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# Purification of sugar beet vinasse – Adsorption of polyphenolic and dark colored compounds on different commercial activated carbons

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## Abstract

The adsorption on activated carbons of dark colored compounds contained in sugar beet vinasse was studied. Four commercial activated carbons with different properties (particle size, residual acidity and microporous properties) were respectively checked for efficiency at two temperature levels (25 °C and 40 °C) and at four pH levels (2, 3.5, 7, 10). The adsorption of organic molecules was determined by quantifying the amounts of total polyphenolic compounds and total organic carbon. The results showed that the adsorption capacity of dark colored compounds was enhanced by the decrease in both temperature and pH values of the solution. In this study, it is shown that this capacity depends on activated carbon characteristics which can be classified in the following order: particle size > residual acidity > microporous volume. Three models (Langmuir, Freundlich and Dubinin–Radushkevich) were tested from experimental data and compared. The Langmuir model provided the best correlation on all the activated carbons studied.

*Keywords:* Activated carbons; Adsorption; Vinasse; Polyphenolic compounds; Total organic carbon

## 1. Introduction

Sugar beet vinasse, a residue produced during the manufacturing of ethyl alcohol, is generally used as an additive for animal feed and as a fertilizer, but demand may be limited by strict environmental restrictions. Therefore, it has become of increasing interest to recover valuable components from distillery vinasse. For example, sugar beet vinasse dry matter contains around 15% of betaine (Caqueret, 2006). This compound possesses amphoteric surfactant properties which allow current industrial applications in toiletries and personal care products. The literature reports that betaine recovery is made by ion exchange (Giacobello et al., 2000; Heikkilä et al., 1999), with strong cationic ion exchange resins. However, before obtaining pure betaine from a natural

substrate like sugar beet vinasse, several operations of pretreatment need to be applied (Caqueret, 2006). Indeed, betaine is mixed with other molecules that damage the resin and reduce its properties (Zagonodni et al., 2002).

A multi-stage process for pure betaine recovery from vinasse was perfected in our laboratory (Caqueret, 2006) and it was shown that betaine was conveniently isolated in three steps: (i) removal of most insoluble compounds from the ethanolic medium, (ii) separation of most polyphenolic and other colored compounds, and (iii) purification of the betaine by ion exchange. In the second stage, it is difficult to remove the polyphenolic and colored compounds by oxidation with classic biological treatments and an adsorption process could be a good alternative to remove these compounds from agro-industrial residues (Ahmedna et al., 2000; Arslanoğlu et al., 2005; Bansode et al., 2004; Caqueret, 2006; Figaro et al., 2006; Garcia-Araya et al., 2003; Pendyal et al., 1999; Satyawali and Balakrishnan, 2007).

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The purpose of this study was to find the best conditions for the discoloration of distillery vinasse by adsorption on activated carbons (ACs). To this aim, it was necessary to determine: (i) the main properties of the four commercial ACs used, (ii) the respective effects of temperature and solution pH on the removing of total polyphenolic compounds (TPP) first and then of total organic compounds (TOC), and (iii) the best adsorption model (Langmuir, Freundlich or Dubinin–Radushkevich (D–R)) that allows to estimate the ACs adsorption capacity and to determine the isotherm parameters.

## 2. Experimental

### 2.1. Characteristics of the distillery vinasse

The sample of distillery vinasse was supplied by a sugar refinery (La Vermandoise, Toury, France). The vinasse was first treated with ethanol in order to remove most of the proteins, pectins and other insoluble compounds (Caqueret, 2006). The content in protein ( $0.51 \text{ g kg}^{-1}$  vinasse) was determined with the Bradford method by using a UV/Vis spectrophotometer (Jasco V-530). The determination of the pectins contents ( $24.50 \text{ g kg}^{-1}$  vinasse) was carried out by “Laboratoire des Biopolymères Interactions Assemblages” (INRA Nantes, France) and the betaine content ( $204.20 \text{ g kg}^{-1}$  vinasse) was determined by high pressure liquid chromatography (HPLC) (Zamarreno et al., 1997). The total organic carbon content ( $376.70 \text{ gC kg}^{-1}$  vinasse) was determined by a TOC analyzer (Shimadzu TOC-V<sub>C<sub>SH</sub></sub>). The Folin–Ciocalteu method was used to estimate the amount of TPP within the vinasse. A calibration curve, obtained from caffeic acid with a spectrophotometer (Jasco V-530), gives the TPP content in equivalent caffeic acid ( $13.51 \text{ g}_{\text{eq}} \text{ kg}^{-1}$  vinasse). Systematically for all the experiments, TPP and TOC contents were determined before and after adsorption.

### 2.2. Characterization of the activated carbons

Three of the commercial ACs used (Picachem 150, 120P and 120PN) were supplied by Pica (Vierzon, France) and the fourth (CXA) by Ceca (Parentis, France). These ACs were used as received from the supplier without further treatment. The porosity of these ACs was characterized through conventional nitrogen adsorption isotherm at  $-196 \text{ }^\circ\text{C}$  (77 K) by Promes (UPR 8521, Perpignan, France) using a Micromeritics ASAP 2000 M. The samples were previously degassed at  $250 \text{ }^\circ\text{C}$  for 24 h under a residual vacuum of less than  $10^{-4}$  Pa. The nitrogen adsorption isotherms were analyzed according to the Dubinin theory (Stoeckli, 1996). Both the specific microporous volume ( $W_0$  in  $\text{cm}^3 \text{ g}^{-1}$ ) and the mean pore size ( $L_0$  in nm) were estimated from the linear part of the Dubinin–Radushkevich (D–R) plot (Stoeckli, 1996; Stoeckli et al., 2001). Besides, the Sing  $\alpha_s$  plots (Sing et al., 1985) were used to determine the external specific surface ( $S_{\text{ext}}$  in  $\text{m}^2 \text{ g}^{-1}$ )

and assuming that for slit-shaped micropores the specific surface of micropores ( $S_{\text{micro}}$  in  $\text{m}^2 \text{ g}^{-1}$ ) could be estimated using the specific microporous volume and the mean pore size (Stoeckli, 1996).

### 2.3. Adsorption isotherms and analysis

All the isotherms were carried out with TOC initial concentrations expressed in  $\text{gC L}^{-1}$  ranging from  $7.5$  to  $113 \text{ gC L}^{-1}$  for TOC and  $0.27$  to  $4.4 \text{ g}_{\text{eq}} \text{ L}^{-1}$  for TPP concentrations, which correspond to dilution factors ranging from 3 to 50 with deionised water. The adsorption isotherm experiments were carried out by adding 4 g of AC to 200 mL of the sorbate solution for different TOC concentrations, under mechanical stirring at 150 rpm, in a thermostated multi-agitation apparatus (Vankel Vanderkamp 600).

It was first verified that the adsorption equilibria at  $25 \text{ }^\circ\text{C}$  were reached in less than 3 h for TOC and TPP adsorptions for all the ACs used (Caqueret, 2006). The results presented in Fig. 1 shows that the TOC adsorption capacity becomes stable after a contact time of 150 min for Picachem 150, 120 min for Picachem 120PN, 100 min for Picachem 120P and 60 min for Acticarbone CXA. Thus, a contact time of 180 min was chosen for all the experiments. Moreover, it was proved that hardly any betaine was adsorbed on ACs ( $<1\%$ ) in these experimental conditions (Caqueret, 2006). At the end of the contact time, the reactor medium was filtered through a  $0.45 \mu\text{m}$  membrane filter. The TOC content of the liquid-phase was analysed by Shimadzu TOC-V<sub>C<sub>SH</sub></sub> and the total phenolic compounds content was determined with the Folin–Ciocalteu method. For all four ACs, two adsorption temperatures were studied ( $25 \text{ }^\circ\text{C}$  and  $40 \text{ }^\circ\text{C}$ ) and the influence of pH was checked on the neutral AC (120PN), by adding HCl (37 wt%) or NaOH (2.5 M) until the expected pH was reached.

### 2.4. Isotherms models

It is well known that the Langmuir equation is used for a monolayer adsorption (Langmuir, 1918). The linear

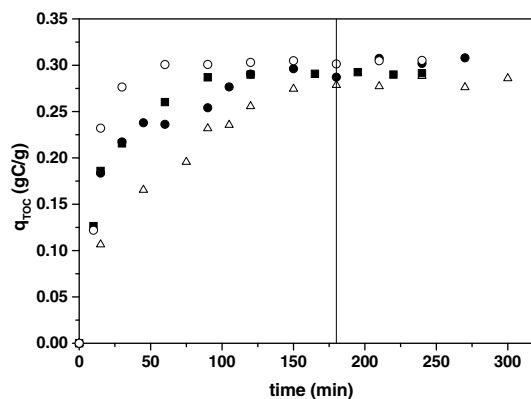


Fig. 1. Evolution of TOC adsorption in sugar beet vinasse as a function of the contact time for the different ACs used in the process at  $25 \text{ }^\circ\text{C}$  (150 (△), 120PN (●), 120P (■) and CXA (○)).

Langmuir equation allows to determine the maximum amount of adsorption corresponding to complete monolayer coverage ( $q_m$  in  $\text{g}_{\text{eq}} \text{g}^{-1}$  for the TPP or  $\text{gC g}^{-1}$  for the TOC):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \quad (1)$$

where  $C_e$  is the equilibrium concentration ( $\text{g}_{\text{eq}} \text{L}^{-1}$  for the TPP or  $\text{gC L}^{-1}$  for the TOC),  $q_e$  is the TPP or TOC adsorbed amount at equilibrium ( $\text{g}_{\text{eq}} \text{g}^{-1}$  or  $\text{gC g}^{-1}$ ) and  $b$  is the Langmuir constant ( $\text{L g}^{-1}$ ). The values of  $q_m$  and  $b$  can be determined from the linear plot of  $C_e/q_e$  versus  $C_e$  from the slope and the intercept respectively.

The empirical Freundlich model can be represented as follows (Freundlich, 1928) but provides no information on the monolayer adsorption capacity:

$$q_e = K \times C_e^{1/n} \quad (2)$$

where  $K$  (dimensionless) is a Freundlich constant that is taken as an indicator of adsorption capacity and  $1/n$  (dimensionless) is an empirical constant which can be related to the adsorption intensity i.e. the affinity of the molecule with the ACs. The values of  $1/n$  and  $K$  can be obtained from the linear plot of  $\log q_e$  versus  $\log C_e$  from the slope and the intercept respectively.

In the case of liquid-phase adsorption, several studies have shown that the adsorption energy could be estimated according to the Dubinin–Radushkevich equation (D–R) (Dubinin and Radushkevich, 1947):

$$q_e = q'_m \exp \left[ -B \left( RT \ln \left( 1 + \frac{1}{C_e} \right) \right)^2 \right] \quad (3)$$

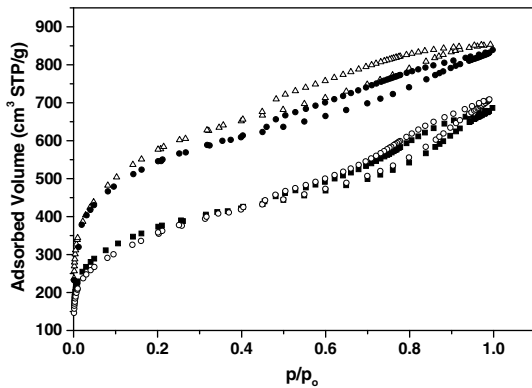


Fig. 2.  $\text{N}_2$  adsorption–desorption isotherms at 77 K ( $-196^\circ\text{C}$ ) of the four activated carbons used (150 ( $\Delta$ ), 120PN ( $\bullet$ ), 120P ( $\blacksquare$ ) and CXA ( $\circ$ )).

where  $q'_m$  ( $\text{g}_{\text{eq}} \text{g}^{-1}$  for the TPP or  $\text{gC g}^{-1}$  for the TOC) is the D–R monolayer adsorption capacity,  $B$  (in  $\text{mol}^2 \text{J}^{-2}$ ) a constant related to the most probable energy of adsorption  $E$  ( $\text{J mol}^{-1}$ ) ( $E = (2B)^{-1/2}$ ),  $R$  the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  the absolute temperature (K). The D–R isotherm constants ( $q'_m$  and  $B$ ) were determined from the linear plots of  $\ln q_e$  versus  $\varepsilon^2$  where  $\varepsilon = RT \ln(1 + \frac{1}{C_e})$ . This linear form of D–R equation allows to determine the values of  $q'_m$  and  $B$  from the intercept and the slope respectively.

### 3. Results and discussion

#### 3.1. Characteristics of the activated carbons

The  $\text{N}_2$  adsorption–desorption isotherms for the four ACs used are presented in Fig. 2 which shows the volume of nitrogen adsorbed (in  $\text{cm}^3 \text{g}^{-1}$ ) in standard conditions of temperature and pressure versus the relative pressure. The ACs used were microporous but they also contained some mesopores as indicated by the shape and the hysteresis loop of the  $\text{N}_2$  isotherms. The isotherm shapes were practically identical for a first couple of ACs (150 and 120PN), and for a second one (120P and CXA). According to Sing et al. (1985), this reveals that the two members of each couple seem to have the same micropores geometrical shape.

The porous properties of the ACs are presented in Table 1. The 150 one is a granular AC whereas the others are in powder form and have the same granulometry. The 150 and 120P ones have a residual acidity due to their activation treatments whereas the 120PN and CXA ones are neutral. As shown in Table 1, the 150 and 120PN ACs exhibit the most important specific microporous volumes ( $W_0$ ) and specific surface of micropores ( $S_{\text{micro}}$ ), with respective values of  $0.72 \text{ cm}^3 \text{g}^{-1}$  and  $543 \text{ m}^2 \text{g}^{-1}$  for the 150 one and  $0.62 \text{ cm}^3 \text{g}^{-1}$  and  $667 \text{ m}^2 \text{g}^{-1}$  for the 120PN one. Nevertheless, the application of the D–R equation is limited to slit-shaped micropores with a value inferior to  $2.50 \text{ nm} \pm 0.05\text{--}0.07 \text{ nm}$  (Stoekli et al., 2001). Thus, the 150 AC, with a  $L_0$  value of  $2.65 \text{ nm}$ , seems to present an over-estimated specific microporous volume. The  $W_0$  exhibited by the 120P and CXA ACs are similar to but lower than those of the two other ACs with respective values of  $0.47$  and  $0.43 \text{ cm}^3 \text{g}^{-1}$  with relatively broad mean pore sizes (respectively  $2.29$  and  $2.51 \text{ nm}$ ).

By comparing their isotherms and their porous properties (in particular microporous volume, microporous surface and external surface), the ACs can be classified by

Table 1  
Textural properties of the commercial activated carbons used

Activated carbons	Nature	Type	$W_0$ ( $\text{cm}^3 \text{g}^{-1}$ )	$L_0$ (nm)	$S_{\text{micro}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$S_{\text{ext}}$ ( $\text{m}^2 \text{g}^{-1}$ )
Pica 150	Acidic	Granular	0.72	2.65	543	671
Pica 120PN	Neutral	Powder	0.62	1.86	667	634
Pica 120P	Acidic	Powder	0.47	2.29	410	517
Ceca CXA	Neutral	Powder	0.43	2.51	343	606

couples: (i) the 150 and 120PN ACs presenting however differences in particle sizes and residual acidity and (ii) the 120P and CXA ones differing in residual acidity.

### 3.2. Effect of temperature and activated carbon characteristics on adsorption

#### 3.2.1. Adsorption of total phenolic compounds on ACs

The experiments were carried out at 25 °C and 40 °C in order to study the influence of temperature on TPP adsorption. The pH value was fixed at 3.5, corresponding to the pH value of the solution obtained from vinasse after ethanol treatment. Fig. 3 shows the adsorption isotherms and these ones have an asymptotic line characteristic of a monolayer adsorption. In the case of the TPP adsorption at 25 °C (Fig. 3a): (i) the 120P AC (acidic, powdered) has a better adsorption capacity than the CXA one (neutral, powdered) although they have almost the same specific microporous volume (respectively 0.47 and 0.43 cm<sup>3</sup> g<sup>-1</sup>), (ii) the 120P one (acidic, powdered) and the 120PN one (neutral, powdered) have about the same particle size but a different  $W_0$  (respectively 0.47 and 0.62 cm<sup>3</sup> g<sup>-1</sup>) however the 120P one adsorbs more than the 120PN AC, (iii) the 120P one has a smaller value of specific microporous volume than the 150 one (acidic, granular) (respectively 0.47 and 0.72 cm<sup>3</sup> g<sup>-1</sup>) but has a more important adsorption capacity and (iv) the 120PN AC (neutral, powdered) adsorbs more TPP than the 150 one (acidic, granular) with comparable specific microporous volumes. These comments allow us to establish a classification of the characteristics of the ACs relative to the adsorption at 25 °C of the polyphenolic compounds contained in the solution. It seems that the efficiency of the process is particularly influenced by the particle size of the solid (granular or powdered), then by the residual acidity and finally by the specific microporous volume.

The same specific shapes of TPP adsorption isotherms at 40 °C are displayed in Fig. 3b. This figure shows that an increase in temperature induces a decrease in efficiency of TPP adsorption on ACs, which confirms the fact that

TPP adsorption is an exothermic process in this case. However, the influence of temperature is different according to the activated carbon used. The most important decrease in adsorption capacity (55%) due to the increase in temperature is observed for the 120P AC to be compared with 26% for the CXA AC, 15% for the 120PN one and only 7% for the 150 one. These values reveal that temperature is less influential for the 150 one than for the other adsorbents and this can be explained by two antagonistic effects. Indeed, adsorption (being an exothermic process) is favored by a decrease in temperature whereas diffusion (being a kinetic phenomenon) is favored by an increase in temperature. Therefore the thermodynamic effect is counterbalanced by the kinetic effect, which seems to show that a contact time of three hours is insufficient for 150 AC at 40 °C. Therefore, the experimental results allow to assume that the efficiency of the ACs, for TPP adsorption, might be classified according to their characteristics in this adsorption process i.e.: particle size > residual acidity > specific microporous volume, and adsorption at 25 °C is more efficient than at 40 °C.

#### 3.2.2. Adsorption of total organic carbon on ACs

The same isotherms were analyzed in order to express the TOC adsorption starting from the solution obtained from vinasse after ethanol treatment (Fig. 4). Fig. 4a shows the adsorption isotherms obtained at 25 °C. It is well known that adsorption is mainly carried out in micropores but the isotherm shapes which do not present a strict plate, suggest that adsorption could also be carried out in larger pores as well as on the external surface (Giles et al., 1974). The maximum of adsorption capacity is almost identical for the 120PN, CXA and 120P ACs (approximately 0.40 gC g<sup>-1</sup>) and slightly weaker for the 150 one (approximately 0.30 gC g<sup>-1</sup>).

Besides, when the temperature is set at 40 °C (Fig. 4b), the tendency is reversed and the 150 AC becomes the most efficient (0.25 gC g<sup>-1</sup>) with nevertheless a drop of 0.05 gC g<sup>-1</sup> in efficiency. As noticed for TPP adsorption, the decrease in adsorption capacity confirms the fact that adsorption is

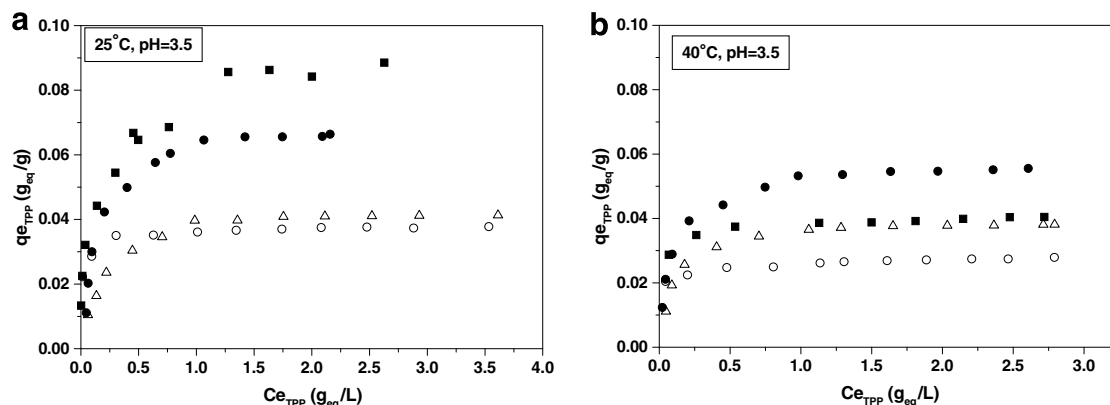


Fig. 3. Influence of temperature on TPP adsorption isotherms at pH = 3.5 on the four activated carbons used at (a) 25 °C and (b) 40 °C (150 (Δ), 120PN (●), 120P (■) and CXA (○)).

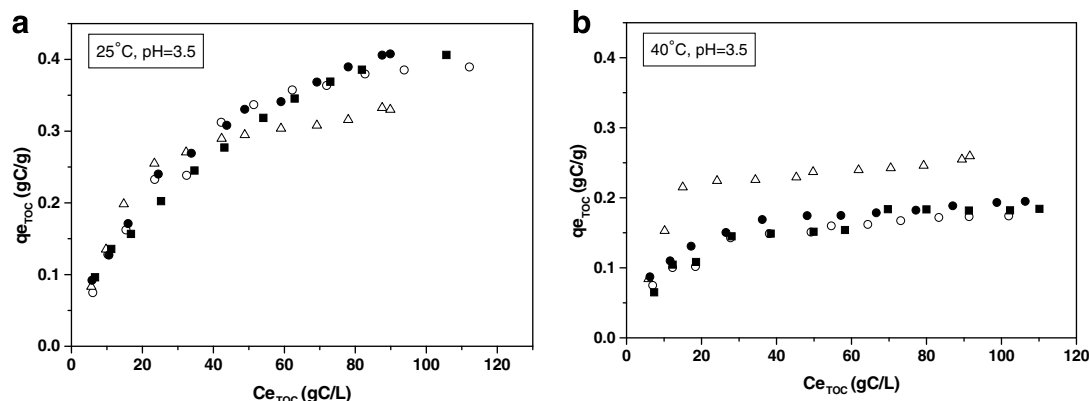


Fig. 4. Influence of temperature on TOC adsorption isotherms at pH = 3.5 on the four activated carbons used at (a) 25 °C and (b) 40 °C (150 ( $\Delta$ ), 120PN ( $\bullet$ ), 120P ( $\blacksquare$ ) and CXA ( $\circ$ )).

an exothermic process favored by low temperatures. But the effect of temperature is more important on the 120P, 120PN and CXA ACs, it leads to a 55% decrease in their adsorption capacity against only 22% for the 150 one. This difference could be explained by a better coefficient of mass transfer in the case of the 150 AC at this temperature as seen previously in the case of TPP adsorption. Moreover, at 40 °C, the isotherms show curves, characteristic of a monolayer adsorption, with asymptotic lines at 0.2 gC g<sup>-1</sup> for the 150 AC and at around 0.15 gC g<sup>-1</sup> for the others. Therefore, adsorption of total organic compounds must be carried out at low temperature (25 °C or below) and is more efficient on ACs in powder form. Besides, residual acidity and microporous volume seem to be less influential than particle size for these materials. Thus, the most effective AC in these experimental conditions is the Picachem 120P.

### 3.3. Effect of pH solution on the adsorption

The pH value of the solution influences the mechanisms of adsorption and interactions between adsorbate and adsorbent. Indeed, the pH value modifies not only the nature of the acidic organic functions of the molecules, but also the protonation of the activated carbon sites. Therefore, the effect of pH on the efficiency of TPP and TOC

adsorptions were studied, at 25 °C on the 120PN AC, the most efficient one without residual acidity. As shown in Fig. 5, adsorption of organic compounds (Fig. 5b) and mostly that of polyphenolic compounds (Fig. 5a) are strongly dependent on pH values; the more acidic the pH is, the more efficient adsorption is. According to Qi et al. (2004), the decrease in adsorption capacity in the basic pH range (7–10) can be due to a deprotonation of (i) the activated carbon acidic functional groups (ii) and of the carboxylated molecules present in the solution like phenolic acids. At higher pH values, the electrostatic interactions are maximal and involve forces of repulsion between the dissociated molecules and the activated carbon surface functional groups. These repulsion forces may prevent the specific interactions of the molecules with the active sites on the carbon surface, especially the hydrogen bondings.

Fig. 5 also shows that the pH is more influential with TPP adsorption than with TOC. In addition, the effect is maximum when pH values are set between 2 and 3.5 for both TPP and TOC adsorptions. Indeed, the proportion of acidic functions in organic compounds is lower in TOC than in polyphenolic compounds. That could be explained by the weaker influence of pH in the case of TOC. The relation between pH and adsorption capacities

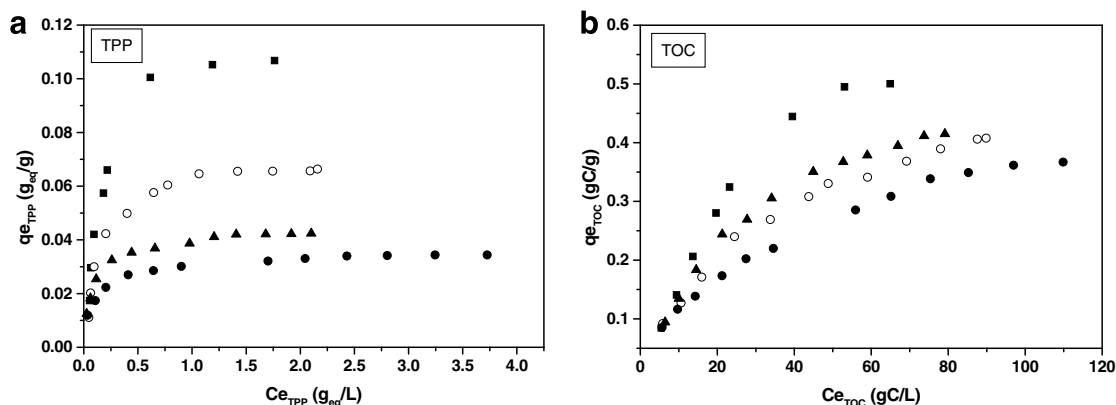


Fig. 5. Influence of pH on adsorption isotherms of 120PN (25 °C) for TPP (a) and TOC (b) (pH = 2 ( $\blacksquare$ ), pH = 3.5 ( $\circ$ ), pH = 7 ( $\blacktriangle$ ) and pH = 10 ( $\bullet$ )).

can be modelled by the plot of adsorption capacity versus pH (figures not shown) that leads to Eqs. (4) and (5) respectively for TPP and TOC:

$$q_{e\text{TPP}} = 0.1675 \times \text{pH}^{-0.7002} \quad (4)$$

where  $q_{e\text{TPP}}$  is the TPP amount adsorbed at equilibrium ( $\text{g}_{\text{eq}} \text{g}^{-1}$ ) and with a regression coefficient of 0.993, and

$$q_{e\text{TOC}} = 0.5392 \times \text{pH}^{-0.1608} \quad (5)$$

where  $q_{e\text{TOC}}$  is the TOC amount adsorbed at equilibrium ( $\text{gC g}^{-1}$ ) and with a coefficient of regression of 0.810.

The better regression coefficients obtained with TPP are due to the fact that this family is clearly defined whereas TOC includes several families of compounds, with or without acidic functions. In conclusion, the adsorption on

120PN AC of TOC and TPP contained in vinasse must be carried out at 25 °C and at a low pH value.

### 3.4. Models

In order to establish the mechanism of adsorption and to determine the isotherm parameters, several equilibrium adsorption isotherm models, (Langmuir, Freundlich and Dubinin–Radushkevich (D–R) equations), were compared and the results are shown in Table 2 for TPP adsorption and in Table 3 for TOC adsorption.

Fig. 6 shows the comparison of the three models with experimental results for 120P and 120PN ACs (the models for the other ACs show the same tendency and are not represented in this figure). For TPP adsorption, the Langmuir

Table 2  
Langmuir, Freundlich and D–R isotherm parameters for TPP adsorption on the activated carbons used at 25 °C

Activated carbons	pH	$q_{\text{max,exp}}$ ( $\text{g}_{\text{eq}} \text{g}^{-1}$ )	Langmuir			Freundlich			D–R		
			$q_m$ ( $\text{g}_{\text{eq}} \text{g}^{-1}$ )	$b$ ( $\text{L g}_{\text{eq}}^{-1}$ )	$R^2$	$K$	$1/n$	$R^2$	$q'_m$ ( $\text{g}_{\text{eq}} \text{g}^{-1}$ )	$E$ ( $\text{J mol}^{-1}$ )	$R^2$
150	3.5	0.041	0.044	5.62	0.999	0.033	0.3211	0.888	0.041	4146	0.986
120PN	2	0.107	0.122	4.82	0.992	0.105	0.4607	0.860	0.116	4002	0.970
	3.5	0.066	0.072	6.08	0.998	0.059	0.3831	0.856	0.064	4495	0.985
	7	0.042	0.044	10.39	0.999	0.039	0.2590	0.931	0.042	6000	0.991
10	0.034	0.036	7.86	0.999	0.029	0.2133	0.931	0.033	5918	0.965	
120P	3.5	0.089	0.090	8.05	0.993	0.075	0.2776	0.989	0.077	7951	0.914
CXA	3.5	0.038	0.038	28.81	0.999	0.035	0.0923	0.920	0.037	10,262	0.911

Table 3  
Langmuir, Freundlich and D–R isotherm parameters for TOC adsorption on the activated carbons used at 25 °C

Activated carbons	pH	$q_{\text{max,exp}}$ ( $\text{gC g}^{-1}$ )	Langmuir			Freundlich			D–R		
			$q_m$ ( $\text{gC g}^{-1}$ )	$b$ ( $\text{L gC}^{-1}$ )	$R^2$	$1/n$	$K$	$R^2$	$q'_m$ ( $\text{gC g}^{-1}$ )	$E$ ( $\text{J mol}^{-1}$ )	$R^2$
150	3.5	0.330	0.390	0.061	0.999	0.4393	0.051	0.891	0.296	243	0.911
120PN	2	0.500	0.930	0.021	0.949	0.7314	0.028	0.965	0.385	224	0.823
	3.5	0.408	0.556	0.029	0.995	0.5453	0.037	0.985	0.370	230	0.767
	7	0.415	0.590	0.031	0.998	0.5733	0.037	0.972	0.344	217	0.839
10	0.367	0.481	0.029	0.987	0.5047	0.037	0.996	0.272	254	0.672	
120P	3.5	0.406	0.557	0.025	0.984	0.5419	0.035	0.993	0.301	222	0.714
CXA	3.5	0.389	0.518	0.031	0.989	0.5530	0.034	0.950	0.320	209	0.823

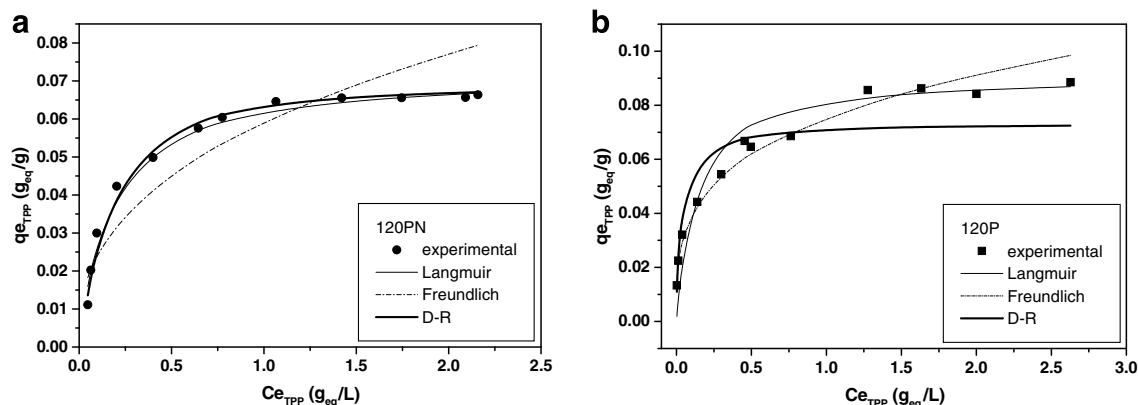


Fig. 6. TPP experimental isotherms (symbols) and predictive isotherms by Langmuir, Freundlich and D–R models (lines) at 25 °C and pH = 3.5 (120PN (a) and 120P (b)).

model was successfully applied for all the activated carbons used under all the experimental conditions. The correlation coefficient is always above 0.99 (Table 2) and then the Langmuir isotherm model provides good fits for TPP adsorption on the four ACs (Fig. 6). These results confirm that TPP adsorption is carried out mainly in a molecular monolayer and are in agreement with the shapes of the isotherms represented in Fig 3a.

The Freundlich model presents the worst values of coefficients of correlation with TPP (Table 2) and cannot be applied as shown on Fig. 6.

The D–R model was successfully applied for TPP adsorption on 120PN (Fig. 6) and 150 (not shown) ACs with correlation coefficients higher than 0.97 (Table 2). These results confirm that the adsorption of polyphenolic molecules within the vinasse is carried out mainly in a molecular monolayer. The D–R model allows to estimate the adsorption energy of the system. The calculated adsorption energies are practically similar for the 150 and 120PN ACs (Table 2), 4146 and 4495 J mol<sup>-1</sup> respectively, that present the same shape of N<sub>2</sub> isotherm at 77 K (Fig. 2). Besides, the calculated energy values are higher for the 120P and the CXA ACs (Table 2), 7951 and 10,262 J mol<sup>-1</sup> respectively, that also present the same shape of N<sub>2</sub> isotherm at 77 K. Thus, this adsorption energy could be closely related to the structure of the activated carbon and seems to be independent of the activated carbon adsorption capacity.

The results obtained for TOC adsorption at 25 °C and at a pH value 3.5 shows that the Langmuir model presents the best coefficients of correlation (generally above 0.98) (Table 3). The monolayer adsorption capacity calculated from this model confirms the results experimentally obtained: (i) 120P and 120PN are the best ACs at pH 3.5 and 25 °C ( $q_m \sim 0.56 \text{ gC g}^{-1}$ ) and (ii) the capacity is enhanced to 0.93 gC g<sup>-1</sup> when the pH is reduced to 2. Nevertheless, it is important to notice that the Langmuir model values ( $q_m$ ) of the monolayer adsorption capacities are always much higher than the experimental ones ( $q_{\text{max,exp}}$ ). That is probably due to the fact that the monolayer adsorption does not fill all the active sites of the ACs. Therefore the TOC adsorption isotherms do not present the plate of saturation (Figs. 4 and 5b) typical of a monolayer adsorption mechanism. Moreover, the vinasse used in this study contains several families of molecules and it is possible that the interactions between all these molecules limit the adsorption. Indeed, these different families of compounds are betaine, polyphenolic compounds, pectins, proteins but also other colored compounds like melanoidins, by-products of alkaline degradation and caramels. Apart from betaine and polyphenolic compounds, these molecules have high molecular weights. This could be the reason why the calculated monolayer adsorption capacity is over-estimated in this case. The Freundlich model does not generally present such good values of coefficients of correlation; it is particularly true for the 150 AC. All the values of the coefficient  $1/n$  are in agreement with the isotherms of Figs. 4 and 5b. The values of the coefficient

$1/n$  are practically similar (close to 0.55) for the 120PN, 120P and CXA ACs at pH 3.5. That means that they exhibit approximately the same affinity for TOC. Moreover, these values decrease for the 120PN activated carbon when the pH value increases. However the anomaly observed in Fig. 5b (inversion of tendency of pH influence for pH 3.5 and 7.0) is confirmed in Table 3 for both 7.0 and 3.5 pH values. Thus, the Freundlich isotherms is better adapted when dealing with TOC adsorption (coefficient generally included between 0.95 and 0.99 (Table 3)) than when dealing with TPP model building (coefficient of determination generally included between 0.86 and 0.93 (Table 2)). Indeed, that confirms that it is better to use the Freundlich isotherms for non ideal systems like those represented by measured TOC of multi-component systems.

The D–R model values of the monolayer adsorption capacities of TOC are always lower than the experimental values of the maximal quantities adsorbed but the D–R model has coefficients of correlation inferior to 0.9 (except for the 150 AC) and cannot be applied in this case.

Finally, the experimental data obtained for TPP adsorption fitted well the Langmuir and D–R models, whereas TOC adsorption fitted well only the Langmuir one. These models are well known to describe the adsorption of mono-component systems. Nevertheless, we have shown in this study that they can also be successfully applied in the case of sugar beet vinasse which contains several types of molecules. Our results confirm similar ones obtained by other authors who used these models with multi-component systems from other substrates (Arslanoğlu et al., 2005; Bansode et al., 2004; Satyawali and Balakrishnan, 2007).

#### 4. Conclusions

This study shows clearly that both TPP and TOC adsorptions on ACs must be carried out at low temperature (25 °C or below) at the lowest pH value; ACs in powdered form are more suitable in term of efficiency. Besides, residual acidity and microporous volume of adsorbents seem to be less influential than AC particle type (granular or powdered form) for the molecules adsorbed. The AC characteristics which favor TPP adsorption at 25 °C can be classified in the following order: particle size, residual acidity, microporous volume. Moreover, the adsorption of organic compounds and particularly that of polyphenolic compounds are strongly dependent on pH values. The proportion of acidic functions in organic compounds is lower in TOC than in polyphenolic compounds. Thus the most effective AC in these experimental conditions is the Picachem 120P. The experimental results were then compared by checking with the models of Langmuir, Freundlich and Dubinin–Radushkevich. The Langmuir one is the adsorption model that allows best to describe the adsorption isotherms and determine the isotherm parameters for both TOC and TPP adsorptions. However, the results are better correlated for the TPP adsorption. Indeed, TPP are a well-defined family of molecules whereas the compounds taken



into account in the TOC content include several families of products. Nevertheless, this high correlation coefficient should mean that the monolayer mechanism or the Langmuir model could also apply to the adsorption of TOC (several families of molecules). However, in the case of TOC which is a measure of several families of molecules, it is more delicate to apply this monolayer mechanism as the values of regression coefficients are weaker. In addition, the monolayer adsorption mechanism in accordance with the Langmuir correlation was confirmed by D-R model. The adsorption process on ACs is thus a good alternative to remove polyphenolic compounds and other organic ones from sugar beet vinasse. This purification step is required to protect the ionic-exchange resins that will be used in the further step of betaine purification. Indeed, this adsorption on ACs permits to remove the colored compounds from the solution and to avoid the alteration of ionic-exchange resins where these compounds are irreversibly adsorbed during the further process.

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