ORIGINAL ARTICLE

ELIMINATION OF PYROMELLITIC ACID WITH ACTIVATED CARBON

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ABSTRACT

Backround: The removal of pollutants by adsorption on activated carbon is widely used. However, in the presence of several pollunates at once, this elimination can be influenced. **Objective**: The objective of this work is the estimation of activated carbon performance when in contact with several solutes. **Methods**: Thus, the elimination of pyromellitic acid was carried out on an activated carbon, in the presence of 0.2 or 0.5 mmol / l of benzoic acid to the concentrations. **Results:** The results show that the adsorption follows the model of Freundlich. The adsorbed amounts of pyromellitic acid are slightly reduced by the presence of benzoic acid in low concentrations. However, high concentrations strongly disfavour the adsorption of acidic examined. **Conclusion**: The study of competitive adsorption is essential to get closer to real effluents.

Keywords*: Competitive adsorption, activated carbon, pyromellitic acid, benzoic acid.*

1. INTRODUCTION

The use of activated carbon in drinking water treatment, to remove many organic trace minerals or water, is an ancient practice. However, despite the importance of the studies of the adsorption of organic compounds on activated carbon, knowledge of the method of attachment of these substances is complex and involves different mechanisms. Understanding these mechanisms requires prior knowledge of the parameters influencing adsorption. Moreover, the adsorption of an organic compound alone on an adsorbent material is, in general, change when that compound is in the presence of other solutes (co-adsorbates). This was appreciated, as we have shown above, if the co-adsorbate is a mineral compound (NaCl or $NaNO_3$) [1].

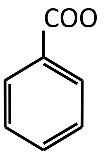
The objective of this work is the study of pyromellitic acid adsorption or benzene-1,2,4,5-tetracarboxylic acid (called Pyr) in the presence of benzoic acid (Ben). Knowledge of these changes will enable the prediction and estimation of activated carbon performance when in contact with several solutes.

2. MATERIALS AND METHODS

2.1 Products

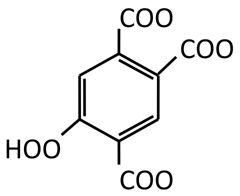
Activated carbon, named (CAG), used by the National Office of Drinking Water in the water treatment, is in the form of grains, particle size 0.4 to 1.7 mm, and effective size 0.55 to 0.65 mm. This activated carbon is washed, in a glass column, at constant distilled water until the pH and conductivity, dried in an oven at 110 ° C overnight and then stored in closed vials until use. According to Irwin (1981), this operation significantly reduces the amount of surface impurities mineral coals [2]. The specific surface area calculated by applying the Brunauer, Emmett et Teller (BET) equation [3] in the isothermal N_2 adsorption at 77K was 800 m^2 g. The pH of the point of zero charge pH_{PZN} coal is determined by the method described by Ferro-Garcia et al. (1998) and Sontheimer et al., (1988) is 8.20 ± 0.02 [4,5].

Pyromellitic acid or 1,2,4,5-benzene-tetracarboxylic acid (named **Pyr**) and benzoic acid (named **Ben**) are FLUKA products (greater than 98% purity)



Ben

Figure 1: Structure of 1,2,4,5-benzene-tetracarboxylic acid.



Py

Figure 2: Structure of benzoic acid (named **Ben**).

2.2 Methods: The concentrations of the aqueous solutions are determined using a chromatograph (HPLC) Type JASCO, equipped with a UV detector JASCO 875-UV, Variable wavelength and an isocratic pump JASCO PU-880. Column Spherisorb ODS_2 5. grafted C18 (octadecylsilane bonded phase with), length 25 cm is used for the separation. The elution rate was maintained at 0.4 ml/min and the volume of the injected solution is 20µl. The eluent phase is methanol (Prolabo). All aqueous solutions and solvents are filtered through Whatman 0.45µm membrane and degassed under vacuum.

The chromatographic detector is connected to an integrator-type VARIAN 4400, which allows recording and evaluation of characteristic peaks surfaces adsorbates according to their concentrations.

The quantities of adsorbed per gram of adsorbent are calculated by measuring the concentrations of the solutions before and after adsorption.

The adsorption tests studied acids, are made batch reactor at 25 ° C (± 0.5 ° C). All stock solutions and diluted examined solutes are prepared with double-distilled water. Volumes of the compound solution studied with a known concentration of were placed in Pyrex tubes in the presence of activated charcoal (1 g/l). The tubes were then stirred using a mechanical rotator (100 revolutions/min) for a time corresponding to obtaining the equilibrium of the adsorption. After a predetermined stirring time, the two phases are separated by double filtration on Millipore filters (Whatman 1.2 µm and 0.45 µm). The filtrate is then analyzed by HPLC to determine the residual concentration of adsorbate. All experiments were conducted in protected from light to avoid possible photodegradation adsorbates. Blank tests (without the addition of activated carbon) were performed to monitor for any loss by adsorption on the filters, or the walls of the tubes. All experiments were repeated at least twice, the experimental error does not exceed 4%.

3. RESULTS

3.1 Adsorption Kinetics:

On figure 3, we presented the kinetic curves of adsorption of Ben and Pyr acids on (CAG) from an initial concentration of 1 mmol/l. Analysis of these curves shows that the stirring time required to reach adsorption equilibrium are 20 and 24 hours respectively for Ben and Pyr acids. The amounts adsorbed at equilibrium are 0.61 and 0.28 mmol/g respectively for Ben and Pyr acids.

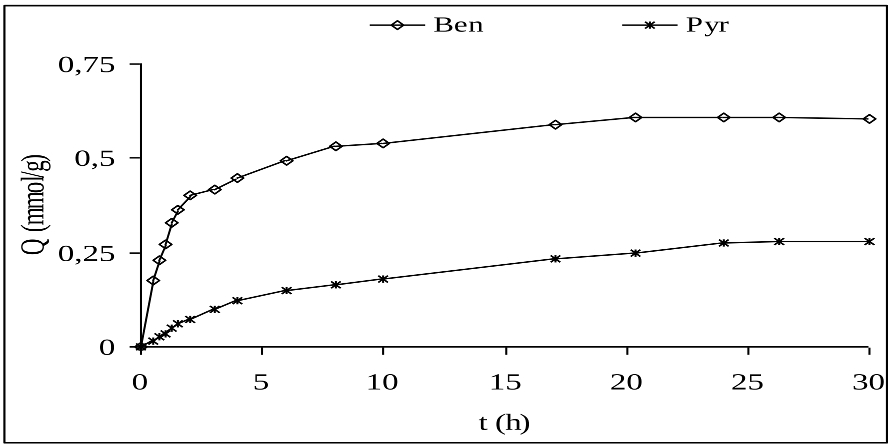


Figure 3: The figure presents the kinetics of the adsorption of benzoic (Ben) and pyromellitic (Pyr) acids on (CAG). C_0 = 1 mmol/l, R = 1 g/l.

It is also observed that, unlike the case of Pyr acid, the adsorption kinetics of Ben exhibite two separate steps. Indeed, 75% of the amount that remains at equilibrium is established after only two hours of contact between the acid and the (CAG). After this period, the amount adsorbed increases slowly until the establishment of equilibrium (20 hours).

Slow kinetics observed on (CAG) may be due to a slow diffusion of the molecules of adsorbate in the porous structure of the grains. To demonstrate the influence of the particle size of the material on the adsorption process, we restored the kinetic curves of the two acids on the (CAG) ground and sieved to 100.mu.m (Figure 4). In this case, the determined equilibrium times are 20 and 30 minutes respectively for Ben and Pyr acids. The amounts adsorbed at equilibrium are equal to those determined on the (CAG) non-milled.

Calculating the initial rates of adsorption of the two acids on the (CAG) and crushed crude highlights the influence of the particle size. Thus, Table 1 shows the initial rates calculated by taking the tangent at the origin of the curves Q = f (t) [6]. This table also gives the values of the quantities adsorbed at equilibrium for both acids on (CAG). Obviously, the initial rates determined on the crushed (CAG) are larger than those on no crushed (CAG) which is consistent with the results reported in the literature [7-9].

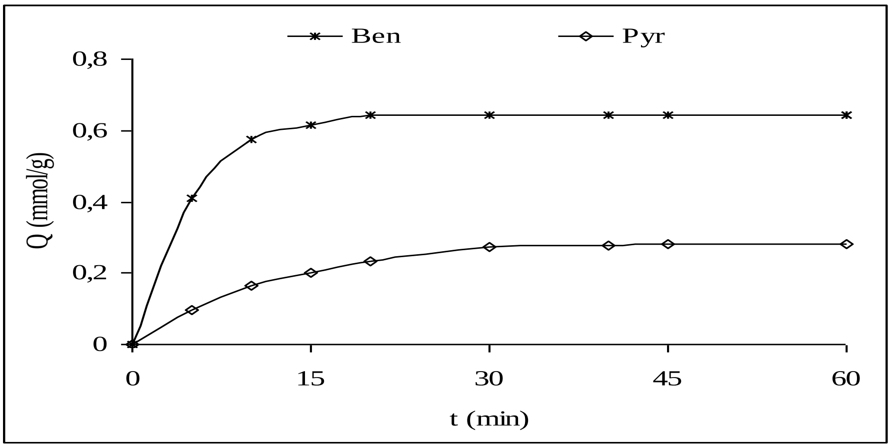


Figure 4: The figure presents the kinetics of adsorption of benzoic (Ben) and pyromellitic (Pyr) on crushed and sieved (CAG) to 100 µm. C_0 = 1 mmol/l, R = 1g/l.

A figure 3 and 4 also shows that the amount of Ben acid retained at equilibrium is greater than that of the Pyr acid. These differences in behaviour between the two acids can be interpreted on the basis of their molecular weight and their solubility's. The Pyr acid has a high molecular weight not allowing it thus rapid diffusion into the pores of activated carbon, which explains its slow kinetics. In addition, because of its high solubility compared to Ben acid, its bonds with water will be higher resulting in low adsorption capacity and slow kinetics

Table 1: The table presents the values of the initial adsorption rates (mmol/g.h) and quantities retained at equilibrium (mmol/g) for benzoic (Ben) and pyromellitic (Pyr) on (CAG).

	(CAG) Brute		**(CAG) crushed**	
	V_0 (mmol/g.h)	**Q (mmol/g)**	**V_0 (mmol/g.h)**	**Q (mmol/g)**
Benzoic acid	0.277	0.606	4,932	0.608
Pyromellitic acid	0.033	0,278	0.798	0.279

3.1 Adsorption Isotherm:

To determine the effect of an organic co-adsorbate on the adsorption of the acid (Pyr), we have established adsorption isotherms of Pyr acid on crushed (CAG) in the presence of a fixed concentration (0.2 or 0.5 mmol/L) of Ben acid. The experimental conditions are the same as those montionned previusly (R = 1g/L; contact time of one hour). At time of equilibrium, the residual concentrations of the two solutes in the filtrate (Pyr + Ben) were determined by HPLC. The equations for the calibration curves for the calculation of these concentrations were performed under the same conditions (binary mixture). We note that we did not observe any interference between the solute mixtures.

The modeling of adsorption isotherms was carried out by applying the classical model Freundlich whose equation is of the form:

$$Q = KC_e^n \qquad \textbf{(1)}$$

Where Q is the amount of solute adsorbed per gram of adsorbent (mmol/g). C_e is the concentration of the solute in the solution at equilibrium (mmol/l), and K and n are constants Freundlich connected respectively, the capacity and the adsorption intensity.

In figure 5, we introduced the acid adsorption isotherms Pyr alone and in the presence of a concentration of 0.2 and 0.5 mmol /L of Ben acid. We note that for low concentrations of Pyr acid (<0.01 mmol/L), the amounts retained in the absence and presence of the Ben acid are substantially equal. When the concentration of Pyr increases, these quantities adsorbed becoming weaker especially in the presence of Ben acid at a concentration of 0.5 mmol/L. The constants K of Freundlich estimated for the adsorption isotherms of the Pyr acid also decreases with increasing concentration of Ben acid. In fact, this constant (K) changes from 0.22 in the case of Pyr acid alone 0.18 to in the presence of 0.2 mmol/L of Ben acid, and then to 0, 155 when the concentration of this last one is 0.5 mmol/L. This shows that Ben acid partially inhibits the adsorption of Pyr acid.

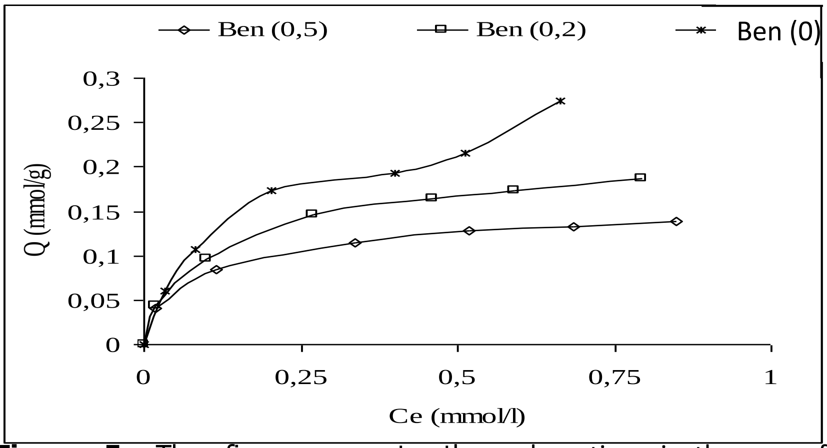


Figure 5: The figure presents the adsorption isotherms of pyromellitic (Pyr) acid alone and in the presence of benzoic (Ben) acid at a concentration of 0.2 and 0.5 mmol/L.

To assess to the effect of the presence of the Pyr acid on adsorption of acid Ben, we brought in "Figure 6", variations in adsorbed amount from the two initial concentrations (0.2 and 0.5 mmol/L) as a function of increasing amounts of Pyr acid. We observe that for Pyr acid concentrations below 0.6 mmol/L, the amount adsorbed of Ben acid is substantially constant. Beyond this concentration, the amount adsorbed Ben especially decreases as the initial concentration of Ben acid is 0.5 mmol/L. These results show that the inhibitory effect of one of the solutes on the other depends on the initial concentration in the mixture, which is in agreement with the findings reported in the literature [10, 11]

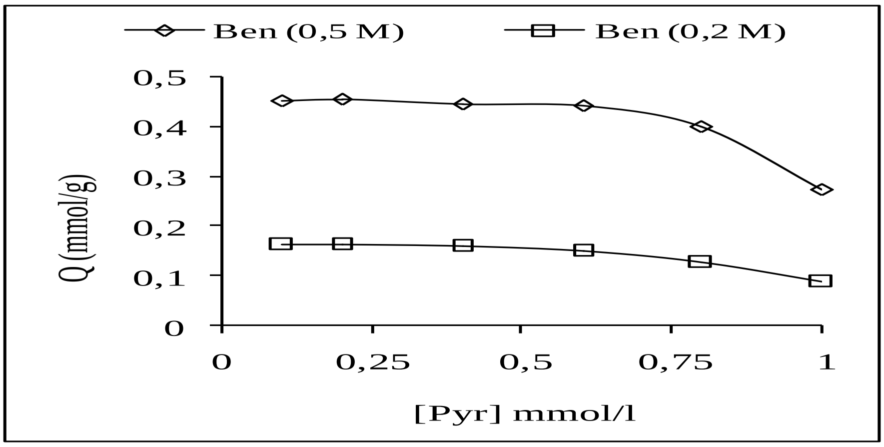


Figure 6: Amount adsorbed of benzoic (Ben) acid as a function of pyromellitic (Pyr) acid concentration. **Pyr**: pyromellitic acid adsorption or benzene-1,2,4,5-tetracarboxylic acid. **Ben** : benzoic acid.

When studying the adsorption of mixtures of two compounds, this latter are capable of binding to the same sites or specific sites for each of the molecules or as a mixed mode with a variable proportion. In the case of fixing two solutes on identical sites (hydrophobic sites for example), each of them will face the competition of the other. In our case, we can explain the results as follows:

- A low concentrations of adsorbates, each solute is adsorbed on specific sites
- with high concentration of adsorbates, the number of sites available for adsorption decreases, and the two solutes adsorb on the same sites.

5. CONCLUSION

In this study, we examined the adsorption of Pyr acid on granular activated carbon (GAC) in the presence of Ben acid. With the coming of this study, we showed that the adsorption kinetics of this material in its granular form is very slow (20 hours). However, this equilibrium time is reduced to 30 minutes after grinding the activated carbon.

The results show also that the adsorption follows Freundlich model. The adsorbed amounts of pyromellitic acid are slightly reduced by the presence of benzoic acid in low concentrations. However, high concentrations strongly disfavor the adsorption of acidic examined. This shows the importance of competition on the adsorption phenomenon for both examined acids.

6. REFERENCES

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