Removal of Antibiotics from Aqueous Solution by Bioadsorbant

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Abstract
In this study, dehydrated wheat bran, which is a natural product grows in the north of Algeria has been used as bioadsorbant for antibiotics removal from aqueous solution. Experimental data showed that the sorption of Tylosin increased with increasing the amount of adsorbent and decreased at high temperature. ΔH° and ΔS° were calculated from the slope and intercept of plots of $ln(k_d)$ versus $1/T$, the adsorption process was found to be exothermic and more favourable at low temperature.

1. INTRODUCTION
Although antibiotics have been used in large quantities for some decades, until recently the existence of these substances in the environment has received little notice [1]. Antibiotics are gaining recognition as being environmental contaminants, classified as recalcitrant bio-accumulative compounds and are thus regarded as hazardous chemicals [2]. Adsorption method is one of the most efficient methods of removing pollutants from wastewater [3]. It is simple to design and operate; and it is relatively inexpensive and unaffected by the potential toxicity as for biologically based processes [4]. The present work is focused on Tylosin adsorption onto dehydrated wheat bran, the experiments were done in a batch system to evaluate the adsorption capacity of carbon, and adsorption characteristics were evaluated as a function of adsorbent dosage, temperature and thermodynamics parameters.

2. MATERIALS AND METHODS
2.1. Preparation of dehydrated wheat bran
The wheat bran provided by SIM Company located in Blida- Algeria; was mixed with sulfuric acid solution in the ratios of 1/1 (starting material/activating agent). The mixture was manually stirred at the beginning to contact wheat bran well with acid and left for 2 h, at the end of the dehydration process, sufficient distilled water was added to the mixture to eliminate dust, impurities and other unwanted chemicals before filtering. This process was repeated until the final pH of the filtrate was about 7.0. The dehydrated material rinsed with distilled water was dried for 24 h in oven at 80 C°. Finally, the powdered sample was kept in a desiccator for future use.

2.2 Adsorption studies
The adsorbed amount of Tylosin (antibiotic selected for study) at equilibrium q_e (mg.g^{-1}) and the percentage removal (R %) were calculated by the following equations:

$$R\% = \frac{(C_0 - C)}{C} * 100 \quad (1)$$

$$q_e = \frac{(C_0 - c_e)}{X} \quad (2)$$

Here C_0 and C_e are the initial and equilibrium concentrations ($g.L^{-1}$), *X (g)* is the weight of dehydrated wheat bran in one litter and *C* is the pollutant concentration at the end of adsorption.

3. RESULTS AND DISCUSSION

3.1. Characterization of the adsorbent

Surface structure of dehydrated wheat was analyzed by Scanning Electron Microscope (SEM), the observation from Fig. 1 enabled us to discern the following aspect.

Highly developed porosity all over the entire sample surface with a certain heterogeneity. This porosity can refer to the evaporation of sulfuric acid from the cavities previously occupied by the chemical agent. The presence of pores indicated that there was a good possibility that Tylosin could be trapped and adsorbed onto the surface of dehydrated wheat bran.

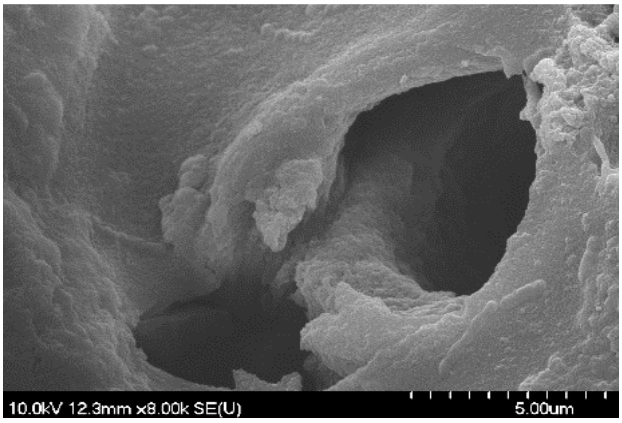

Fig. 1. Scanning electron microscope image of dehydrated wheat bran

3.2. Effect of the operating parameters

3.2.1 Effect of adsorbent dosage

The adsorbent dosage is an important parameter because this determines the capacity of a biosorbent for a given initial concentration. The biosorption efficiency for as a function of biomass dosage was investigated. The results are presented in Fig. 2.It can be seen that percentage of Tylosin adsorption steeply increases with the biomass loading up to 0,8 g/L. This result can be explained by the fact that the biosorption sites remain unsaturated during the biosorption reaction whereas the number of sites available for biosorption site increases by increasing the biosorbent dose [5].

3.2.2. Effect of temperature

Effects of temperature on Tylosin removal are presented in Figure 3. It is concluded from Fig. 3 that Tylosin adsorption decreases with increasing the temperature, which indicated that the lower temperature could be more favourable for Tylosin adsorption onto the dehydrated wheat bran. For further understanding the mechanism of Tylosin adsorption onto the dehydrated wheat bran, thermodynamic analysis was performed. The thermodynamic parameters represented by the change in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) have an important role to determine spontaneity and heat change for the adsorption process. Equilibrium constant can be used to evaluate the thermodynamic parameters [6].

The van't Hoff equation is used to determine the value of the equilibrium constant with temperature changes. The equation is given as:

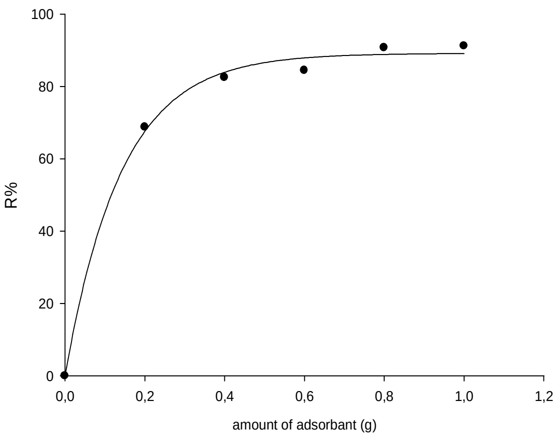

Fig. 2. Adsorbent dosage effect

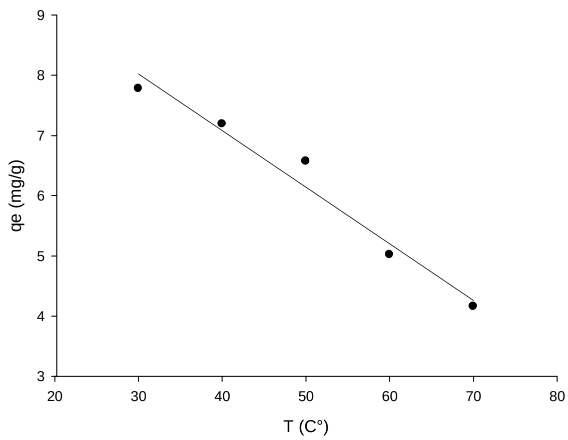

Fig.3. Temperature effect

$$\boldsymbol{ln(k_d) = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}} \tag{3}$$

R is the gas constant, T is temperature and $\Delta H°$ and $\Delta S°$ are the standard enthalpy and entropy changes of adsorption, respectively.

The distribution coefficient k_{d} [7] can be calculated by using the following equation:

$$\boldsymbol{k_d = \frac{q_e}{C_e}} \tag{4}$$

Fig. 5 shows that ln(k_{d}) vs. 1/T can be fit by the linear equation of van't Hoff (Eq. 3), from which the the values $\Delta H°$ and $\Delta S°$ were calculated from the slope and from the intercept of the straight line.

The Gibbs free energy of specific adsorption $\Delta G^{°}$ is calculated using the equation:

$$\boldsymbol{\Delta G^O = \Delta H^o - T\Delta S^o} \tag{5}$$

The calculated thermodynamic parameters of Tylosin adsorption on activated carbon were listed in Table1.

The negative value of enthalpy change $\Delta H°$ indicates that the adsorption of Tylosin was an exothermic process. The $\Delta G°$ values were negative at all temperatures and became less negative with increasing temperature, which indicated the spontaneity of the sorption process [8, 9].

Both the negative value of $\Delta H°$ and the increase in $\Delta G°$ with an increase in temperature suggested that the reaction was less favourable at higher temperatures.

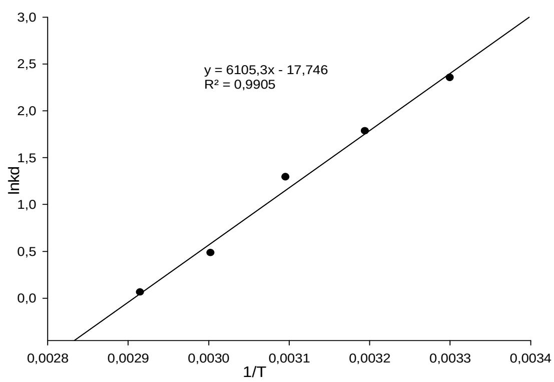

Fig.4. Ln(k_d) according to the reverse of temperature 1/T

Table 1: Thermodynamic parameters for Tylosin adsorption on dehydrated wheat bran.

T (K)	K_d (L.g^{-1})	*ΔG°* (kJ.mole^{-1})	*ΔH* (kJ.mol^{-1})	*ΔS* (kJ.mol^{-1})
303	10.52	-6.057	-50.750	-0.147
313	5.96	-4.582		
323	3.64	-3.107		
333	1.62	-1.632		
343	1.07	-0.157		

4. CONCLUSION

The present investigation shows that the dehydrated wheat bran is an effective bioadsorbant to remove antibiotics compound such as Tylosin from aqueous solutions. The negative value of ΔG confirms the spontaneous nature adsorption process. The negative value of ΔH indicated the adsorption process was exothermic. The experimental results indicated that Tylosin adsorption is favored for adsorbent dosage higher than 0.8 g.L and at low temperature.

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