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Benzene biosorption by activated carbon from orange peel.

C. M. Santos[1], A. H. Rosa[1], A.A.D. Maia[1], L. C. Morais[1]

1- Department of Environmental Engineering, Sao Paulo State University Júlio de Mesquita Filho, Sorocaba, Sao Paulo, Brazil.
Avenue Três de Março, 511, Alto da Boa Vista, 18087-180 – Sorocaba, Sao Paulo, Brazil.
Contact number +55 (15) 3238-3400, Extension line: 3429 – Fax: +55 (15) 3228-2842
E-mail: s.carolmonteiro@hotmail.com

RESUMO: No presente estudo foi investigada a possibilidade da utilização de cascas de laranja, resíduo agroindustrial da produção do suco de laranja, como um possível material adsorvente do contaminante orgânico benzeno. A adsorção de benzeno por carvões ativados de casca de laranja foi estudada com relação a concentração inicial do contaminante, tempo de contato e a temperatura de pirólise do carvão. A cinética e as isotermas de equilíbrio da adsorção foram ajustadas pelos modelos cinéticos de primeira e segunda ordem e pelas isotermas de Langmuir e Freundlich, respectivamente. O carvão ativado de 450°C apresentou os melhores resultados de sorção quando comparado aos de 250°C e 350°C, com aproximadamente 78% de remoção do contaminante. A adsorção foi melhor ajustada a isoterma de Langmuir quando comparada a de Freundlich, apresentando coeficientes próximos de 1. Esses resultados sugerem que este produto apresenta aplicação potencial para a remoção desse contaminante orgânico de soluções aquosas.

PALAVRAS-CHAVE: Adsorção, casca de laranja, pirólise, contaminante orgânico.

In the present study the possibility of using orange peels, agroindustrial residue of the production of fruit juice, as a possible sorbent of the contaminant monoaromatic extremely toxic benzene was investigated. The adsorption of benzene onto coals from orange peels was studied in relation to the initial benzene concentration, contact time and sorbent dose. Adsorption kinetics and equilibrium adsorption isotherm were fitted by pseudo first and second orders kinetic model and Langmuir and Freundlich isotherms, respectively. The coal pyrolyzed at 450°C showed the best rate of sorption compared to the pyrolyzed coals at temperatures 250°C and 350°C, with approximately 78% removal of the contaminant. The adsorption of benzene by different coals was better adjusted to the Langmuir isotherm compared to Freundlich, presented coefficients ratio close to 1. These results suggest that this product has potential application for removal of the organic contaminants in aqueous solution.

KEYWORDS: Adsorption, orange peels, pyrolysis, organic contaminant.

1. INTRODUCTION

Benzene is a highly toxic monoaromatic hydrocarbon classified as flammable, toxic, carcinogenic, and / or mutagenic agent, one of the most presents organic pollutants in groundwater (Yu *et al.*, 2012). Humans exposed to this contaminant may have several health problems: weakened nervous systems, reduced bone marrow function, and cancers (Costa, 2012). However, this compound is used in different industries for various chemical processes as a raw material, even as a solvent. Consequently, the treatment of waste waters containing such pollutants is of utmost importance.

Several methods were tested for removal of this contaminant, such as membranes (Rohricht *et al*. 2,009), polymers (Frimmel *et al*. 2002; Robberson *et al*. 2006) and carbon nanotubes (Yu, *et al*., 2012), but which are highly dependent on experimental conditions and have a high cost manufacturing and deployment, restricting the use.

Studies show that the use of activated carbon has shown satisfactory results (Ayranci, Duman, 2006), however, this material has a high production cost.

For these reasons, particular attention has been paid to the production alternative adsorbent materials. Of all materials used can highlight the fruit peel or parts of plants, mainly because they are reused, since they are waste of agricultural activity (Vieira *et al.*, 2011), such as chestnut waste (Yao; Qi, Wang, 2010), peanut shells (Liu, Sun, Li, 2010), rice husks (Ajmal *et al*., 2003; Bishnoi *et al.*, 2004), sugar cane bagasse (Santos *et al* ., 2011; Anoop Krishnan, Sreejalekshmi, Baiju, 2011), palm husks (Chong, Chia, Ahmad, 2013), waste orange (Feng *et al.*, 2011; Souza *et al.*, 2012), and other materials.

The fruits production is the primary segment of the Brazilian economic, being the leading country in the production of orange (*Citrus sinensis*). Its cultivation is present in all Brazilian states, being the fruit with more plantations in the country, with more than 800 000 hectares. As a result, the country is the largest generator of fruit waste reaching 25,000 tons per day, most of the manufacturing process of the juice, resulting in several environmental adversities due to high load of improperly disposed waste (IBGE, 2010).

The aim of this work was to study the benzene adsorption from aqueous solutions by using coals from pyrolyzed orange peel at different temperatures. In particular, in this work, adsorption kinetics and equilibrium adsorption isotherm were studied by pseudo first and second orders kinetic model and Langmuir and Freundlich isotherms, respectively.

2. METHODS

***2.1. Orange peels treatment*:** The Orange peels (OP) - *Citrus sinensis* - were obtained in industries which produce the juice. The OP were dried at 110ºC to constant weight, the control was done by weighing every 24 hours. The OP were ground and milled, passed an ABNT 200 sieve to decrease the size of its particles and increase their contact surface, making the sample more homogeneous and thus more representative (Brown, Gallagher, 1998). To get activated carbon from orange peel (ACOP) a thermochemical conversion of the resulting powder was performed. The resulting powder was pyrolyzed in a muffle furnace up to peak temperatures of 250°C, 350°C and 450°C degrees.

2.2. Adsorbate: The solutions were prepared by adding the required volume of benzene to obtain mg/L^{-1} in the concentrations: 50.24, 100.49, 150.74 and 200.99, respectively.

2.3. Adsorption experiments: The adsorption experiments were conducted by mechanically agitating 0,2 g of activated carbons from orange peels (ACOP) with 250 mL of adsorbate solution (benzene and deionized water) solution in orbital shaker (Protech Model 721) at 120 rpm for 15 min for the homogenization of the solution, with concentrations varying between 0,05–0,23 ml.L^{-1}. After the solution was filtered in a filter paper, the filtrate was analyzed using a UV-visible spectrophotometer (UV-VIS), FEMTO 700 plus, at 252 nm for estimation the remaining amount of benzene, value found by scanning through a Varian Cary 100 spectrophotometer. Effect of various contact times 24, 48, 72 and 96 hours were studied. The experiment was performed in triplicate for the ACOP of 250ºC, 350ºC and 450ºC.

2.4. Isotherm studies: The amount of benzene adsorbed at equilibrium, Qe (mg/g), was calculated using the equation:

$$Q_e = (C_o - C_t)\frac{V}{W} \tag{1}$$

Where Co and Ce (mg/L) are concentrations of benzene at initial and equilibrium stages, respectively. While V (liter) is the volume of benezene solution and W (gramme) is the mass of adsorbent.

The adsorption capacity and intensity were calculated by the Freundlich (1906) and Langmuir (1918) isotherms. The Langmuir isotherm model assumes a monolayer adsorption in a homogeneous surface having a finite number of adsorption sites. This model is expressed by the equation:

$$\mathrm{Qe} = \frac{Q_m K_l C_e}{1 + K_l C_e} \tag{2}$$

Where Q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg.g^{-1}), Qm the monolayer adsorption capacity (mg.g^{-1}), K_l the Langmuir or equilibrium constant of adsorption (m.g^{-1}) and C_e the equilibrium concentration (mg.L^{-1}). The linearized expression of the Langmuir equation is given by:

$$\frac{1}{Q_e} = \left(\frac{1}{K_l Q_m}\right)\frac{1}{C_e} + \frac{1}{Q_m} \qquad (3)$$

In contrast, the Freundlich isotherm model assumes heterogeneous surface energy. This model is represented by the equation:

$$Q_e = K_f . C_e^{1/n_f} \qquad (4)$$

Where K_F is the Freundlich constant (mg.g^{-1})(L.mg^{-1})$^{1/n}$, Q_e the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg.g^{-1}), C_e the equilibrium concentration of the solute in the liquid phase (mg.L^{-1}) and $1/n_F$ heterogeneity factor. The linearized model is given by:

$$logQ_e = logK_f + \frac{1}{n_f}logC_e \qquad (5)$$

3. RESULTS AND DISCUSSIN

3.1. Characterization of activated carbons: The available surface area is an important parameter to be determined in the adsorption capacity of the material. The surface area (SB.ET (m^2/g) was calculated using the BET ASAP 2000.

The ACOP pyrolyzed at temperatures of 250°C, 350°C and 450 ºC showed superficial areas of 0.280, 0.279 and 0.410 m²/g, respectively. The BET surface area analysis of the ACOP 450°C shows greater surface area, probably due to the decomposition of more resistant volatile compounds. This ACOP also showed the best sorption which was 78,77%.

3.1. Percentage of mass loss: Initially it was determined the mass loss of samples of ACOP in relation to the dry powder. The samples after removal from the muffle furnace were placed in a desiccator in order to reach equilibrium with the ambient temperature and humidity. The mass loss percentage obtained of ACOP 250°C, 350°C and 450°C were 46.53%, 61.89% and 77.09% respectively.

3.2. Effect of initial concentration: The initial concentration range of 50.24-200.99 mg/L^{-1} was studied and it was observed that the adsorbed amount of benzene by the differents ACOP increased with the increased of initial concentration. The ACOP 450 °C showed the best results (Figure 1).

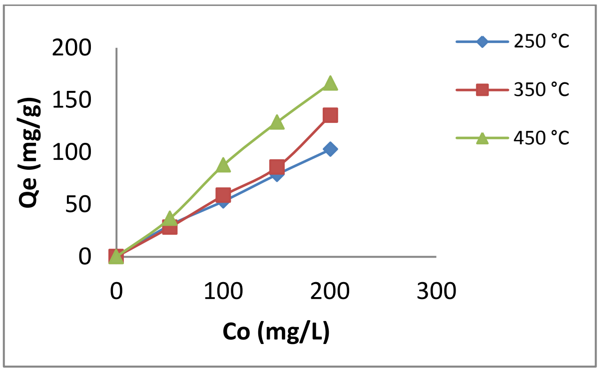

Figure 1. Effect of initial concentration on adsorption of benzene by activated carbon from orange peel.

This may be explained due to a higher superficial surface area of such ACOP and thus a greater availability of sorption sites, in agreement with the Langmuir hypothesis (Converti *et al.* 1992).

3.3. Adsorption study: The percentage removal of benzene is shown in Figure 2.

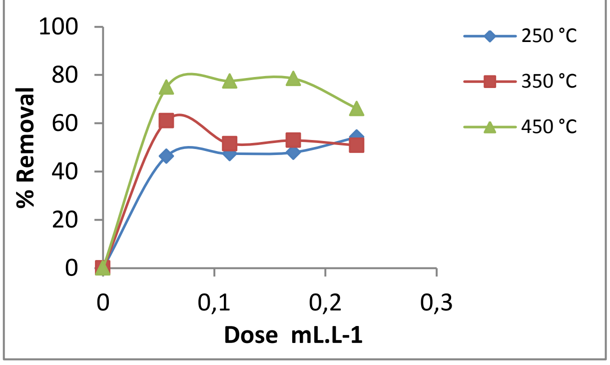

Figure 2. Effect of dose on benzene adsorption.

It has been found that ACOP pyrolyzed at a temperature of 450°C showed the best sorption compared to 250°C and 350°C. This because due to pyrolysis mass loss of ACOP 450°C presented in relation to the powder of OP was higher than the values observed for the ACOPS of 250ºC and 350ºC.

Thus, the ACOP when pyrolyzed at a higher temperature was more reactive, probably due to decomposition of volatile elements.

Most of benzene adsorption occurred during the first 24 hours, this behavior was observed for the three pyrolysis temperatures. The ACOP 450°C showed an average rate of adsorption around 50% for the first 24 hours.

<u>3.4. Adsorption isotherms:</u> The fitting of Langmuir and Freundlich isotherm models and their isotherm constants for the studied adsorption systems are shown in Figures 3 and 4, and Table 1.

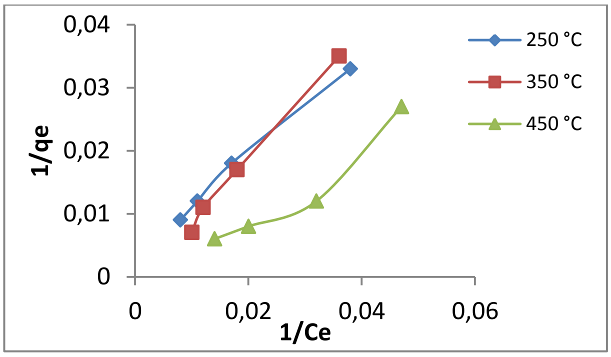

Figure 3. Langmuir isotherm modeling for diferrents solutions concentrations.

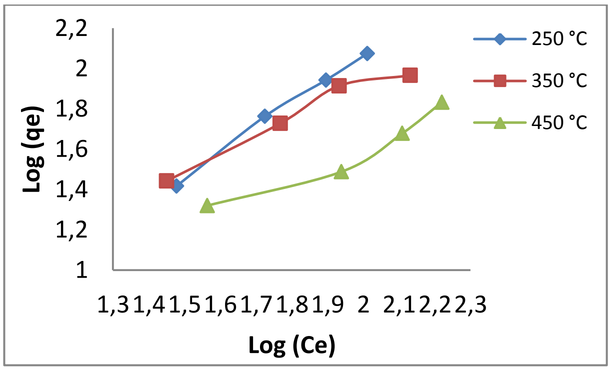

Figure 4. Freundlich isotherm modeling for diferrents solutions concentrations of benzene onto activated carbon from orange peel.

It is observed R² values near 1, especially for ACOP 250ºC. In this way, the data for this type of coal are better adjusted than the others. For ACOP 450°C the R² values are slightly lower than ideal, but it is still valid for comparative purposes. Analyzing the values for the Langmuir model can observe they all have separation factor R_L, which is a dimensionless parameter that allows predicting the viability of the process, a range between 0 and 1.This indicates that in all cases of adsorption processes for this type of activated coal are favorable.

The K_a parameter indicates the strength of interaction between the activated carbon and benzene. According to the values observed, ACOP 450°C has the highest adsorption power. This finding is in agreement with values measured on UV-VIS, which is greater adsorption of benzene solutions for this activated coal.

In the Freundlich isotherm model the parameter n_f is related to the intensity of the interaction of activated carbon with benzene.

How $1/n_f$ factor measures the deviation from the linearization of adsorption, we find that for solutions containing ACOP 350°C and 450°C the value of n_f is less than 1, indicating that the adsorption process is favorable chemical. However, for solutions containing ACOP at 250°C the value of n_f is greater than 1, indicating that the adsorption process is favorably physical.

In pyrolysis has thermal decomposition of the material with elimination of compounds of increased temperature, according to its decomposition temperature. Thus, the ACOP 250 ° C, pyrolyzed at lower temperature, also has in its structure compounds that give the material high stability, having minimal interaction between the adsorbate and with the adsorbent surface, thus characterizing a physical adsorption. Already the ACOP 350 °C and 450 °C having been pyrolyzed at higher temperatures the decomposition of them

Table 1. Langmuir and Freundlich isotherm constants and regression correlation coefficients for the adsorption of benzene onto activated carbon from orange peel

	Langmuir isotherm model				**Freundlich isotherm model**		
Adsorbate	**K_l(L/mg)**	**Q_m(mg/g)**	**R_L**	**R²**	**K_F (mg/g)(L/mg)1/n**	**n_F**	**R²**
250ºC	0.0043	294.11	0.4416	0.9940	2.0801	1.23	0.9953
350ºC	0.0022	434.78	0.5111	0.9951	1.9107	0.8387	0.9612
450ºC	0.0071	222.22	0.3901	0.9283	1.0060	0.8078	0.9283

was more marked, conferring a different characteristic to the adsorbent surface. That way, contaminants from aqueous solution chemically reacted with the surface of these ACOP featuring a more stable and stronger chemical adsorption.

3.5. Adsorption kinetic: The adsorptions of benzene for the different ACOP at different contact time are shown in Figures 5, 6 and 7, and their correlation coefficients in Table 1.

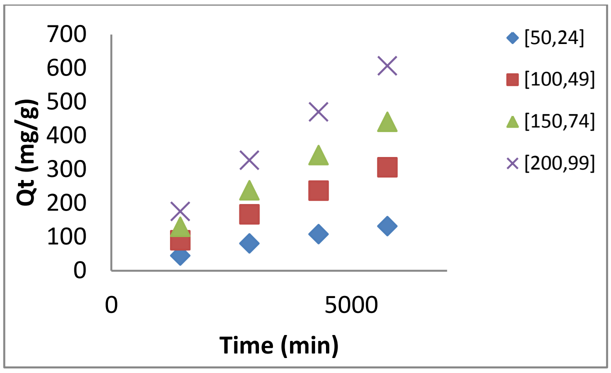

Figure 5. Kinetics modeling of benzene adsorption onto activated carbon from orange peel of 250°C.

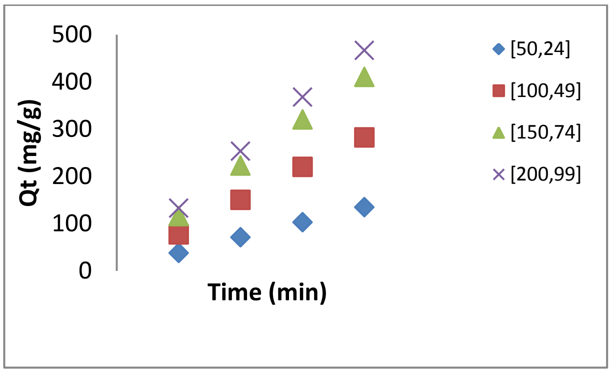

Figure 6. Kinetics modeling of benzene adsorption onto activated carbon from orange peel of 350°C.

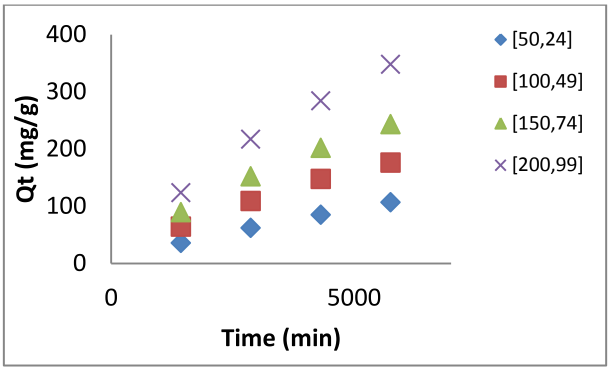

Figure 7. Kinetics modeling of benzene adsorption onto activated carbon from orange peel of 450°C.

The largest amount of benzene adsorbed by ACOP was during the first 24 hours of the experiment, this value being increased with increasing contact time. This may be due to the large amount of empty available sites links at the beginning of the adsorption process, therefore, the initial rate of adsorption was faster. The kinetic models were used to investigate the kinetics of benzene adsorption onto ACOP were the pseudo-first-order (Lagergren, 1898) and the pseudo-second order (Ho and McKay, 1999). The linear equations of the pseudo-first-order and the pseudo-second-order are represented in equations (6) and (7), respectively:

$$log\ (Q_e - Q_t) = logQ_e - \frac{k_1}{2.303}.t \qquad (6)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e}.t \qquad (7)$$

Where k_1 (1/min) is the pseudo-first-order rate constant and k_2 (g/mg.min) is pseudo-second-order rate constant.

Table 2. Regression correlation coefficients for the adsorption of benzene onto activated carbon from orange peel.

Concentrations mg.L^{-1}	**Temperatures of activated carbons from orange peels**		
	250 °C R^2	**350 °C R^2**	**450 °C R^2**
50.24	0.9994	0.9999	0.9982
100.49	0.9994	0.9988	0.9903
150.74	0.9994	0.9986	0.9916
200.99	0.9903	0.998	0.9911

The comparison between the experimental data time profile against the theoretical calculated values given by pseudo-first-order and pseudo-second-order for the different concentrations used are shown in Figure 8 and 9, where the temporal profile of experimental data of the pseudo-first-order showed the best results.

This is confirmed by the highest correlation coefficients (R^2) given by the pseudo-second model (Table 3), which suggests that the limiting factor for adsorption of benzene from ACOP is physical.

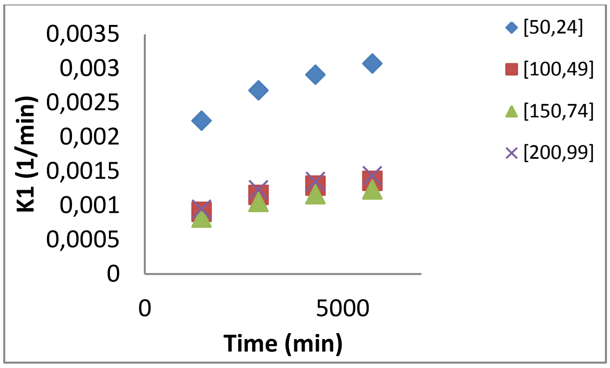

Figure 8. Pseudo-first-order kinect model of benzene adsorption onto activated carbon from orange peel.

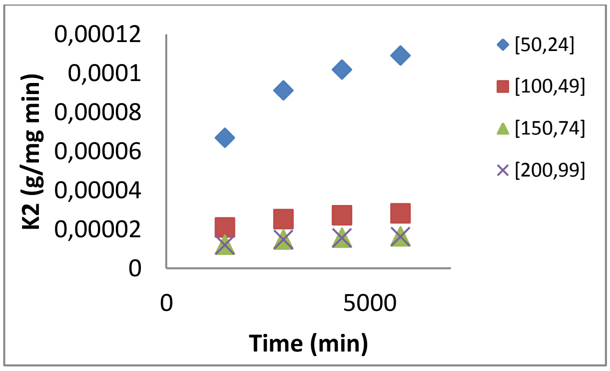

Figure 9. Pseudo-second-order kinect model of benzene adsorption onto activated carbon from orange peel.

4. CONCLUSION

It was found that the adsorption capacity of the ACOP 450°C for the time reaction of 96 hours was over 78%. For all the ACOP most of the adsorption occurred during the first 24 hours, with an average 50% removal

The Langmuir isotherm model was more suitable, in view of the values closer to 1 for the correlation coefficient R^2 and values within the range of 0 and 1 for the separation factor R_L.

Results from the pseudo-first-order model fitting suggest that the limiting factor for adsorption of benzene from ACOP is physical.

ACOP can become an economically viable and environmentally sound for fruit producing countries.

5. ACKNOWLEDGEMENTS

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Table 3. Pseudo-first-order and pseudo-second-order model constants and regression correlation coefficients for the adsorption of benzene onto activated carbon from orange peel.

Concentrations mg.L^{-1}	**Pseudo-first-order**		**Pseudo-second-order**	
	K_1 (1/min)	**R^2**	**K_2 (mg/g)**	**R^2**
50.24	0.0027	0.9988	0.000092	0.9928
100.49	0.0046	0.9951	0.000025	0.9901
150.74	0.0042	0.995	0.000059	0.9896
200.99	0.0049	0.9915	0.000014	0,9809

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