content was for microwave synthesized tea powder in 300 gram KOH solution having only 43.34% of carbon content. It can be observed that more the carbon content more is the adsorption capacity. We can also infer that microwave synthesis increased the carbon content of the tea powder sample however, when the concentration of the KOH solution was increased, the carbon content decreased. The surface area of commercial carbon was given as 102.11 m²/g and thus the adsorption was also significantly large. Surface area was analyzed using BET analysis and it was found that untreated tea powder waste had lowest surface area of 14.6 m²/g while the microwave synthesized tea powder waste had the highest surface area of 86.6 m²/g. It is observed that the surface area of microwave synthesized tea powder in 80 gram KOH solution has surface area of 59.1 m²/g while the surface area of microwave synthesized tea powder in 300 gram KOH solution was found to be 29.4 m²/g. From these results, we can assume that microwave synthesis increased the surface area of the adsorbent. This might be possible due to high power levels which might have caused the carbon structure to expand. During microwave synthesis, the temperature of the adsorbents increase rapidly and this results in the increase of pores. However, this effect is observed for micropores and mesopores. Thus, microwave treatment has very little effect on the pore width or pore volume. But, by increasing the basicity in the adsorbent, the surface area reduced significantly. The maximum adsorption capacities for the adsorbents are shown in Table 2. It was observed that the maximum adsorption capacity was obtained for 1 gram microwave synthesized tea powder waste at 294 kPa. It was also found that the adsorption capacity of the commercial carbon was lower at 294 kPa but increased with increase in pressure and was even more than microwave synthesized tea powder at 392 kPa and 490 kPa.

Adsorption studies

The maximum adsorption capacities for the adsorbents are shown in Table 2. It was observed that the maximum adsorption capacity of 0.00892 mmol/g was obtained for 1 gram microwave synthesized tea powder waste at 294 kPa and the lowest adsorption capacity of 0.00018 mmol/g was obtained for 1 gram microwave synthesized tea powder waste at 392 kPa. The graphical representation of the adsorption values are shown in Figures 5-9.

Kinetic data

The experimental data was fit into Langmuir adsorption isotherm

by using the equation,

$$1/q_e = 1/q_m + 1/(q_m \cdot K_L)$$

Here, q_m and K_L are the values of constants and need to be determined in order to find if the data fits into the adsorption isotherm. The values of q_e is,

$q_e = [(\text{initial pressure} - \text{final pressure}) \times \text{volume of adsorbent}] / \text{mass of adsorbent}$

Sample No	Name	Elemental Analysis (in %)							
		C	O	Mg	Al	Si	K	Ca	Fe
1	Untreated tea powder	56.93	40.52	0.10	0.47	1.03	0.14	0.49	0.24
2	Tea powder without solvent and with mw synthesis	62.08	37.16	0.08	0.07	0.07	0.22	0.21	0.10
3	Tea powder with 80 mg KOH	50.66	40.04	0.17	0.43	1.23	5.64	0.69	0.58
4	Tea powder with 300 mg KOH	43.34	43.73	0.14	0.48	0.98	10.50	---	0.41

Table 1: Elemental Analysis of the adsorbents.

Pressure (kPa)	Untreated Tea Powder (mmol/g)	Microwave synthesized Tea powder (mmol/g)	MW synthesized TP in 80 g KOH (mmol/g)	MW synthesized TP in 300 g KOH (mmol/g)	Commercial Carbon (mmol/g)
294.06	0.00267	0.00892	0.00112	0.00201	0.000781
392.08	0.00357	0.00018	0.00212	0.00290	0.00167
490.1	0.00457	0.00029	0.00290	0.00390	0.00268

Table 2: Maximum Adsorption Capacities obtained for different adsorbents.

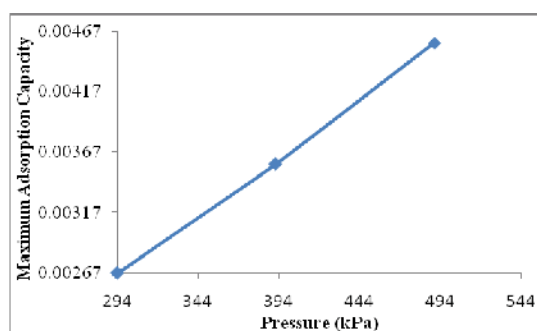


Figure 5: Pressure v/s Maximum Adsorption Capacity for untreated tea powder waste.

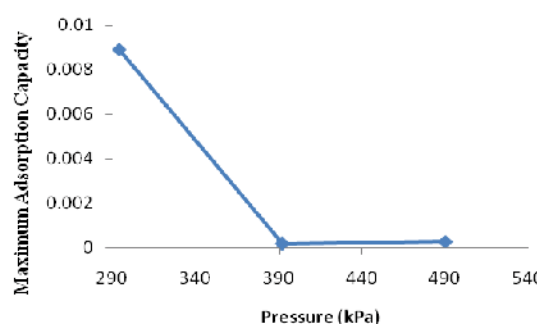


Figure 6: Pressure v/s Maximum Adsorption Capacity for Microwave synthesized tea powder waste.

where initial and final pressures are in pascal (Pa), volume of the adsorbent in cubic meter (m^3), mass of the adsorbent in kilogram (kg). The volume of the adsorbent was found using ideal gas law.

Once the values of q_e were determined, graph was plotted for $1/q_e$ v/s $1/P_f$ and the value of constants q_m and K_L was found by using slope of graph formed. For the experimental data to fit in the isotherm, the r^2 value should be lower than 1 and this was observed in all cases. In order to fit any experimental data, r^2 value is important because its value will determine which adsorption isotherm model it will be fit. Thus, the experimental data fit the Langmuir adsorption isotherm. The values of constants calculated are given in Table 3.

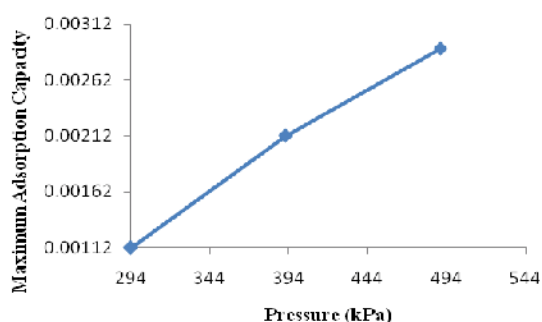


Figure 7: Pressure v/s Maximum Adsorption Capacity for Microwave synthesized tea powder waste in 80 gram KOH solution.

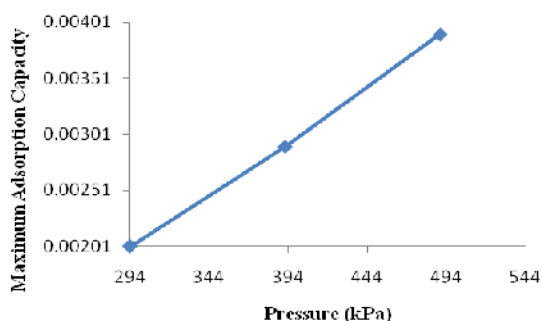


Figure 8: Pressure v/s Maximum Adsorption Capacity for Microwave synthesized tea powder waste in 300 gram KOH solution.

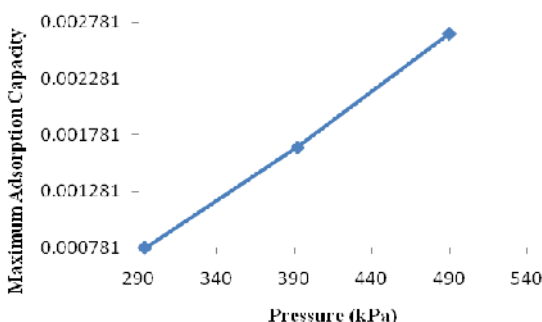


Figure 9: Pressure v/s Maximum Adsorption Capacity for commercial activated carbon.

Constants	Synthesized Tea Powder	Microwave synthesized Tea powder	MW synthesized TP in 80 g KOH	MW synthesized TP in 300 g KOH
K_L	8.333×10^3	-3333.33	-70	25000
r^2	0.112	0.045	0.1159	0.0047

Table 3: Determination of K_L and q_m using Langmuir isotherm.

Conclusion

With all the observations and data above, we can conclude that adsorption capacity of microwave synthesized tea powder waste was maximum. It was observed that microwave synthesis of tea powder waste increased the surface area significantly. It can also be concluded that more the carbon content in the adsorbent, more is the adsorption. Surface area and adsorption capacity can further be improved by using more technologically advanced methods which have easy steps and easily feasible. Further studies, for example, by increasing the time of synthesis in microwave or by addition of additives to enhance the adsorption capacity provides a larger scope of improvement.

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