WASTES III

solutions
treatments
opportunities

Editors:
Cândida Vilarinho, Fernando Castro, Margarida Gonçalves & Ana Luísa Fernando

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Wastes: Solutions, Treatments and Opportunities III

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Wastes: Solutions, Treatments and Opportunities III – Vilarinho et al. (Eds)
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Capture of CO_2 in activated carbon synthesized from municipal solid waste compost

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ABSTRACT: In this study, municipal solid waste composts obtained from mechanical biological treatment has been considered as a source of adsorbents for CO_2 capture. Three samples derived from the maturated compost in the municipal solid wastes were modified to produce activated carbon. The first sample was treated with sulfuric acid, the second one was thermally treated at 800°C and the last one was modified chemically and thermally with sulfuric acid and at 800°C. Then, the CO_2 uptake capacity of prepared samples was measured through breakthrough adsorption experiments at the post combustion operational conditions to collect isotherm data. Also a fixed bed adsorption mathematical model was developed by applying mass and energy balances. Results showed the municipal solid wastes have an excellent capacity to be considered as source of adsorbent for CO_2 capture also the mathematical model is able to predict breakthrough data.

1 INTRODUCTION

1.1 *CO_2 capture*

Global warming has been one of the major concerns of mankind in the recent decades, which it needs significant attempts to reduce the greenhouse gases (GHGs) emissions (Karimi et al., 2014). Among all GHGs, CO_2 has the main role, which has contributed to several adverse effects on the ecosystem and environment, and if the current dangerous level of the GHGs is not controlled, it can face the life on this planet with several serious challenges. According to reports, the coal and natural gas fired power plants released 11.1 Gt of carbon dioxide, nearly 30% of the total global emissions in 2012 (Stocker et al., 2013; IEA). In this way, the combustion of coal, also oil and natural gas industries including naphtha refineries (Iranshahi et al., 2014; Karimi et al., 2018a), and petro-chemical complexes (Karimi et al., 2016), are the main industrial sources of CO_2 emissions. As consequence of these industrial activities, the CO_2 percentage has exceeded 50 ppm in the atmosphere from the maximum allowable level in the pre-industrial period until now (280 ppm to 400 ppm) (Karimi et al., 2018b). Thus, strict policies, better strategies and more attention for capturing and sequestering CO_2 are required.

1.2 *Municipal Solid Wastes Management*

Municipal solid waste (MSW) is a term usually referred to the unwanted or useless solid materials originated from the combined residential, industrial and commercial activities in the urban areas. The characteristics and qualities of the MSWs depend on several parameters, including: the income, lifestyle and living standards of region's inhabitants also, climate and natural resources of region. For

example, the generated solid wastes in the humid, tropical, and semitropical areas are rich with plant debris, while in the areas with seasonal climate changes it has more ash. Thus, the classification of MSWs can be based on the origin, content or hazardous potentials, but the category which considers the content (organic or inorganic materials) is the most popular one (Hoornweg and Bhada-Tata, 2012). There are some main treatment techniques for solid wastes such as employing extremely high temperatures, dumping on the land, also applying the biological processes to treat the wastes and producing the compost, which is one of the most popular strategies (Karak et al., 2012). The results can be contributed to reduce the GHGs emission, conserve the natural resources, energy saving, environment protection and finally, a healthier life.

2 MATERIALS & METHODS

2.1 *Synthesis of Activated Carbon from compost*

The employed compost was obtained in mechanical biological treatment plants for municipal solid waste, supplied by the company "Resíduos do Nordeste, EIM". In order to homogenize and remove the soluble compounds and suspended solids, the compost was first mixed with water and washed. Then, the first sample was prepared by carbonization at 800 ^{o}C (C-800). The second sample was synthesized by treating the washed compost with sulfuric acid. In addition, the other samples were prepared by treating with sulfuric acid before the carbonization at 800^{o}C.

2.2 *Experimental breakthrough measurements*

The measurement of uptake capacities of the prepared samples for CO_2 capture was performed through the breakthrough experiments in the fixed bed adsorption unit at LSRE-LCM. To this goal, an adsorption column was packed with prepared samples, then, the adsorption process takes place by passing the gas mixture (career gas and CO_2) on the fixed bed, which has been putted in the oven and it has a constant partial pressure and temperature. Then, the mass flow rate was continuously measured at the output of the packed bed by TCD, until getting the saturation condition at output of adsorption column. More details about this unit can be found in author's previous studies (Karimi et al., 2018b).

2.3 *Objective*

In this work, based on the scopes of Carbon Capture and Storage (CCS) technique and municipal solid waste management a novel strategy has been proposed. In this way, the obtained compost in the mechanical biological treatment from municipal solid wastes has been considered as a source of adsorbents for CO_2 capture and its performance for CO_2 capture evaluated through breakthrough adsorption experiments.

3 MODELLING OF BREAKTHROUGH DATA

Breakthrough data for CO_2 adsorption, were modeled with mass and energy balances based on the following assumptions:

- The ideal gas law was assumed for the gas phase.
- The pressure drop was considered negligible.
- The adsorption equilibrium was described by Langmuir's isotherm;
- The external resistance and macropore diffusion can be combined in a global resistance to a lumped model for the adsorbent particle (Linear Driving Forge model – LDF).

Accordingly, the mass and energy balances results in the of partial differential equations (PDEs):

Global mass balance:

$$\frac{\partial F}{\partial z} + \varepsilon_b \frac{\partial C}{\partial t} + (1 - \varepsilon_b) \sum_{i=1}^{n} \frac{\partial \bar{q}_i}{\partial t} = 0 \quad (1)$$

Component mass balance (Adsorbate specie):

$$-\varepsilon_b D_{ax} \frac{\partial}{\partial z}\left(C \frac{\partial y_i}{\partial z}\right) + \frac{\partial (F y_i)}{\partial z} + \varepsilon_b \frac{\partial (C y_i)}{\partial t} + \rho_p (1 - \varepsilon_b) \frac{\partial \bar{q}_i}{\partial t} = 0 \quad (2)$$

Mass transfer (LDF Model):

$$\frac{\partial \bar{q}_i}{\partial t} = k_{LDF}(q^* - \bar{q}_i) \quad (3)$$

Energy balance:

$$-K_{ax} \frac{\partial^2 T}{\partial z^2} + F c_{pg} \frac{\partial T}{\partial z} + \varepsilon_b C c_{pg} \frac{\partial T}{\partial t} +$$
$$+(1 - \varepsilon_b) a_p h_p (T - T_s) + a_c h_w (T - T_w) = 0 \quad (4)$$

Energy balance in the solid phase:

$$c_{ps} \frac{\partial T_s}{\partial t} = a_p h_p (T - T_s) + \sum_{i=1}^{n} (-\Delta H_i) \frac{\partial \bar{q}_i}{\partial t} \quad (5)$$

The initial and boundary conditions are summarized below:

Initial condition:

$$t = 0: \forall z; \;\; F = F_f; \;\; C = C_f; \;\; \bar{q}_i = 0; y_i = 0; \;\; T = T_s = T_f;$$

Boundary condition:

$$z = 0, t > 0: \qquad F = F_f, \quad F y_{if} = F y_i - \varepsilon_b D_{ax} C \frac{\partial y_i}{\partial z},$$

$$F c_{pg} T_f = F c_{pg} T - K_{ax} \frac{\partial T}{\partial z} \;\; z = L, t > 0: \qquad \frac{\partial y_i}{\partial z} = 0 \quad \frac{\partial T}{\partial z} = 0$$

Here, L, ε_b and $\overline{q_i}$ are the length of adsorption column, void fraction and the average adsorbed concentration of absorbable species i in the solid phase, respectively. Also, y_i, D_{ax} and q^*represent the molar gas fraction of solute i, the coefficient of axial dispersion and the adsorbed phase concentration of species i in equilibrium with gas phase. In addition,k_{LDF} is called the Linear Driving Force (LDF). To solve the considered model, the set of partial differential equations (PDEs) are converted into a system of ordinary and algebraic differential equations (DAEs) via method of lines (MOL) and solved by numerical integrator ode15s method, available in the MATLAB library. The ode15s integrator was considered as a variable order method and robust strategy to solve stiff equations (Shampine & Reichelt, 1997). The MOL method is based on a library of differentiation routines provided by Schiesser & Griffiths, 2009 This model is also important for the design of cyclic processes for CO_2 capture (e.g Pressure Swing Adsorption). In addition, this model can be coupled with proper isotherm (Langmuir isotherm) that describe the measured CO_2 adsorption experimental data

Table 1. Elemental analysis of the prepared samples.

Sample	C (%)	H (%)	S (%)	N (%)	Remaining (%)	Ashes (%)
C-800	17.5	0.4	0.4	0.0	81.6	80.6
C-S	20.1	2.3	0.6	1.7	70.4	34.3
C-S-800	20.5	1.9	0.4	1.4	75.8	65.9

Table 2. Textural properties of materials determined from BET and t-plot methods.

Sample	Burn-off (%)	S_{BET} ($m^2 \cdot g^{-1}$)	S_{ext}	V_{mic} S_{mic}	($mm^3 \cdot g^{-1}$)	V_{mic}/V_{Total} (%)	W_{mic} (nm)
C-800	39.9	77	52	25	12	14.0	1.9
C-S	59.6	11	11	0	0	0.0	–
C-S-800	76.3	279	56	223	92	53.4	1.6

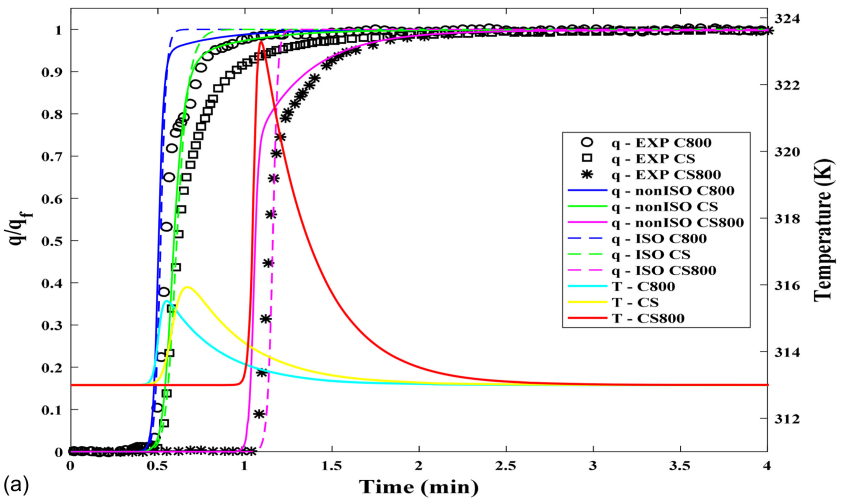
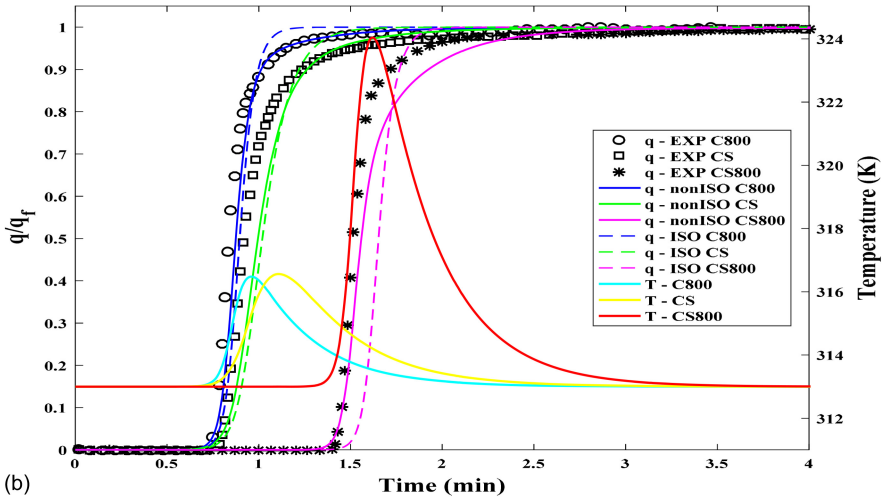


Figure 1. Breakthrough adsorption RUNs in samples C-800, C-S and C-S-800 at 40 C and total pressure: (a) 1 bar, (b) 3 bar and (c)5 bar. Points are experimental data and lines model predictions.

4 RESULTS & DISCUSSION

The textural properties of the materials were determined from N_2 adsorption–desorption isotherms at 77 K, obtained in a Quantachrome NOVA 4200e adsorption analyzer. The specific surface area was calculated using the S_{BET} method. The external surface area (Sext) and the micropore volume (V_{mic}) were obtained by the t-method (thickness was calculated by employing ASTM standard D-6556-01). The total pore volume (V_{Total}) was calculated at $p/p_0 = 0.98$. The microporous surface area (S_{mic}) was determined as the subtraction of Sext from SBET and the average pore width (W_{mic}) by approximation ($W_{mic} = 4\, V_{mic}/S_{mic}$). The results of elemental analysis and textural properties of the prepared samples are presented in Table 1 and Table 2, respectively.

The breakthrough adsorption runs on the synthesized samples were performed at 40°C and different pressures (in the range of 1-5 bar) to collect the isotherm data. Figure 1 (a-e) shows



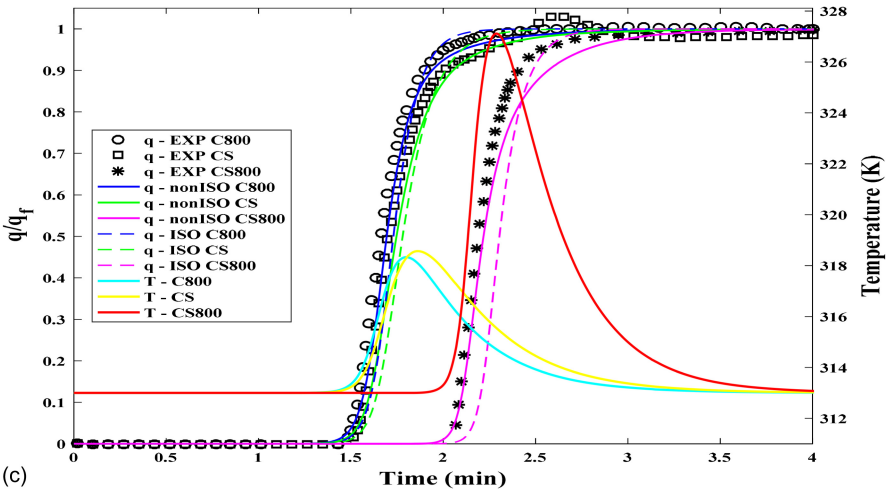


Figure 1. (*Continued*)

the examples of breakthrough experiments (points) with the mathematical modelling (lines). It is clear that the developed model is capable to describe the experimental data being a valuable tool to design cyclic processes for CO_2 capture. In addition, maximum loadings (around 2.5 mmol/g) can be considered reasonable value for CO_2 capture (since municipal waste has been considered) when compared to literature. Accordingly, results are very promising in view of developing a cyclic process for CO_2 capture using municipal solid wastes as source of activated carbon. It also clear from the Figures that sample C-S-800, is the best sample for CO_2 capture since the breakthrough time is much higher than the other ones. In addition, as can be observed, the enhancement of adsorption pressure has a positive effect on the adsorption capacity, which by increasing the pressure, the loading of different prepared samples has increased.

5 CONCLUSION

In this study, the potential of municipal solid wastes as a source of adsorbents for CO_2 capture were investigated at the post-combustion operational conditions. The composts from municipal solid

wastes are converted to activated carbons and then breakthrough experiments were performed to collect isotherm data and simultaneously, the mathematical model was developed to fit the experimental results in view of the design of cyclic processes for CO_2 capture. The equilibrium adsorption capacity of the considered samples revealed that the adsorption capacity of the sample treated with sulfuric acid and thermally calcinated is the best one with CO_2 loadings comparable with commercial carbon materials. Finally, it can be concluded that the obtained results through this work can be significant for CO_2 capture and reducing the global warming, also high added value to the waste by using these materials as a source of Activated Carbons.

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