

Removal and recovery of diethyl phthalate (DEP) onto activated carbon from Albizzia Julibrissin Pods: operating parameters effect and equilibriums modeling

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Abstract

Diethyl phthalate (DEP), a disrupting compound, is one of major environmental issues, due to its harmful effects on the human health and the ecological systems. It is frequently detected in drinking water mainly as a consequence of its widespread use as plasticizer and non-plasticizer and its characteristic not to bind to materials, hence its migration into various systems like surface marine water, freshwater, sediments, etc. to end up in the human body to possibly cause cancer, liver damage, genetic disorders, etc. Therefore this has encouraged the present study considering the phthalate retention onto an activated carbon.

The adsorption of DEP onto a new activated carbon prepared from waste material and chemically activated by H_3PO_4 , was investigated, combining non-recovered waste recycling and reduction of phthalate water contamination. In fact, Albizzia Julibrissin Pods AJP was used for preparing activated carbon, which is a by-product widely abundant in both Asia and Africa. It may be considered as an invasive tree, providing a high volume of pods non-valued constituting an environmental problem. In addition, Albizzia Julibrissin pod is characterized by a high lingo-cellulosic composition, making it a promising feedstock for the production of activated carbon with a high specific surface area.

The main objective was to determine the phenomenon which governed the DEP adsorption onto activated carbon from waste material. Batch experiments were carried out to evaluate the effect of adsorbent dose, temperature and DEP concentration on adsorption efficiency. The optimum conditions were obtained at 1 g L^{-1} of activated carbon, 20°C and 150 g L^{-1} of DEP. The equilibrium data were very well represented by Langmuir isotherm with a maximum adsorption capacity of 435 mg/g, confirming the mono-layer coverage. Finally these results encouraged the possibility to treat, this type of pollutant, by activated carbon prepared from waste material.

Keywords: Diethyl phthalate; Activated Carbon, Albizzia Julibrissin Pods, Equilibrium, parameters effect.

I. Introduction

Nowadays, the endocrine disrupting compounds like diethyl phthalate (DEP) is one of the environmental problematic issues owing to harmful effects on human health and ecological systems. The development of new analytical techniques reveals the presence of DEP at the entrance and exit of the treatment plant that have escaped all pollution treatment. The DEP is frequently detected in surface marine water, sediment and atmosphere as a consequence of their widespread use as plasticizers [1] and also as no plasticizers like pharmaceuticals, cosmetic additives or domestic applications [2]. Since the phthalates are not chemically bound to the materials and can easily migrate from the plastics to various systems [3] including freshwater, foods, toys and cloth then ending in the human body causing cancer, liver damage and genetic disorders [4].

In this context, many researches proposed several treatment technologies for complete elimination of phthalates from water and wastewater such as advanced oxidation processes [3, 5], microbial degradation [6], and adsorption [7]. For the present case, adsorption is mainly dependent on the DEP properties, structure and to an equal extent on the surface chemistry of the adsorbent. Therefore, this study focused on the behavior and mechanism of DEP adsorption onto activated carbon by waste materials from aqueous phase. The influence of independent variables were investigated, additionally, the suitable modeling kinetic and isotherm were proposed to describe the experimental data

II. Materials and methods

II.1. Adsorbent preparation

The activated carbon from waste materials was chemically activated by phosphoric acid in 40 wt %, with weight H₃PO₄/precursor ratio 8:1 for 1 h at 100 °C. After that, the impregnated sample was calcinated in thermally controlled tubular furnace. Finally, the obtained activated carbon was washed mainly by hot water until pH of wash water became constant [8].

II.2. Adsorbate preparation

Analytical grade DEP (purity > 99 %, E. Merck; C₁₂H₁₄O₄; MW= 222.24 g mol⁻¹), which is characterized by a high toxicity, was used as a model pollutant, the structure is given in Fig. 1. The required amount of DEP was dissolving in distilled water to obtain 500 mg L⁻¹ concentration. The solution test at desired concentration of DEP was prepared by diluting the stock solution with distilled water.

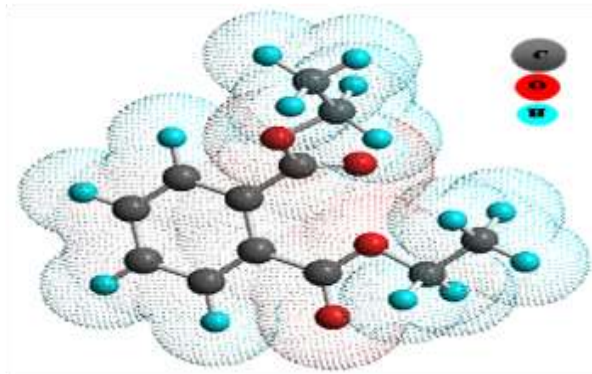


Fig. 1: 3D DEP structure

II.3. Batch adsorption experiments

A series experiment batch was carried out in 100 mL DEP aqueous solutions at controlled temperature. The operating parameters effect such as contact time equilibrium, DEP concentration (150 to 500 mg L⁻¹) and temperature of solution (283 TO 313 K) were investigated. The removal percentage of DEP and q_e the amount of adsorbate adsorbed at equilibrium (mg g⁻¹) were determine using the following equation:

$$Removal \% = \frac{(C_o - C_e)}{C_o} * 100 \quad (1)$$

$$q_e = \frac{C_o - C_e}{W} * V \quad (2)$$

Where, C_o and C_e (mg g⁻¹) are the initial and the equilibrium concentration, respectively. V is the volume of the solution (L) and W is the weight of adsorbent (g).

In order to ensure the accuracy and to evaluate the best fitting between the experimental and predicted

data, all equilibrium date were performed in triplicate and the mean values were used in the data analysis. Statistical functions of Absolute Percentage Error (APE) were applied to validate the models using the following expressions:

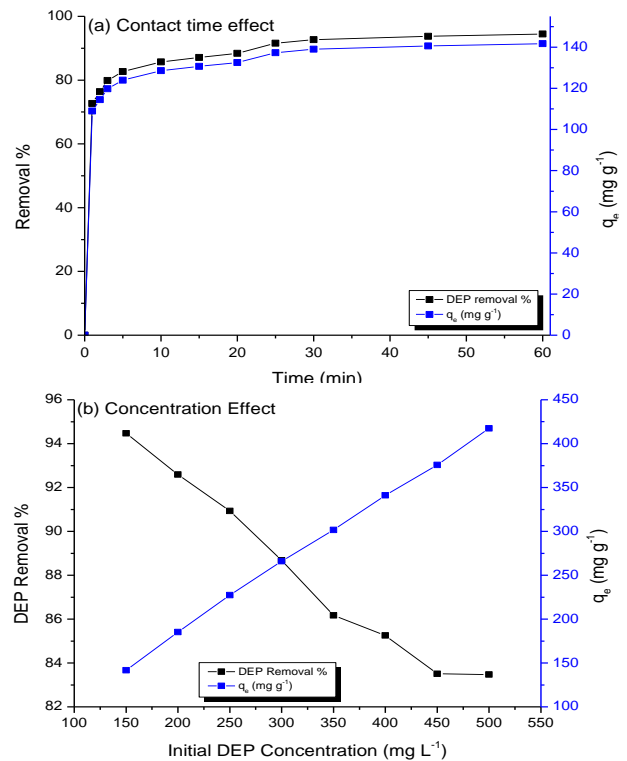
$$APE = \frac{1}{N} \sum_{i=1}^N \left| \frac{q_{e\ exp} - q_{e\ pred}}{q_{e\ exp}} \right| * 100 \quad (3)$$

Where, q_{eexp} and q_{epred} (mg g⁻¹) are the experimental and predicted values of equilibrium capacity adsorption and N the number of experimental data.

Results and discussion

III.1. parameters affecting the DEP adsorption

In Fig. 2 (a), DEP molecules were rapidly adsorbed on the external surface onto adsorbent at the beginning 10 min. Then, between 10 and 30 min, they were slowly diffusion at inner on surface particle.



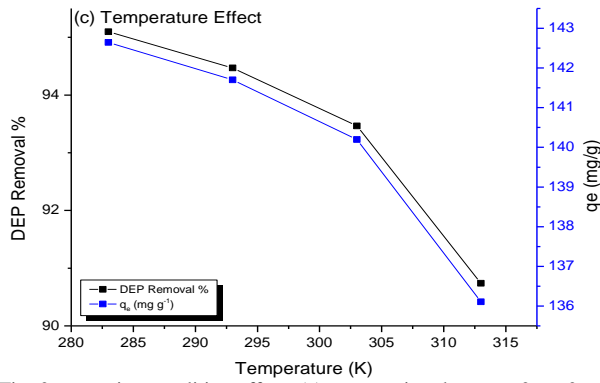


Fig. 2: operating condition effect: (a) contact time between 2 – 60 min, (b) initial DEP concentration between 150 – 500 mg g⁻¹ and (c) Temperature between 283 – 313 K.

Finally, the equilibrium was reached at 30 min, as no significant changes were observed after about 60 min.

The variation in the extent of adsorption may be due to the fact that initially all sites on the surface of sorbent were vacant and the solute concentration gradient was relatively high.

From the Fig. 2 (b), it seems with rise of the initial DEP

concentration the removal percentage decreased from 95% to 83 %, suggesting an exothermic adsorption process. This phenomenon was due to saturation the availability of adsorption sites, expressed by the number of adsorbate moiety to the available active sites of adsorbent ratio. On the other hand, this ratio was also related to the surface coverage that increased with rising

Table 1: Empirical equation of isotherm models

| Model | Equation | Parameters | Ref |
|------------|---|--|---------|
| Langmuir | $q_e = \frac{q_{max} k_L C_e}{1 + k_L C_e}$ | q_e (mg g ⁻¹) equilibrium adsorption capacity q_{max} (mg g ⁻¹) maximum monolayer adsorption capacity k_L (L mg ⁻¹) Langmuir equilibrium constant | [9, 10] |
| Freundlich | $q_e = k_F C_e^{1/n}$ | C_e (mg L ⁻¹) Equilibrium solution concentration k_F (L g ⁻¹) Freundlich constant of adsorption capacity n (mg g ⁻¹) Freundlich adsorption capacity constant | |
| Temkin | $q_e = \frac{RT}{h} \ln (AC_e)$ | A Temkin constant h Temkin constant R (J mol ⁻¹ K ⁻¹) gas constant equal to 8.314 T (K) Temperature | |

adsorbate moiety per unit volume of solution at fixed dose, this explains the increase of adsorption capacity with rise temperature until attained the maximum capacity at 420 mg g⁻¹.

The temperature plays an important role in the adsorption process, hence the interest to study the effect of thermal variation. Adsorption capacity increased slightly from 143.53 to 136.11 mg g⁻¹ with rising temperature (Fig. 2 (c)), indicating an exothermic process. Qureshi et al., [9] and Tümay Özer et al., [10] reported the similar trends onto activated carbon and biocomposite beads, respectively.

III.2. Equilibrium adsorption study

For solid-liquid system, the equilibrium adsorption isotherm is a basis of the thermodynamic studies of separation process describing behavior between liquid/solid phase distributions at equilibrium state. A number of empirical equations of two parameters namely: Langmuir, Freundlich and Temkin (Table1).

Originally, the Langmuir isotherm was developed to describe the gas-solid phase adsorption on the assumption that the adsorbent surface was homogenous with energetically equivalent sites, which saturated by one adsorbate monolayer.

Freundlich model is based on the assumption that the adsorption occurs in multilayers with heterogeneous adsorbent surfaces applied to non-ideal systems.

The Temkin and Pyzhev considered the effects of indirect adsorbent/adsorbate interactions on adsorption isotherms. According to the Temkin isotherm, the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions.

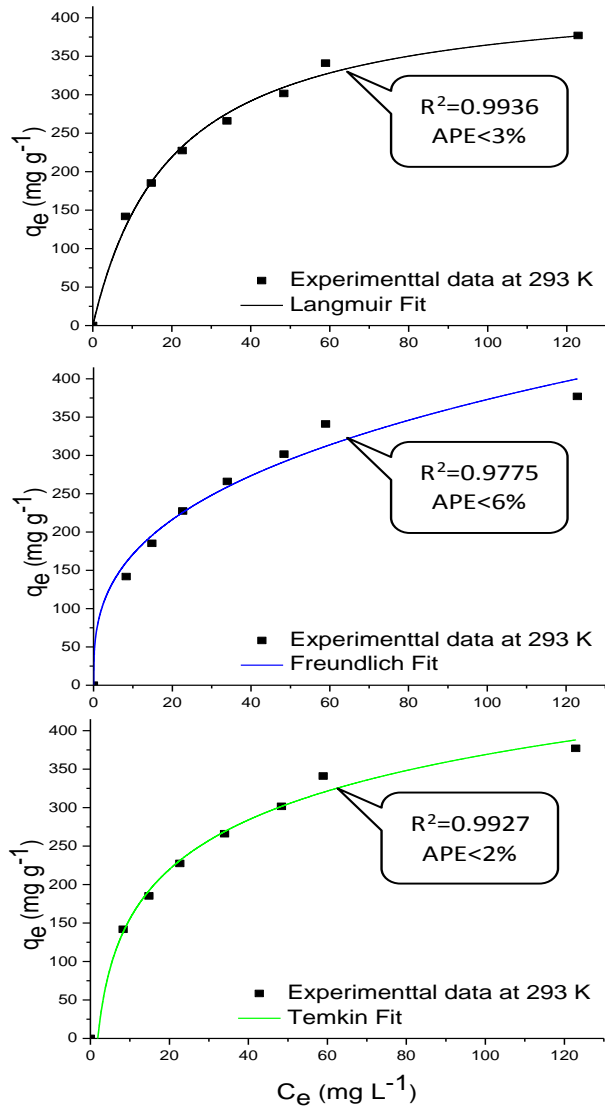


Fig. 3: Langmuir, Freundlich and Temkin plots

Fig. 3 illustrates the Langmuir, Freundlich and Temkin plots from non linear regression at 289 K, where a good agreement between the experimental and theoretical results was observed for all isotherms. The correlation coefficient (R^2) and Absolute Percentage Error (APE) given in Table 2 are the order Langmuir > Temkin > Freundlich with percentage error < 10 % for all investigation.

The K_{Lg} , k_f and k constant decreased with rise temperature indicating an endothermic nature of adsorption process. The maximum adsorption capacities were ranged between 437 to 457 $mg\ g^{-1}$, higher than th values reported in [8, 9].

Table 2: Isotherm parameters for the DEP adsorption

| Température | 10°C | 20°C | 30°C | 40°C | |
|-------------|-----------|--------|--------|--------|--------|
| qe cal | 389 | 377 | 375 | 370 | |
| Langmuir | q_{max} | 437 | 438 | 452 | 457 |
| | k_{Lg} | 0,0601 | 0,0501 | 0,0408 | 0,0347 |
| | R^2 | 0,9922 | 0,9936 | 0,9928 | 0,9947 |
| | APE | 4% | 3% | 4% | 2% |
| Freundlich | n_f | 2,9748 | 2,9527 | 2,7651 | 2,6401 |
| | k_f | 84 | 78 | 70 | 62 |
| | R^2 | 0,9869 | 0,9775 | 0,9745 | 0,9742 |
| | APE | 4% | 6% | 7% | 6% |
| Temkin | B | 92 | 93 | 99 | 103 |
| | K | 1,9199 | 1,7084 | 1,4975 | 1,3734 |
| | R^2 | 0,9971 | 0,9927 | 0,9903 | 0,9921 |
| | APE | 2% | 2% | 3% | 2% |

Additionally, the $1/n$ values for both molecules range between 0 and 1, indicating a favorable adsorption process. Therefore, this would suggest that the adsorption was physical, with weak adsorption bonds.

On the basis of statistical analysis, Langmuir model displayed the better coefficient correlation and the lower APE (< 10 % of error), confirming monolayer adsorption. In this case, the molecules had equal activation energy and that adsorbate–adsorbate interaction was negligible.

III.3. DEP adsorption kinetics

The $\ln(q_e - q_t) = \ln q_e - k_1 t$ pseudo-first-order model proposed by Lagergren was based on solid capacity for the adsorption of liquid/solid system. The pseudo-second-order kinetic expression developed by Ho and McKay was based on the assumption that the adsorption followed second-order kinetics of adsorption. The used expressed are given by the following:

$$(4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

Where, q_t (mg g^{-1}) adsorption capacity at time t , k_1 (min^{-1}) pseudo-first-order rate constant and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) pseudo-second-order rate constant.

The fit plots of $\ln(q_e - q_t)$ and t/q_t versus t were represented in Fig. 4 (a) and (b), show the good agreement between the experimental data and the fit of first and second order models. However, the theoretical equilibrium capacities of adsorption q_e values from the first order model did not agree with the experimental q_e . While the theoretical q_e values from the second order model were closer to the experimental q_e values with good correlation coefficient greater than 0.990 for all concentrations of DEP.

The error function values of first-order model had higher, range 2.9 to 10 % comparatively to APE values for the second-order that are lower and 0.4 to 5.1 %. The higher R^2_{adj} and the lower APE for the pseudo-second-order model also indicating chemical reaction of adsorbent surface. Similar phenomenon has observed in the literature on various adsorbents [9].

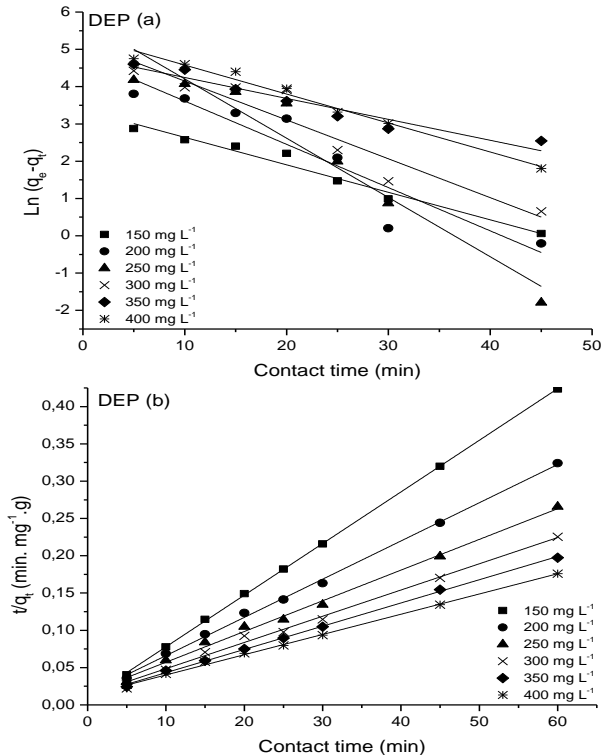


Fig. 4: Kinetic plots: (a) pseudo-first-order and (b) pseudo-second-order.

IV. Conclusion

According to the operating parameters effects study, the initial concentration has a significant effect of DEP adsorption onto activated carbon. It seems also that the equilibrium is reached rapidly after 30 min favoring application on a larger scale. The equilibrium data was well fitted by the Langmuir isotherm suggesting the monolayer adsorption. The parameters results of isotherm fit indicated a favorable and exothermic DEP adsorption process onto activated carbon. The kinetics data tended to fit very well in the pseudo-second-order kinetics model with high correlation coefficients. The maximum adsorption capacity was 438 mg g^{-1} , indicating the high capacity of the considered activated carbon in removing DEP as compared to others adsorbents.

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