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ARGENTINIAN SUGAR CANE VINASSE: CHARACTERIZATION OF PHENOLIC COMPOUNDS AND EVALUATION OF ADSORPTION AS A POSSIBLE REMEDIATION TECHNIQUE

***Maricel Caputo*[1, 2], *Francisca Aparicio*[3], *Sergio Laurella*[1, ✉],**
***Marнa de las Mercedes Schiavoni*[1]**

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Abstract. Chemical composition of sugar cane vinasse (Tucumán, Argentina) was studied finding high concentration of organic compounds. Phenolic compounds were partially characterized, finding mostly flavonoids, anthocyanins, as well as resorcinol and ferulic acid derivatives. Adsorption isotherms of phenolic compounds and total organic compounds were measured on four commercial activated carbons with different physical and chemical properties at two temperatures. The isotherm shape depends on the type of carbon and the adsorption capacity is enhanced as temperature increases. Enthalpies of the adsorption process were estimated, revealing that the adsorption of organic compounds is a chemisorption process, while the adsorption of phenolic compounds is a physisorption process on three of the tested carbons and a chemisorption process on the other one (CONCARBO).

Keywords: vinasse, adsorption, phenolic compounds, remediation.

1. Introduction

Every year sugar refineries in Argentina (settled mainly in the Province of Tucumán) produce great quantities of vinasse, a liquid residue obtained from the distillation of the alcoholic fermentation of sugar cane. The total production of this residue surpasses two billion liters per year, 13 l per litter of distilled ethanol. Taking into account its polluting effects, it is necessary to pretreat this liquid before pouring it into the rivers (which is not a common practice among the sugar refineries). Vinasse is an organic liquid material that might contain substances proceeding from the extraction and fermentation processes as impurities.[1]

Its pH is moderately acid and it has a biochemical oxygen demand (BOD) ranging from 70 to 80 g/L. It is typically composed of 93 % of water, 2 % of inorganic substances (containing principally potassium, calcium, sulfate, chloride, nitrogen, phosphorus, *etc.*) and 5 % of organic compounds (that are volatilized when heating over 923 K). This effluent also contains a high proportion of phenolic compounds and flavonoids, which contribute with 33 % of its chemical oxygen demand.

The studies carried out on sugarcane vinasse have shown that it is a highly corrosive and polluting waste of water, which presents in its chemical composition high contents of organic matter, potassium and calcium, as well as moderate amounts of nitrogen and phosphorus.[2,3] However, the chemical composition of vinasse depends on the raw material being used, the climatic conditions, the soil and the alcohol production process.[4] Several works have reported the physico-chemical characteristics of different types of vinasse, obtained from grapes, beets, sugar cane, and fruits (pears and apples), produced in different distilleries.[5-7]

Several remediation treatments have been so far studied for reduction of the polluting effects of vinasse, such as combustion, microbiological processes (using aerobic and anaerobic bacteria), coagulant treatments and utilization of semipermeable membranes.[8-13]

Adsorption has also been proposed as a pretreatment for vinasse and has proved successful in drawing organic matter off the liquid using activated carbon as an adsorbent.[14-17]

The purpose of the present study is to compare the adsorption characteristics of vinasse and individual

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[1] CEDECOR (Centro de Estudio de Compuestos Orgánicos),
Facultad de Ciencias Exactas, Universidad Nacional de La Plata (UNLP),
Calle 115 y 47, (1900) La Plata, Argentina
[2] CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas), Argentina
[3] Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA),
Departamento de Química, Facultad de Ciencias Exactas,
Universidad Nacional de la Plata,
CONICET. Diag 113 y 64, La Plata (1900), Argentina
✉ *sllaurella@quimica.unlp.edu.ar*

compounds contained in it (phenolic compounds, flavonoids, *etc.*) on four commercial activated carbons. For this aim,[18-20] it is necessary: (i) to carry out a physico-chemical characterization of the solution; (ii) to compare the main properties of the four commercial activated carbons being used; (iii) to study the adsorption isotherms of some selected compounds (in this case, total organic carbon and total phenolic compounds), regard specially the effects of temperature on the processes; (iv) to find the best adsorption model (Langmuir, Freundlich, *etc.*) that allows to estimate each activated carbon adsorption capacity and to determine the isotherm parameters, and (v) to carry out a desorption study.

2. Experimental

2.1. Characteristics of the Distillery Vinasse

The sample of distillery vinasse was supplied by a sugar refinery (Santa Bárbara, Tucumán, Argentina).

Total solid content and humidity were determined by evaporating water from a 50 mL of vinasse sample in a heating bath at 368 K up to a constant weight. Total solid content and humidity were calculated from initial and final masses by means of usual calculations. The pH measurements were carried out with an Altronix EZDO-PC pH meter. Conductivity was measured by means of HM COM-100 digital conductometer.

For the rest of determinations, vinasse was first treated with ethanol in order to remove most of the proteins, pectins and other insoluble compounds.[14]

Bradford method was used to measure the protein content by using the UV/Vis spectrophotometer Hewlett Packard 8452A. The Folin-Ciocalteu method was used to estimate the amount of total phenolic compounds (TPC) within the vinasse. A calibration curve, obtained from protocatechuic acid (3,4-dihydroxibenzoic acid) with a spectrophotometer (Hewlett Packard 8452A) at 700 nm, gives the TPC content in the equivalent protocatechuic acid. Total organic carbon content (TOC) of all solutions was measured by means of a TOC analyzer (TOC-5000A SHIMADSU).

2.2. Analysis of Phenolic Compounds

Phenolic compounds (TPC) were isolated from 50 mL of vinasse by extracting with ethyl acetate. The obtained organic fraction was then washed with 5% $NaHCO_3$ solution and finally extracted with NaOH 5% solution. This alkaline extract was drawn to the neutral pH by means of 0.1M HCl.

The analysis of phenolic compounds within the extract was made by means of HPLC-MS. The chromatograph was an Agilent 1100 LC system (Agilent Technologies Inc., USA) equipped with a binary pump and a diode array detector (DAD), and coupled with MSD VL quadrupole (Agilent Technologies, USA) with an electrospray ionization (ESI) interface. A Rheodyne 7725i injector with a 20 μL loop was used. Data acquisition and analysis were performed using LC/MSD Agilent ChemStation. The chromatographic separations were performed on a C-18 Gemini column (150 mm×4 mm, 3 m). The column was maintained at room temperature (295±1 K).

The optimum chromatographic conditions for phenolic compound separation were achieved using two mobile phases A (methanol) and B (water containing 0.1% formic acid) at the following gradient profile: constant 20% A (2 min), from 20% A to 90% A at 7 %/min (10 min), constant 90% A (8 min), from 90% A to 10% A at 7 %/min (10 min), constant 20% A (2 min). The total run time was 32 min and the flow rate was kept constant at 0.5 mL/min.

The electrospray ionization was performed using nitrogen to assist nebulization, at a flow rate of 7 L/min, and a nebulizer pressure of 275.8 kPa. The capillary temperature and voltage were set at of 603 K and 3000 V, respectively. Positive scan ion mode was used for identifying the base peaks *m/z* values for each chromatographic peak. The *m/z* values were scanned between 50 and 1000 amu.

Different phenolic compounds were identified by means of their m/z values and checking the fragments obtained within each mass spectrum by comparison with phenolic compounds previously found in literature.[18-20]

2.3. Characterization of the Activated Carbons

Four types of commercial activated carbon were used, each one with different physical and chemical properties. The four activated carbons used within this work were: 1) Hydrogen sulfide CAT-Ox 4 mm pellet activated carbon (UMI 2000), 2) CARBOPAL MB 4S (Donau), 3) CHAC (F & M Sc. Corp. 30–60 mesh) and 4) CONCARB, activated carbon supplied by INTA Prov. de Entre Ríos. Adsorbents were ground and then calcined at 423 K in a stove for 24 h in order to eliminate adsorbed water, and no further treatment was made on them. Four adsorbents will be named from now on as CAT, CARBOPAL, CHAC and CONCARB. These materials were analyzed considering their physical and chemical properties.

Superficial areas and textural properties of carbons were determined using conventional adsorption/desorption of N_2 at 77 K using a Micromeritics ASAP 2020 equipment. The samples were previously degassed at

523 K for 24 h under a residual vacuum of less than 104 Pa. The nitrogen adsorption isotherms were analyzed according to Brunauer, Emmett and Teller (BET) method.[21,22]. The pore distribution was determined by Barrett-Joyner-Halenda (BJH) method[23] from the analysis of the micropore isotherm by the test taking the curve of Harkins and Jura;[24] the total pore volume was determined by the rule of Gurvitsch.

Surface chemical characterization of all adsorbents was performed with the Boehm method, which is widely used for determination of acidic and basic surface groups of activated carbons.[25] For acid groups: NaOH was used. It is assumed that NaOH neutralizes carboxylic acids, phenols, lactones and carbonyls. HCl was used for neutralizing basic groups. 0.1000 g of carbon were placed in a 100 mL Erlenmeyer, then 100 mL of 0.0563M HCl solution were added. The system was kept under constant stirring for 24 h. After this time, the mixture was filtered, and 20 mL of each solution were taken. They were titrated with 0.0539M NaOH using phenolphthalein asa pH indicator. For acidic groups, measurements were made following the same procedure, using 0.0539M NaOH and methyl orange as the pH indicator. A blank experiment was also performed in order to verify the pH value of charcoal dispersion in distilled water.

Also, pH of the point of zero charge (pH_{PZC}), was determined by a drift method.[26] pH_{PZC} is the pH value at which the charge on the activated carbon surface is zero. Constant amounts of solids (0.1000 g) were weighted into a closed 25 mL Erlenmeyers. 10.0 mL of 0.1000M NaCl solution were added. pH adjustment was performed using 0.1000M HCl and 0.1000M NaOH solutions with the pH values of 2–12. The initial pH of the solutions were measured with pH Meter Altronix-Mod EZDO-PC and noted as $pH_{initial}$. The system was magnetically stirred for 24 h. After this time, the dispersion was centrifuged and pH_{final} of the solution was measured and plotted against $pH_{initial}$. The pH_{PZC} value of the activated carbon sample is the point when $pH_{initial} = pH_{final}$.

2.4. Adsorption Experiments

All isotherms were obtained by batch adsorption experiments with initial concentrations ranging from 360 to 9000 $mg{\cdot}L^{-1}$ for TOC and 5 to 35 $mg{\cdot}L^{-1}$ for TPC concentrations, which correspond to dilution factors ranging from 20 to 500 with deionized water.

The adsorption isotherm experiments were carried out by adding 0.020 g of activated carbon to 50 mL of the diluted vinasse under mechanical stirring at 150 rpm in a thermostated multi-agitation apparatus (SHZ-88). The samples were shaken for 24 h finding that the adsorption equilibrium was achieved within this time under all the tested operation conditions. Systematically for all the experiments, TPC and TOC contents were determined before and after adsorption as described for vinasse characterization.

The equilibrium adsorption capacity, q_e ($mg{\cdot}g^{-1}$), was calculated according to Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 and C_e are the liquid-phase concentrations of TOC or TPC at initial and at equilibrium time, respectively, $mg{\cdot}L^{-1}$; V is the solution volume, mL; W is the weight of activated carbon, g.

Each adsorption test was performed in duplicate. The pH values of all solutions were measured before and after adsorption.

2.5. Desorption Experiments

To evaluate TPC and TOC desorption, the residual solids retained on the filter paper after adsorption were collected in Erlenmeyer flasks and dried under vacuum for 24 h. To each flask, 50 ml of deionized water were added. The flasks were then shaken for 24 h. The suspensions were filtered and TOC and TPC contents were analyzed by the methods described above.

3. Results and Discussion

3.1. Characterization of Vinasse

The physico-chemical properties of vinasse: the pH value of the vinasse was 4.74, the total solids content was 83.0 $g{\cdot}L^{-1}$ and it has a humidity of 92.4 %. The content of phenolic compounds (TPC) was 0.675 $g{\cdot}L^{-1}$ and the total organic compounds (TOC) of 182.05 $g{\cdot}L^{-1}$.

The measured conductivity was 28 $dS{\cdot}cm^{-1}$ and the total protein content value was <0.1 $g{\cdot}L^{-1}$.

Over 60 different phenolic compounds could be detected within the phenolic fraction (as defined in the experiment). Table 1 shows the mass of the pseudo molecular ion corresponding to peaks bearing a relative concentration (measured as area) greater than 2 %.

Such pseudomolecular ions appear, as commonly in the positive ESI mode, as protonated molecules (noted as $[M+H]^+$) or adducts with sodium and ammonium ($[M+Na]^+$ and $[M+NH_4]^+$, respectively). Although one of the adducts is (in each case) more abundant than the other two, their appearance in the spectrum (even in low abundance) is taken as a confirmation of the ion forming the adduct with

M (H^+, Na^+ or NH_4^+). The only peak that does not appear as an adduct is the one assigned as malvidine derivative (peak J), since this compound is cationic.

Nevertheless, it is important to state that this identification is just tentative, as we associate molecular weights with compound identities assuming that they belong to the phenolic compounds so far identified in literature.

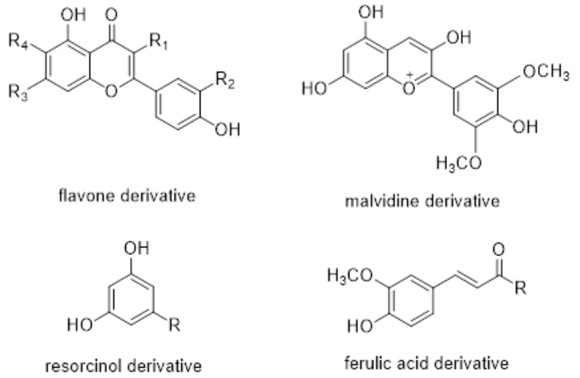
As a general remark, the most abundant phenolic compounds in vinasse (even when some identities have more than one known possibility) can be classified as flavones and flavone derivatives (compounds A, D, E, G, L, M, N, P and R), resorcinol derivatives (compound H and I), malvidine derivatives (J), and ferulic acid derivatives (C, F and S). The basic structures are displayed in Scheme 1.

3.2. Characteristics of the Activated Carbons

The N_2 adsorption–desorption isotherms for the four used activated carbons which show the volume of nitrogen adsorbed (in $cm^3 \cdot g^{-1}$) in standard conditions of temperature and pressure *versus* relative pressure. These isotherms have been analyzed in the light of the newest IUPAC Technical Report.[27] Considering these recommendations, the four physisorption isotherms correspond to Type IVa isotherms, typical of mesoporous adsorbents. The adsorption behaviour in mesopores is determined by the adsorbent–adsorbate interactions and by the interactions between the molecules in the condensed state. For Type IVa isotherm, a capillary condensation is accompanied by hysteresis.

Table 1. Phenolic compounds found in vinasse

Peak	Retention time, min	Relative peak area, %	*m/z* (relative abundance), %	Tentative identification [pseudomolecular ion]
A	16.20	2.64	581.4	Luteolin 7-O-(2-apiosyl-glucoside) $[M+H]^+$ Kaempferol 3-O-xylosyl-glucoside $[M+H]^+$ Naringin$[M+H]^+$
B	17.20	3.55	932.6	Unknown
C	17.55	4.97	983.4	1,2,2'-Trisinapoylgentiobiose $[M+Na]^+$
D	18.20	2.45	595.8	Apigenin 6,8-di-C-glucoside $[M+H]^+$ Chrysoeriol 7-O-apiosyl-glucoside $[M+H]^+$ Luteolin 7-O-rutinoside $[M+H]^+$ Kaempferol 3-O-galactoside 7-O-rhamnoside $[M+H]^+$ Kaempferol 3-O-rutinoside $[M+H]^+$ Didymin$[M+H]^+$ Poncirin$[M+H]^+$
E	18.30	2.74	826.0	Spinacetin 3-O-glucosyl-(1->6)-[apiosyl(1->2)]-glucoside $[M+Na]^+$
F	18.50	6.02	594.6	24-Methylcholesterol ferulate $[M+NH_4]^+$ 24-Methylenecholestanol ferulate $[M+NH_4]^+$ 24-Methyllathosterol ferulate $[M+NH_4]^+$
G	18.85	2.27	485.5	Chrysoeriol 7-O-glucoside $[M+Na]^+$ Isorhamnetin 3-O-rutinoside $[M+Na]^+$
H	18.95	2.56	337.7	5-Pentadecylresorcinol $[M+NH_4]^+$
I	19.05	2.09	289.0	Phlorin$[M+H]^+$ Eriodictyol$[M+H]^+$
J	20.50	2.14	655.5	Malvidin 3,5-O-diglucoside$[M]^+$ Malvidin 3-O-(6''-caffeoyl-glucoside) $[M]^+$
K	20.90	3.39	343.8	Unknown
L	21.40	2.52	619.1	Quercetin 3-O-glucosyl-xyloside $[M+Na]^+$ Eriocitrin$[M+Na]^+$ Neoeriocitrin$[M+Na]^+$
M	21.70	2.58	632.8	Quercetin 3-O-xylosyl-glucuronide $[M+Na]^+$
N	21.80	2.75	806.3	Patuletin 3-O-glucosyl-(1->6)-[apiosyl(1->2)]-glucoside $[M+NH_4]^+$
O	22.00	3.28	646.5	Unknown
P	23.10	2.52	653.7	Quercetin 3-O-(6''-acetyl-galactoside) 7-O-rhamnoside $[M+H]^+$
Q	23.70	2.09	531.5	Unknown
R	24.30	3.08	293.5	Apigenin$[M+Na]^+$ Baicalein$[M+Na]^+$ Galangin$[M+Na]^+$ Genistein$[M+Na]^+$
S	25.10	3.17	352.1	Avenanthramide 2f $[M+Na]^+$



flavone derivative

malvidine derivative

resorcinol derivative

ferulic acid derivative

Scheme 1. Main phenolic compounds characterized in sugar cane vinasse

The textural properties of the activated carbons are presented in Table 2.

The micropore surface (S_{micro}) decreases in the order CONCARB > CAT > CHAC > CARBOPAL. The area of micropores is significantly lower for CARBOPAL (98 $m^2 \cdot g^{-1}$) than for others (having 459.5, 579.5 and 659.5 $m^2 \cdot g^{-1}$). Also, the micropore volume W_0 has the same order (0.039, 0.20, 0.25 and 0.28 cm^3 g^{-1} for CARBOPAL, CAT, CHAC and CONCARB, respectively). However, the total surface (S_{BET}, $m^2 \cdot g^{-1}$) has a rather different order CARBOPAL (1288) > CAT (1189) > CONCARB (981) > CHAC (638).

The surfaces of the four activated carbons were chemically characterized by means of titration of acid and basic functional groups and also by the determination of pH of zero-charge-point (pH_{ZCP}). The results are summarized in Table 3.

Three of the activated carbons (CAT, CHAC and CONCARB) appear as neutral materials in the aqueous solution but bearing potential acidic groups on their surfaces. CHAC is the only one of the three that also shows basic functional groups. On the other hand, CARBOPAL shows a marked acidic reaction towards water, containing both acidic and basic groups on its surface.

As a conclusion, four carbons can be classified as mesoporous materials. CARBOPAL is the only one with acidic characteristics, CAT, CONCARB and CHAC have rather neutral surfaces. CAT and CONCARB have only acidic functional groups on their surfaces; CARBOPAL and CHAC have acidic and basic functional groups on their surfaces.

3.3. Adsorption Experiments

Fig. 1 shows the adsorption of phenolic compounds and total organic compounds from vinasse on four different activated carbons at 298 K.

Regarding phenolic compounds, the adsorption isotherms on CHAC and CARBOPAL can be described as type Ib (or L2) isotherms, the ones on CAT are type II (or L3) isotherms, and on CONCARBO, they appear as type V (also called S2 type) curves [27, 28]. At low concentrations, CAT, CHAC and CARBOPAL show similar adsorption behavior, being more effective than CONCARBO. Nevertheless, they are overcome by CONCARBO at phenolic compounds concentrations higher than 10 ppm.

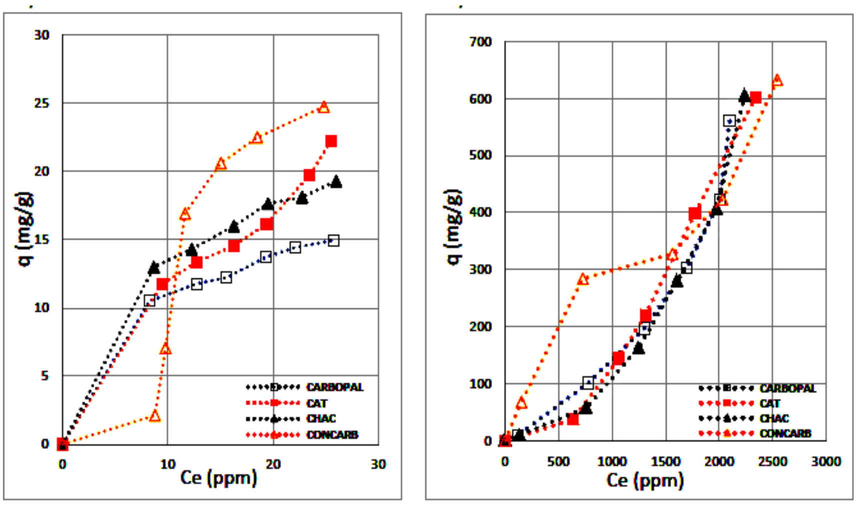
It is observed that the efficiency in adsorption depends on the micropore area S_{micro}. The more efficient adsorbent (CONCARBO) is the one that has higher micropore area. When considering the isotherms obtained for total organic carbon, it can be seen that CHAC, CARBOPAL and CAT can be described as type III (or S1) isotherms, but CONCARBO shows a type II (or L3) isotherm. CONCARBO produces a very high adsorption at low concentration but when TOC concentration reaches 1500 ppm, four carbons show similar capacity. Within the concentrations studied the isotherms did not reach the plateau.

Table 2. Textural properties of the activated carbons

Activated carbon	Surfaces, $m^2 \cdot g^{-1}$			W_0, $cm^3 \cdot g^{-1}$	L_0, nm
	S_{micro}	S_{ext}	S_{BET}		
CARBOPAL	98.5	1189.2	1287.7	0.039	3.89
CAT	579.5	609.9	1189.4	0.25	2.23
CHAC	459.5	178.4	637.9	0.20	2.24
CONCARB	659.5	321.8	981.3	0.28	2.00

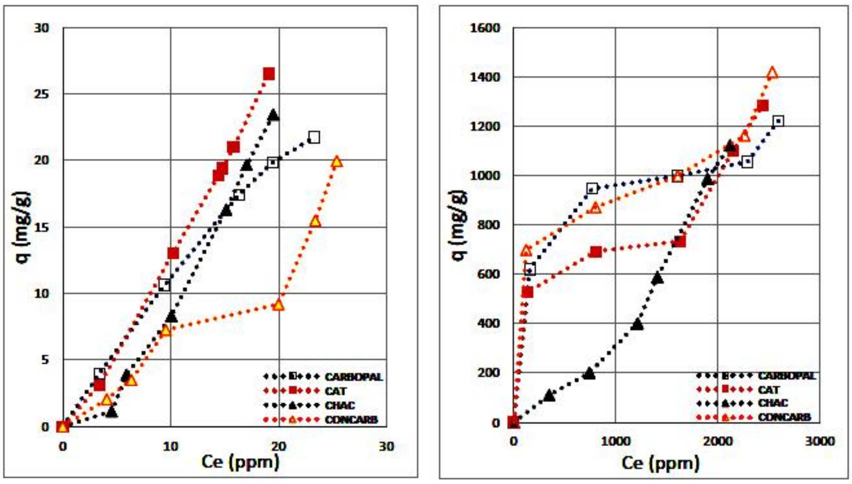
Table 3. Chemical properties of the activated carbons

Activated carbon	Functional groups, $mmol \cdot g^{-1}$		pH_{ZCP}	Nature
	acidic	basic		
CARBOPAL	0.8	0.8	4.4	Acidic
CAT	0.6	0.0	7.5	Neutral
CHAC	0.3	0.1	7.4	Neutral
CONCARB	0.1	0.0	7.5	Neutral



a) b)

Fig. 1. Adsorption isotherms for phenolic compounds (a) and total organic carbon (b) on four activated carbons at 298 K



a) b)

Fig. 2. Adsorption isotherms for phenolic compounds (a) and total organic carbon (b) on four activated carbons at 313 K

In this case, the correlation between the adsorption and the adsorbent surface is not observed.

3.4. Temperature Effect

Fig. 2 shows the adsorption of phenolic compounds and total organic compounds from vinasse on four different activated carbons at 313 K.

As a general remark, it is noticeable that when rising temperature, the values of q_e for TOC are higher than the ones observed at room temperature. Since this behavior has been found typical of chemisorption processes in several systems involving activated carbon as the adsorbent and phenolic and other organic compounds,[29-32] it can be assumed that, in this case, the adsorption is a chemical (rather than physical) process.

In the case of TPC adsorption, the q_e values get lower as temperature rises in the case of CAT, CARBOPAL and CHAC, suggesting an exothermic adsorption process. In the case of CONCARBO, and especially at low concentrations, the effect is opposite (adsorption is favored by temperature and the process is endothermic).

In order to estimate the enthalpy value for the adsorptions, the initial slopes of all isotherms have been approximated by modeling them as Freundlich isotherms and not considering the second order adsorptions. Table 4 shows the initial slope values for each isotherm and the estimated ΔH for the adsorption process.

Table 4. Initial slope values for each isotherm and the estimated Δ*H* for the adsorption process

Carbon	TPC adsorption			TOC adsorption		
	initial slope, $L \cdot g^{-1}$		Δ*H*, kJ/mol	initial slope, $L \cdot g^{-1}$		Δ*H*, kJ/mol
	298 K	313 K		298 K	313 K	
CHAC	2.1±0.2	0.328±0.1	-96±28	3.10^{-5}±3.10^{-5}	0.006±.005	273±110
CAT	2.2±0.5	0.8662±0.1	-48±20	0.001±0.001	36±5	535±51
CONCARB	$3.5.10^{-4}$±5.10^{-5}	0.304±0.1	350±26	4±7	50±27	131±123
CARBOPAL	1.7±0.1	1.3776±0.2	-10±5	0.002±0.001	46±12	510±43

Previous works[33] have shown that Δ*H* in physisorptions has negative and low values (lower than 84 kJ/mol), while chemisorptions are associated with higher Δ*H* values (typically between 84 and 240 kJ/mol), which can be positive or negative. Regarding these facts, then it is clearly seen that the adsorption of TOC is a chemical process, as it is also the adsorption of TPC on CONCARBO. In the case of adsorption of phenolic compounds on CAT, CHAC and CARBOPAL, the adsorption is a physical process, and then depends directly on the surface of the adsorbent.

3.5. Desorption Experiments

After desorption experiments, it was found that the concentration of TPC and TOC in all the experimental conditions were below the detection limit. Then, it is seen that in all cases the adsorption of TOC and TPC is an irreversible process.

4. Conclusions

This study shows that sugarcane vinasse has a high organic load. The phenols present in it belong mostly to flavonoids, anthocyanins, derivatives of resorcinol and ferulic acid.

Adsorption of vinasse samples was performed on four classes of activated carbon CARBOPAL, CONCARBO, CAT, CHAC. CONCARBO coal presented the highest room temperature adsorption capacity for phenolic compounds because this adsorbent has the largest micropore surface. No correlation was observed between the adsorption and the surface charge of the activated carbons.

An increase of approximately 100% in the adsorption capacity of total organic compounds of four adsorbent materials is observed when the temperature increases by 15 K, this is since the process is endothermic.

For the adsorption of phenolic compounds, the CONCARBO carbon decreases its adsorption capacity with the increase in temperature, while the remaining three carbons increase their adsorption capacity by approximately 13 %. It can be concluded therefore that in carbon CONCARBO the adsorption of phenols at high temperatures is not a priority, being adsorbed more effectively by another type of organic compounds.

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АРГЕНТИНСЬКА ЦУКРОВА БАРДА: ХАРАКТЕРИСТИКА ФЕНОЛЬНИХ СПОЛУК ТА ОЦІНКА АДСОРБЦІЇ ЯК МОЖЛИВОГО МЕТОДУ ВІДНОВЛЕННЯ

Анотація. *Вивчено хімічний склад барди цукрового очерету (Тукуман, Аргентина) та встановлено високу концентрацію органічних сполук. Серед фенольних сполук виявлено переважно флавоноїди, антоціани, похідні резорцину та ферулової кислоти. Описано ізотерми адсорбції фенольних сполук та загальних органічних сполук на чотирьох комерційних активованих вугіллях з різними фізико-хімічними властивостями за двох температур. Встановлено, що форма ізотерми залежить від типу вуглецю, а адсорбційна здатність посилюється із збільшенням температури. Визначені ентальпії процесу адсорбції, та доведено, що адсорбція органічних сполук є хемосорбційним процесом, тоді як адсорбція фенольних сполук є фізичною адсорбцією для трьох типів вуглецю та хемосорбцією для четвертого (CONCARBO).*

Ключові слова: *барда, адсорбція, фенольні сполуки, відновлення.*