Adsorption of Acetic and Benzoic Acids from Aqueous Solutions on Activated Carbon

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Summary

Adsorption of acetic and benzoic acids at different temperatures range from 298K to 503K has been carried out on activated carbon from an industry. The results obtained show that adsorption decrease for acetic acid and is constant for benzoic acid when the temperature increases. Furthermore, whatever temperature, benzoic acid adsorption is superior to acetic acid one. The difference in adsorption is associated to the contribution of benzene ring which gives to this molecule a high polarisation than acetic acid. This contribution has inhibited the action of temperature excepted over adsorption.

Keywords: adsorption, activated carbon, benzoic acid, acetic acid,

Résumé

L'adsorption des acides acétique et benzoïque à différentes températures allant de 298K à 503K a été étudiée sur du charbon actif provenant de l'industrie. Les résultats obtenus ont montré que l'adsorption diminue pour l'acide acétique et est constante pour l'acide benzoïque lorsque la température augmente. En plus quelle que soit la température, l'adsorption de l'acide benzoïque est supérieure à celle de l'acide acétique. La différence en adsorption est associée à la contribution du cycle benzénique qui confère à la molécule une plus grande polarisation que l'acide acétique. Cette contribution a inhibé l'action attendue de la température sur l'adsorption.

Mot-clés : adsorption, charbon actif, acide benzoïque, acide acétique,

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1. Introduction

Activated carbons are widely used for the removal of various pollutants from gases, and especially for adsorption of volatile organic compounds ^[1,2]. Their porous allowed extending structures their [3, water application in treatment ⁴ chemicals ^[5] and medicals industries ^[6]. This is one of the reasons these materials are used to remove pollution from water infected by pesticide. The capacity of activated carbon to remove organic and inorganic substances is usually represented by Langmuir and Freundlich models ^[7-9]. The aim of this work is to study removal of acetic and benzoic acids from aqueous solutions. These molecules were selected because acetic acid gives sour taste to water and benzoic acid has molecular with similarities some pesticides chlorophenols). (benzonitriles, Thus, temperature is one of the most important factors that influence adsorption of organic compounds from aqueous solutions onto carbon materials. The expected effect of temperature on adsorption isotherms is a decrease in adsorption with increasing temperature. since adsorption is а spontaneous process. However, different been examples have reported with increases in the amount adsorbed with temperature ^[10-16]. This is opposite to the effect of temperature on the physical adsorption of a single component, leading us to investigate the behaviour of adsorbate at different temperatures.

2. Experimental

The benzoic acid (M = 122.12 g/mol, purity \geq 99%) from Merck (E. Merck D 6100 Darmstadt, Fr Germany) and acetic acid (M = 60.05 g/mol, purity \geq 96%, d=1.06) from Merck (E. Merck Darmstadt, Germany) were used as adsorbates. Powder activated carbon from industry (Polychimie, Abidjan, Côte d'ivoire) was used as adsorbent. The characteristics of the carbon were: $S_{BET}=200 \text{ m}^2.\text{g}^{-1}$, and $V_p=$ 0.6 cm³.g⁻¹ porous diameters $2nm \le d \le$ 60nm. The solutions were prepared with respectively volumes of adsorbate (benzoic or acetic acid) and diluted to obtain different solutions concentrations (C_0) . These solutions were introduced in small bottles and put in a thermostatic bath adjusted at different temperatures 298K to 503K. One gram of activated carbon was added and homogenised during 30 min. Since equilibrium was taking place, the mixing is screened with filter paper. We took 10 mL of this new solution and dosed with phenolphthalein by NaOH checked by oxalic acid solution. We calculated the residual concentration (Ce) of benzoic acid after adsorption and the amount adsorbed by 1g of activated carbon was calculated according to the following equation: $a = V \times \frac{(c_0 - c_e)}{m}$ where V (mL) is the volume of the liquid phase, m (g) is the mass of the activated carbon, and C_0 is the

3. Results and discussion

initial concentration.

The measured adsorption isotherms were described using the (1) Langmuir equation $a = \frac{a_m b c_e}{1 + b c_e}$, and (2) Freundlich equation, $a = k c_e^{1/n}$ where a (mol/g) is the amount of solute adsorbed per unit weight of adsorbent, C_e (mol/L) is the equilibrium concentration of solute, a_m (mol/g) is the amount of solute adsorbed per unit weight of adsorbent, required for monolayer coverage of the surface, b (L/mol) is a constant related to the heat of adsorption, k (mol/g)(L/mol)^{1/n} and n Ereundlich

(mol/g)(L/mol)^{1/n} and n Freundlich constants. The adsorption isotherms from aqueous solutions of benzoic and acetic acids at different temperatures are presented in figure 1a) and figure 1b). There are different behaviours depending on temperature for the both adsorbates. For acetic acid, adsorption decreases with temperature, from a_m = 2.2 mmol/g at 298



Figure1: 1a) : Adsorption isotherms of Benzoic acid **1b**) : Acetic acid on activated carbon at $\diamond 298$ K, $\Box 303$ K, $\blacktriangle 308$ K, $\times 413$ K, *418K and $\bigcirc 503$ K

Concerning benzoic acid, it remains fairly constant whatever temperature, $a_m = 2$ mmol/g. The decrease of adsorption is expected, given the spontaneity of adsorption phenomenon and thermodynamic predictions. The behaviour of acetic acid does not thus fit with of these predictions. Table 1 presents the Langmuir and Freundlich constants values for both acids. The adsorbates have shown slightly variation value of the coefficient k (range 0.0018-0.0179) to acetic acid and constant value (k = 0.005) to benzoic acid. The obtained values are consistent with those from the last works published ^[17-19]. Freundlich constant (1/n) is practically

K to $a_m = 0.1 \text{ mmol/g at 503 K}$.

constant for benzoic acid (1/n = 0.2) and is in the range (0.15 - 0.6) for acetic acid. These ranges of Freundlich parameter equation values 1/n (0.19 - 0.5) have been already obtained ^[20] and shown that the surface is not heterogeneous. Acetic and benzoic acids values from Langmuir X_m and b are represented (Table 1). For acetic acid, a_m and b respectively decreases and increases with temperature, but for benzoic acid, a_m is a constant (2 mmol/g) and b seems to be decreasing. The observation of k value has shown a higher capacity of adsorption for benzoic rather than for acetic acid. We can claim that the formation of apparent monolayer coverage onto carbon surface to the both adsorbents is not reached. It can be expected that apparent monolayer coverage would happened at higher adsorbate concentrations. These types of isotherms in which the saturation of the surface has not been reached. due to experimental difficulties can be classified as L1 isotherms^[7]. These isotherms are similar to those obtained by other authors during adsorption at different temperatures over [21] solid surfaces They could be interpreted as isotherms resulting of physical adsorption in the micro porous having molecular dimensions. In this case, the Langmuir isotherm usually predicts better the adsorption behaviour than the exponentially increasing Freundlich isotherm^[22]. The results enable us to trace the function Inb according to 1/T and to obtain a line of equation: $lnb = -\Delta H^{\circ}/RT + \Delta S^{\circ}/R$ (R: noble gas constant, T: temperature (K))

Thus, we could determine the enthalpy of adsorption (ΔH°) and entropy of adsorption (ΔS°) .

For benzoic acid: $\Delta H^{\circ} = -53.62$ KJ/mol and $\Delta S^{\circ} = -90.84$ J/mol.K.

For acetic acid: $\Delta H^{\circ} = -26.25$ KJ/mol and $\Delta S^{\circ} = -1.20$ J/mol.K.

Acetic and benzoic acids adsorption have a negative heat of adsorption values. These

values confirm an exothermic reaction. All times, an increase of temperature would not further the adsorption reaction that we observed this acid. The energy of benzoic acid is more than acetic acid adsorption, which confirm the high interaction between benzoic acid and the

Table 1: Apparent Langmuir and Freundlich isotherm parameters adsorption at different temperatures 298K,303K,308K,413K,418K,503K

Temperature(K)	a _m (mmol/g)		b (L/mol)		1/n [*]		k **	
	acetic	benzoic	acetic	benzoic	acetic	benzoic	acetic	benzoic
	acid	acid	acid	acid	acid	acid	acid	acid
298	2.2	2	95	3437	0.6132	0.1920	0.0179	0.0050
303	2.2	2	95	3935	0.3342	0.1850	0.0052	0.0050
308	1.1	2	357	2656	0.4079	0.2147	0.0060	0.0057
413	0.9	2	1819	3221	0.1557	0.1984	0.0018	0.0053
418	1	2	1313	3152	0.1971	0.2090	0.0024	0.0057
503	0.1	2	357	2814	0.2746	0.2124	0.0027	0.0055

 $^{*}1/n$ is the slope of straight line on the isotherm.

**k is the empirical constant corresponding to a segment cut off by the straight line with the axis of ordinates.

adsorption is characterised by the value of b. It is also indicating the interaction between adsorbate and adsorbent. This value is very higher for benzoic acid than acetic acid. This adsorption is the physical type that involves very low bond and promoted by the drop in temperature ^[23]. When temperature is enhanced, it occurs desorption to the surface of the adsorbent. Benzoic acid, adsorption is always physical and should follow to the same phenomenon for elevated temperature. To this molecule, benzene ring provides his high electronic density giving the benzoic acid a new high negative polarisation superior to acetic acid. The change in the apportionment of the molecule electronic creates a stronger adsorption which means, the bonds became strengthened cause to electrostatic attraction with the the adsorbent. This could lead to formation of the monolayer that is observed (2mmol/g). molecule For this increasing the temperature will eliminate the contribution of physical adsorption as well as for acetic acid but did not diminish adsorption. It will be relayed by the contribution of the benzene ring that is not the case for acetic acid. Figure 2 shows the comparison at the adsorption of the two molecules on activated carbon. The adsorption of

adsorbent. Even at 503K benzoic acid more adsorbed than acetic acid at 303K. This difference in adsorption is therefore due to the benzene ring electronic contribution and the weight of benzoic acid. The effect of temperature is attenuated by the contribution of the electronic density.





4. Conclusion

The experiments of acetic and benzoic acids adsorption were carried out at different temperatures. The results have shown that the models of Langmuir and Freundlich are appropriate to describe the isotherms gracefulness to the values of the constants obtained. The values of heat of adsorption and entropy have shown that adsorption is exothermic which take place with decreasing entropy. Benzoic acid adsorption is greater than acetic acid one, due to the contribution of benzene ring which increases its electronic density thereby furthering adsorption.

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