



Fullerene C60 for Tyrosol Retaining

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Abstract The main aim of this work is to determinate the adsorption of tyrosol on fullerene C60. By varying the amount of carbon fullerene C60 and maintaining tyrosol solution concentration constant, the adsorption percentage was evaluated. Detailed analysis on the adsorption isotherms were accomplished successfully. Four isotherms which are Freundlich, Langmuir, Sips and Redlich-Peterson were adopted to predict the experimental works and Sips model was the most appropriate to fit the experimental data. In fixed experimental conditions, the adsorption of tyrosol on C60 could reach 80%.

Keyword: Fullerene C60, Tyrosol, adsorption isotherm

1. Introduction

Tyrosol, also known as 2-(4-hydroxyphenyl) ethanol is an aromatic organic compound that is a type of phenol containing two hydroxyl groups. It is an active compound that is widely present in nature mainly in olives, wine and other varieties of plants. Tyrosol is one of the most important phenolic compounds due to its wide medicinal and chemical utilization and its high biological activity [1-3]. This compound and its derivatives, especially hydroxytyrosol have very important antioxidant activity and play an important role as cardioprotective agent [4]. Also, tyrosol gains several biological activities such as antibacterial, neuroprotective, anticancer, anti-inflammatory and prevents the human LDL oxidation [5, 6]. Many efforts have been expanded to extract tyrosol from biological matrix [7, 8]. However, the total purification of this compound causes generally technical process problems. If totally purified, the process yields a small quantity [9].

In the past two decades, carbon based materials with organized structure, especially, fullerene and carbon nanotubes have been one of the most active fields. Since their discovery [10], fullerenes have been intensively studied and wide varieties of related compounds have been synthesized. The chemistry of fullerenes is a very dynamic field in systematic evolution; several authors from different areas of expertise are concentrated in the synthesis and the use of functionalized fullerenes or not by different methods. In fact, this development is largely due to the ability of this structure to allow a many chemical reactions: radical reactions, polymerizations and cycloadditions and many others [11-13]. The largest use of fullerene is also due to its large surface area, and thermal stability and its mechanical properties [14].

Thus, many research works have been focused on the interaction of fullerene with other atoms and molecules [15].

In this work, the adsorption of Tyrosol on fullerene C60 was explored, different adsorption models were examined to determinate the best model to fit the experimental data.



2. Materials and methods

2.1. Materials

C60 (purity 99.98%) was obtained from SES Research Corporation (USA) and used without further purification. Tyrosol (99.5 %) was obtained from Fluka and used as received.

2.2. Adsorption experiments

Adsorption experiments were executed under static conditions at 298 K in batch agitated Pyrex flasks (150 rpm). The equilibrium adsorption isotherms were obtained by varying C60 Concentration in a tyrosol solution. All experiments were performed over 24 h. After filtration, the resulting liquid phase was analyzed by UV spectrophotometer at 280 nm.

Tyrosol adsorption (% Tyrosol) was measured by the following equation;

$$(\% \text{ Tyrosol}) = \frac{C_0 - C_F}{C_0} \times 100$$

Where C_0 and C_F are the initial and the final concentrations of the phenolic compounds, measured as total phenols.

The amount of each polyphenol adsorbed at equilibrium q_e (mg g^{-1}) was calculated by:

$$q_e = \frac{(C_0 - C_{eq})}{X} V$$

Where, V is the volume (L) and X is the amount of C60 (g) and C_0 and C_{eq} are the concentration of Tyrosol initially and at equilibrium.

2.3. Adsorption isotherms

In order to characterize the adsorption equilibria, the following isotherm models (Freundlich, Langmuir, Sips and Redlich-Peterson) were used to correlate the experimental data:

Langmuir model

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

Whose linearized form is:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

where:

q_m : Tyrosol amount at saturation of monolayer that is the adsorption capacity (mg g^{-1}).

K_L : the Langmuir constant.

1) Freundlich model

$$q_e = K_F C_e^{1/n}$$

whose linearized form is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

where:

K_F : the Freundlich constant.

n : the Freundlich exponent.

2) Sips model

$$q_e = \frac{q_m K_S C_e^{1/n}}{1 + K_S C_e^{1/n}}$$

whose linearized Form is:

$$\frac{C_e^{1/n}}{q_e} = \frac{1}{q_m K_S} + \frac{C_e^{1/n}}{q_m}$$

q_m : the Sips maximum adsorption capacity (mg g^{-1}). K_S : Sips equilibrium constant (mg L^{-1}) $^{-1/n}$.



3) Redlich–Peterson

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^\beta}$$

whose linearized Form is:

$$\ln\left(K_{RP} \frac{C_e}{q_e} - 1\right) = \ln(a_{RP}) + \beta \ln(C_e)$$

Where K_{RP} ($L g^{-1}$) and a_{RP} ($mg L^{-1}$) ^{β} are the Redlich–Peterson isotherm constants.

3. Results and Discussion

The adsorption percentage of tyrosol on C60 was determined by varying the amount of adsorbent. The obtained results for the adsorption percentages of tyrosolare shown in Fig. 1. When the adsorbent dose increases, the adsorption percentage increases.

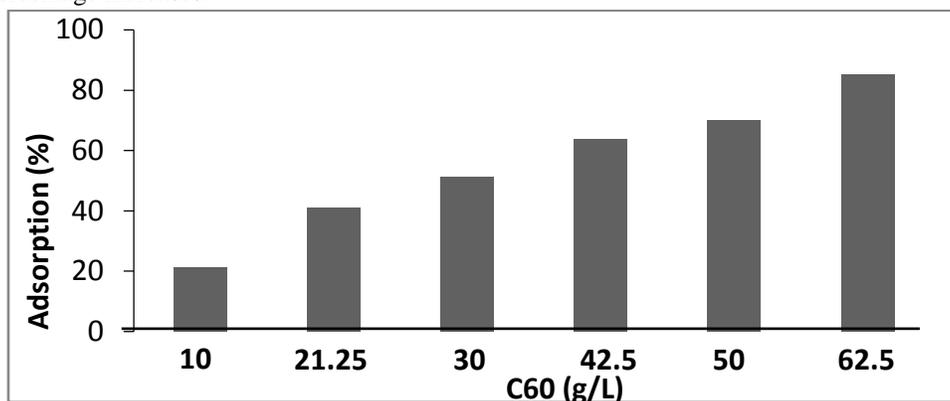


Figure 1: Adsorption percentages of tyrosol on fullerene C60 with different concentrations

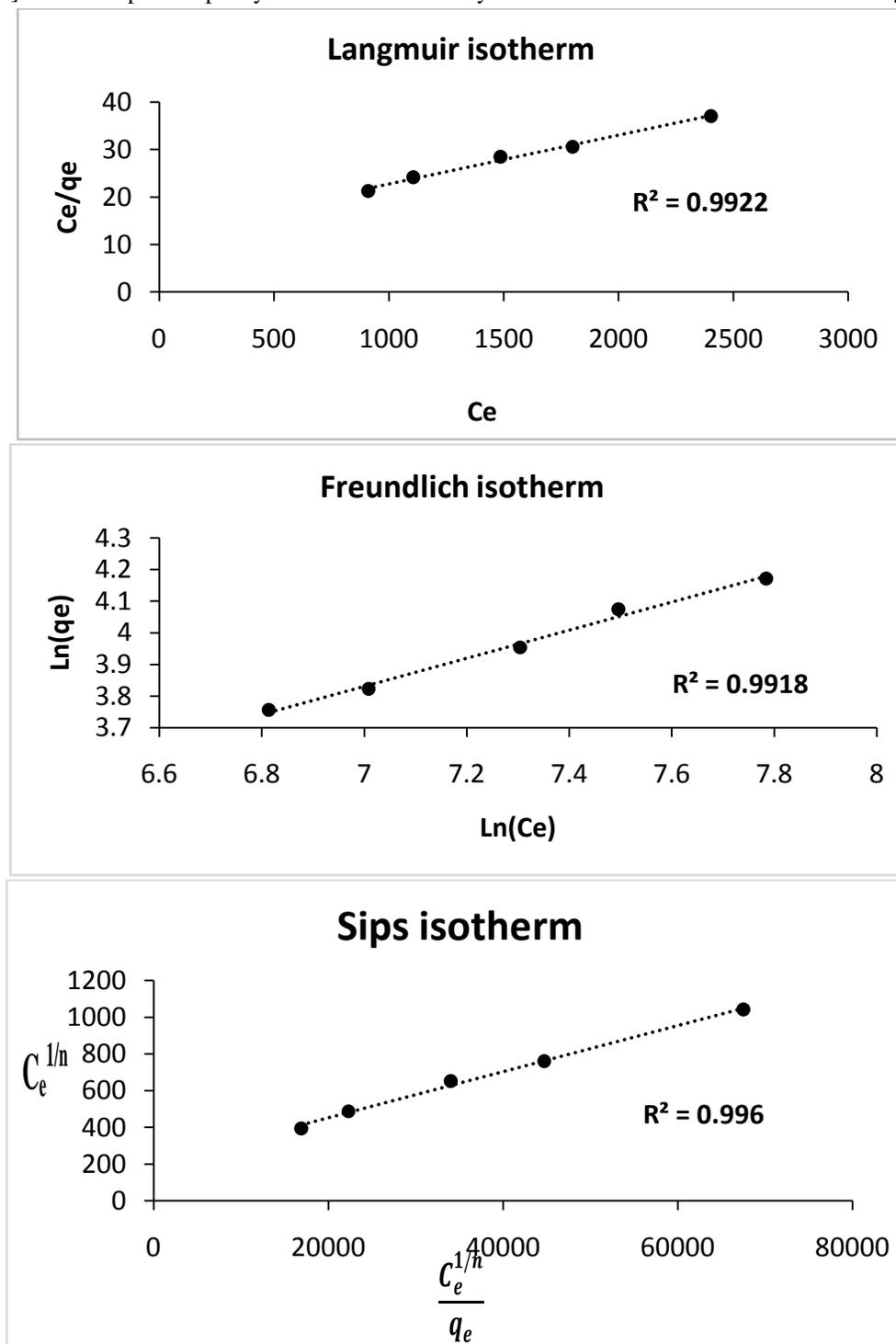
The adsorption experimental data were evaluated using some models and the equilibrium parameters related to these models were determined. Four models: Langmuir, Freundlich, SIPS and Redlich-Peterson were used to fit the adsorption of tyrosol on fullerene C60 (Fig. 2).

Table 1: Adsorption models for tyrosol on fullerene C60

Adsorption models	Values
Langmuir	
q_m ($mg g^{-1}$)	97.36
K_L ($g L^{-1}$)	$8.22 \cdot 10^{-4}$
R^2	0.9922
Freundlich	
K_F	2.05
n	2.25
R^2	0.9918
Sips	
q_m ($mg g^{-1}$)	79.720
K_s	$6.21 \cdot 10^{-5}$
n	0.7
R^2	0.996
Redlich-Peterson	
K_{RP} ($L g^{-1}$)	1
a_{RP}	0.4023
β	0.5766
R^2	0.9947



The best adsorption parameters and regression coefficients are shown in Tables 1. The parameter “n” of the Freundlich model is in the range between 0 and 10, demonstrating that the adsorption of tyrosol on fullerene C60 was favorite [16]. The values of the regression coefficients show that the best fitting of the adsorption data are revealed by the Sips equation, which is resulting from the limiting behavior of the Langmuir and Freundlich isotherms [8]. The adsorption capacity of fullerene C60 to Tyrosol in these conditions attains 79.720 mg g⁻¹.



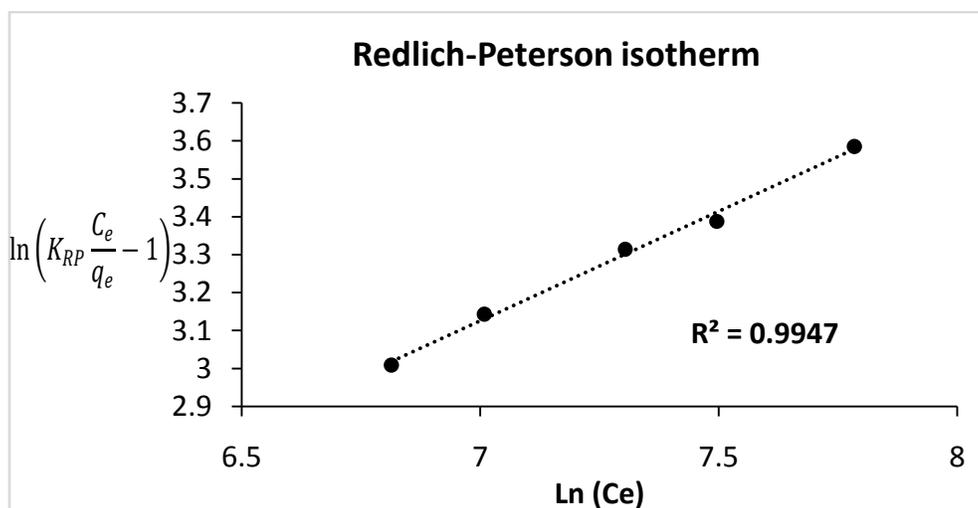


Figure 2: Adsorption isotherms of Tyrosol on fullerene C60

4. Conclusion

The adsorption of tyrosol on fullerene C60 was evaluated and the experimental data show that when the adsorbent concentration increases, the adsorption rate increases. Also, the equilibrium models showed a good fit to the experimental data with a good adsorption capacity.

Reference

1. Fernández-Bolaños, J., Rodríguez, G., Rodríguez, R., Heredia, A., Guillén, R. & Jiménez, A. (2002). Production in large quantities of highly purified hydroxytyrosol from liquid-solid waste of two-phase olive oil processing or "Alperujo". *Journal of Agricultural and Food Chemistry*, 50: 6804-6811.
2. Ben Abdallah, F., Hmani, E., Bouaziz, M., Jaziri, M., Abdelhedi, R. (2017). Recovery of hydroxytyrosol a high added value compound through tyrosol conversion by electro- Fenton process. *Separation and Purification Technology*, 188: 260-265.
3. Yangui, A., Abderrabba, M. (2018). Towards a high yield recovery of polyphenols from olive mill wastewater on activated carbon coated with milk proteins: Experimental design and antioxidant activity. *Food Chemistry*, 262: 102–109.
4. López-Villodres, J.A., Abdel-Karim, M., De La Cruz, J.P., Rodríguez-Pérez, M.D., González-Correa, J.A., (2016). Effects of hydroxytyrosol on cardiovascular biomarkers in experimental diabetes mellitus. *The Journal of Nutritional Biochemistry*, 37: 94-100.
5. Sun, Y., Zhou, D., Shahidi, F., (2018). Antioxidant properties of tyrosol and hydroxytyrosol saturated fatty acid esters. *Food Chemistry*, 245:1262-1268.
6. Yangui, A., Abessi, M.H., Abderrabba, M., (2015). Antioxidant activity of olive mill wastewater extracts and its use as an effective antioxidant in olive oil; kinetic approach. *Journal of Chemical and Pharmaceutical Research*, 7(3):171-177.
7. Yangui, A., Abderrabba, M., Sayari, A., (2017). Amine-modified mesoporous silica for quantitative adsorption and release of hydroxytyrosol and other phenolic compounds from olive mill wastewater. *Journal of the Taiwan Institute of Chemical Engineers*, 70: 111–118.
8. Yangui, A., Njimou, J.R., Cicci, A., Bravi, M., Abderrabba, M., Chianese, A. (2017) Competitive adsorption, selectivity and separation of valuable hydroxytyrosol and toxic phenol from olive mill wastewater. *Journal of Environmental Chemical Engineering* 5, 3581–3589.
9. Potocká, E., Mastihubová, M., Mastihuba, V. (2015). Enzymatic synthesis of tyrosol glycosides. *Journal of Molecular Catalysis B: Enzymatic*, 113, 23-28.



10. Kroto, H.W., Heath, J.R., O'Brien, S.C., Curl, R.F., Smalley, R.E., (1985). C60: Buckminsterfullerene. *Nature*, 318: 62-163.
11. Hirsch, A., Brettreich, M. (2006). Fullerenes: Chemistry and Reactions. John Wiley & Sons, Weinheim.
12. Liu, Z.Q. (2017). Modification on Fullerene. *Current Organic Synthesis*. 14: 999–1021.
13. Rasovic, I. (2017). Water-soluble fullerenes for medical applications. *Journal of Materials Science & Technology*, 33:777–794.
14. El Mahdy, A.M. (2106). Density functional investigation of CO and NO adsorption on TM-decorated C60 fullerene. *Applied Surface Science*, 383: 353-366.
15. Ergürhan, O., Parlak, C., Alver, Ö., Şenyel, M. (2018). Conformational and electronic properties of hydroquinone adsorption on C60 fullerenes: Doping atom, solvent and basis set effects *Journal of Molecular Structure*. *Journal of Molecular Structure*, 1167: 227-231.
16. Barkakati, P., Begum, A., Das, M.L., Rao, P.G., (2010). Adsorptive separation of Ginsenoside from aqueous solution by polymeric resins: Equilibrium, kinetic and thermodynamic studies. *Chemical Engineering Journal*, 161: 34–45.

