

Supplementary file

Preparation and modification of activated carbon for removal of pharmaceutical compounds by adsorption and photodegradation process: A comparative study

B. Samir¹, N. Bouazizi¹, P.N. Fotsing¹, J. Cosme¹, V. Marquis, G.L. Dotto^{1,2}, F. Le Derf¹, J.

Vieillard^{1*}

1. Experimental part:

Table.S1: properties of Atenolol and propranolol

molecules	Propranolol	Atenolol
Group	Beta blockers	Beta blockers
Molecular Formula	C ₆ H ₂₁ NO ₂ .HCl	C ₁₄ H ₂₂ N ₂ O ₃
Molecular weigh	295.8	266,3
Color	White	White
Form	Powder	Powder

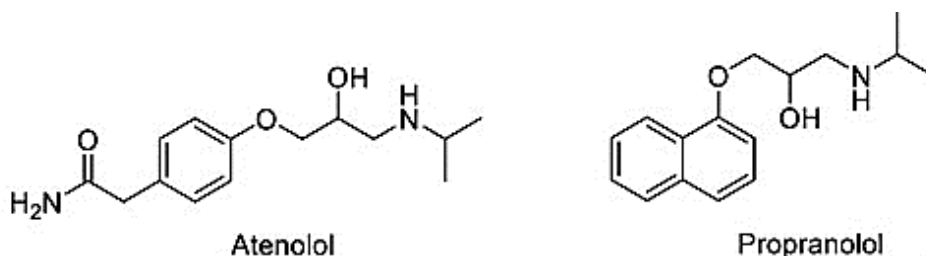


Figure S1: Chemical structure of Propranolol and Atenolol

2. Adsorption studies

2.1. Effect of Temperature

Temperature can influence the adsorption uptake as it changes the reaction rate between the adsorbate and adsorbent. In this study, the effect of temperature is investigated and the results are summarized in **Figure S2**. Different temperatures, 22 °C, 30 °C, 40 °C and 50 °C are used to evaluate the adsorption capacity of (AT, PR) over AC-OH. As seen, the adsorption rate of AT and PR are decreased, with increasing temperature from 22 °C to 50 °C. Results, showed

that adsorption capacity is declined from 220.11 mg/g to 194.29 mg/g and from 314.33 mg/g to 207.34 mg/g, at 22°C and 50°C for AT and PR, respectively. The above results can be explained by the adsorption temperature of the AT and PR molecules, suggesting that high temperature is not suitable for the adsorption of organic molecules due to these stability in temperature.

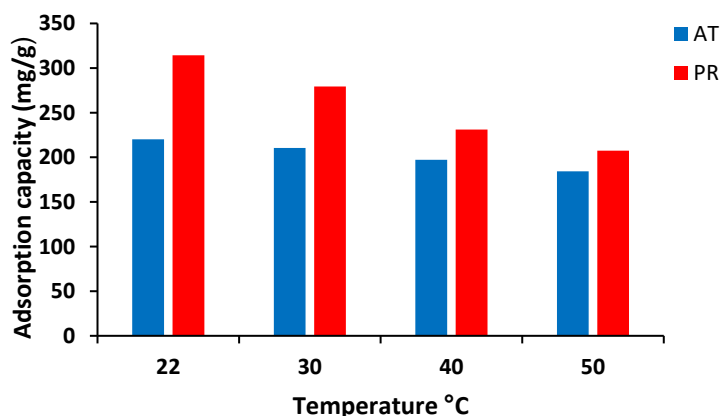


Figure S2: The effect of temperature on the adsorption capacity of AT ad PR.

2.2. Initial concentration of pollutants

Often, the concentration of pollutant affects the adsorption uptake of the adsorbents. **Figure S3** showed the adsorption capacity of AC-OH for AT and PR at different concentrations from 30 to 150 mg/L. Results showed that the adsorption capacity increased with increasing the initial concentration of pollutants. While, when the initial concentration of AT and PR increased, the adsorption capacity reached the maximum, and then the adsorption equilibrium is reached. Here, the results are attributed to the achievement of the saturation of active sites, resulting in the stabilization.

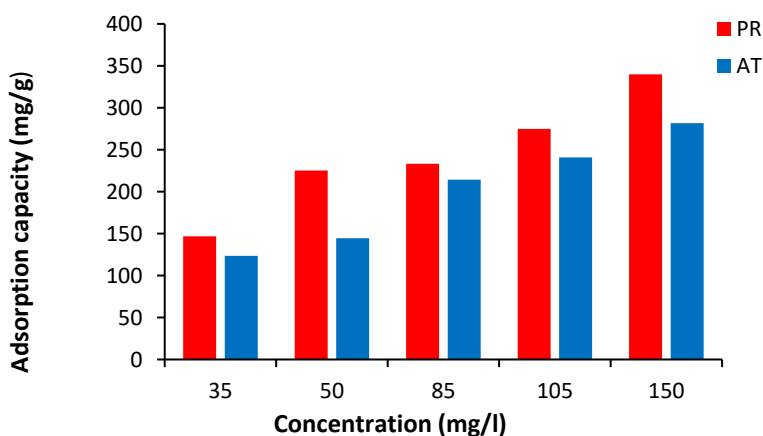


Figure S3: Effect of concentration variation in the adsorption capacity of AT and PR

2.3. Effect of pH

Figure S4-a and Figure S4-b show the effect of pH in the adsorption of AT and PR by AC-OH. As observed in figure 8, the high adsorption uptake 67% for AT and 92% for PR in the pH range of pH 6.30 - 9.50. Regarding to the acidic constant of 9.4 of both AT and PR, the positively charged molecules with the negatively charged of AC-OH can occurred and electrostatic interaction and then the adsorption phenomena is observed. Therefore, adsorption of pharmaceutical molecules could be performant in basic media, while the acidic solution avoid competition with proton.

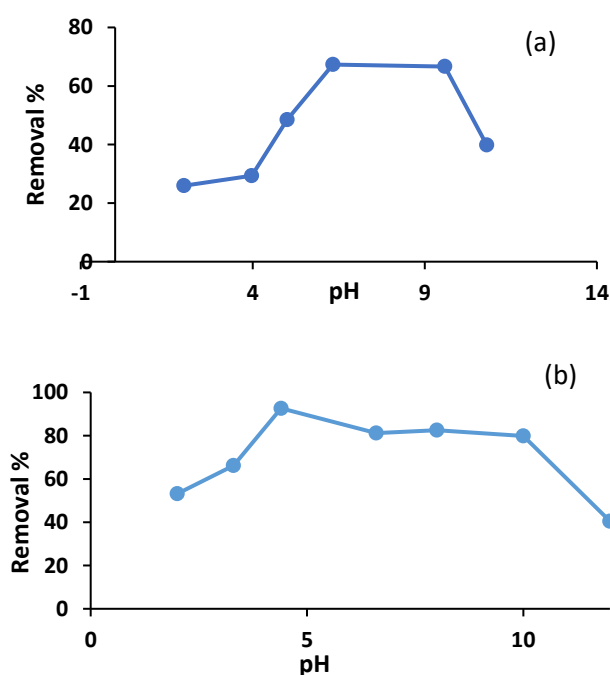


Figure S4: The effect of pH variation in the removal of (a) Atenolol and (b) Propranolol.

2.4. Adsorption isotherms

To elucidate the adsorption process of AT and PR on AC-OH adsorbent, the adsorption isotherms were studied for various concentration from 20 to 150 mg/L. The Langmuir and Freundlich isotherm models were used to describe the adsorption behavior, the dedicated equations were shown in Eq. (S1) and Eq. (S2), respectively.

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (\text{eq.S1})$$

$$\text{Log} Q_e = \text{Log} K_F + \frac{1}{n} \text{Log} C_e \quad (\text{eq.S2})$$

Where, C_e was the residual pharmaceutical products concentration at adsorption equilibrium (mg/L), Q_e was the adsorption capacity at the equilibrium (mg/g), Q_m was the maximum adsorption amount (mg/g), K_L was the Langmuir adsorption equilibrium constant (L/mg) and K_F was the Freundlich adsorption capacity constant (mg/g), $1/n$ represents the heterogeneity factor related to the adsorption strength and the heterogeneity of the adsorbent surface. **Table S2** reports the parameters feature obtained from each model, and their plotters are shown in **Figure S5**. It was found that Freundlich model fit more better than the Langmuir model, as supported by the correlation coefficient values 0,99. The analysis of the parameter $1/n$ obtained for Freundlich model confirmed that adsorption process is favorable. The n -value obtained in our work are 2.02 and 3.67 for both propranolol and atenolol, respectively, which was in good agreement with those described by Kyzas et al. using graphene oxide as solid adsorbent. However, in their work, not only the very expansive adsorbent but also the adsorption isotherm is reached in 24 hours compared to 2 hours in this work. These observations were confirmed by Haro and al. who demonstrated that adsorption on granular activated carbon fitted well with Freundlich model.

Table S2. Thermodynamic parameters for Langmuir and Freundlich models

AT				PR			
Freundlich		Langmuir		Freundlich		Langmuir	
K_F	33.87	q_m	357.14	K_F	92.89	Q_m	344.82
n	2.02	K_L	0.04	n	3.67	k_L	0.10
R^2	0.98	R^2	0.97	R^2	0.95	R^2	0.93

2.5. Thermodynamic parameters

The thermodynamic experiments were carried out at 25 °C, 35 °C and 45 °C with an initial concentration of 50 mg/L, and pH = 7.0. using the following equations. The thermodynamic parameters are calculated and the adsorption mechanism is determined through the thermodynamic equilibrium constant K_d . K_d can be calculated using **Eq. (S3)**:

$$K_d = C_{ad}/C_e \quad (\text{eq.S3})$$

Where the distribution coefficient (K_d) is a dimensionless parameter, and represents the ratio of the concentration of solute adsorbed on the AC-OH(C_{ad}) to the residual concentration of the solute in solution at equilibrium (C_e). The decrease of K_d when temperature increased indicated that the adsorption process is exothermic (**Figure S5**). The ΔG° , ΔH° , and ΔS° were calculated using the equations:

$$\Delta G^\circ = -RT \ln(K_d) \quad (\text{eq.S4})$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S \quad (\text{eq.S5})$$

$$\ln(K_d) = -\Delta G^\circ / RT \quad (\text{eq.S6})$$

As depicted in **Figure S5**, the plot of $\ln(K_d)$ versus $1/T$ was found to be linear, ΔH° and ΔS° were determined from the slope and intercept of the plot, respectively. It can be observed in **Table S3** that ΔG^0 , ΔH^0 and ΔS^0 are in negative values, indicating that adsorption behaviors of AT and PR over AC-OH was a spontaneous and exothermic phenomenon. This adsorption process is more favorable at low temperature, as confirmed in the above section. It was in good agreement with the result obtained by Zhang et al. which confirm that the spontaneous and exothermic adsorption of atenolol into modified montmorillonite;

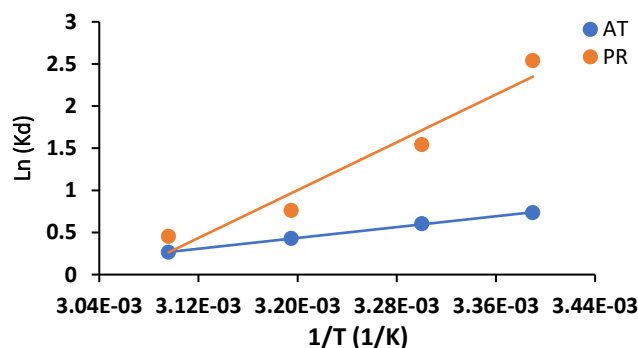


Figure S5: Thermodynamic adsorption of AT and PR on AC-OH.

Table S3: Thermodynamic adsorption parameters for AT and PR.

	$\Delta G^\circ(\text{kJ/mol})$				$\Delta S^\circ(\text{J}/(\text{mol/K}))$	$\Delta H^\circ(\text{kJ/mol})$
	22 °C	30 °C	40 °C	50 °C		
AT	-1.80	-1.52	-1.13	-0.71	-39.18	-13.13
PR	-6.22	-3.88	-1.98	-1.22	- 180.47	-59.00

3. Photocatalysis studies

3.1. Effect of TiO₂ concentration

In order to ensure the role of TiO₂ concentration in activated carbon, the photocatalytic activity of AC-TiO₂ are measured for various quantity of TiO₂ (30%, 50% and 70%). The results are reported in (**Figure S6**). As seen, the photocatalytic degradation is increased considerably from 84% to 94 % and from 65% to 73% for PR and AT, respectively. This increase is obtained with increasing of TiO₂ from 30% to 70%. This can be explained by the rise of photocatalyst radicals. the degradation continued until reaching an optimum close to 50%. An overloading of TiO₂ didn't improve significantly the degradation of the organic molecule (**Figure S6**).

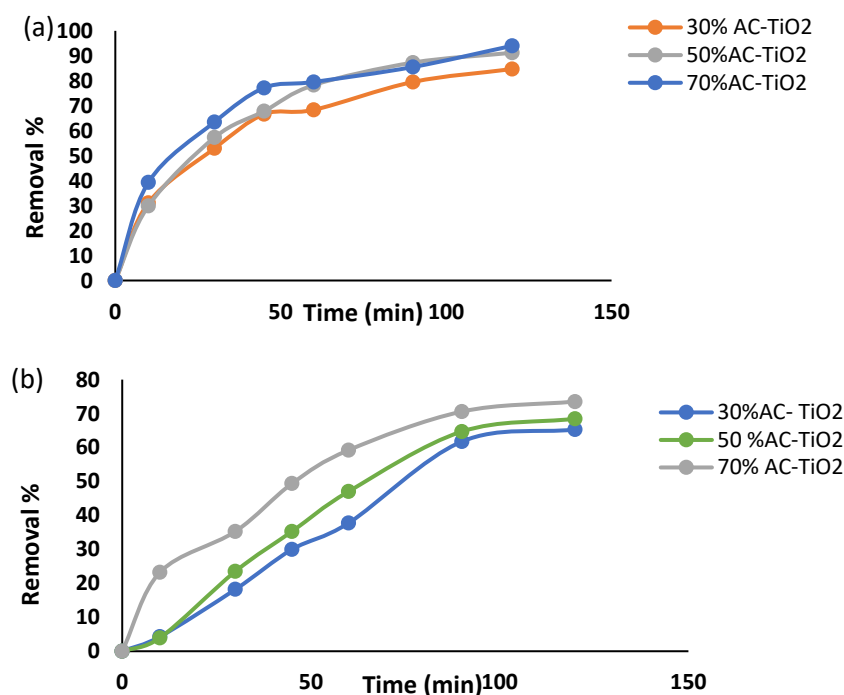


Figure S6: Removal capacity of (a) PR and (b) AT AC doped with various % TiO₂.