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Studies on adsorptive removal of an antibiotic drug using ion exchange resin.

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ABSTRACT/RESUME

Abstract: *This study explores the adsorption feasibility of an antibiotic (rifampicin) onto the amberlite IRA-420 resin. The effect of rifampicin concentration (10–30 mg/L), contact time, adsorbent dose (1-3 g/L), solution pH (4-10.5) on the pharmaceutical adsorption on amberlite IRA-420 is investigated. The experimental results indicate that the optimal pH for the rifampicin elimination is the free pH for an adsorbent dose of 1 g/L. The Langmuir model describes well the isotherm data with a high correlation coefficient (R2> 0.944) and a maximum monolayer adsorption capacity of 77.04 mg/g at 295 K. The comparison of the pseudo-second-order and Temkin kinetic models; shows that the experimental data are well fitted by the pseudo second-order kinetic model.*

I. Introduction

Water is one of the most precious resources for the life on earth, but infortunately this treasure is menaced by the presence of a complex mixture of organic and inorganic chemicals, such as pharmaceuticals products.

Findings of drugs in the aquatic environment were reported in the 1970s [1, 2,3]. Some investigations showed the existence of pharmaceuticals in public-owned treatment work's (POTWS) effluents. They have been mainly carried out in the UK in the eighties [4,5,6]. The concentrations in surface waters and STEP effluents were in the ng/L to µg/L range [7-18].

Rifampicin a bactericidal antibiotic drug of the Rifamycin group antibiotic [19], introduced in 1967 [20] as a major addition to the cocktail-drug treatment of tuberculosis and Tuberculosis-related mycobacterial infections. However, less than 30% of the dose consummate is excreted in the urine as Rifampin or metabolites and some of these compounds are not completely removed by conventional wastewater treatment systems due to its not ready biodegradability.

For this reason, it has become extremely important to find solution to remediate Rifampicin polluted environment and thereby preserve the health of the deteriorating environment. Sorption onto resin is one of the promising techniques for removing pharmaceutical from wastewater.

The purpose of this work was to investigate adsorption kinetics and the mechanism of adsorption of Rifampicin onto a strong-base anion exchanger (Amberlite IRA-420). A linear method of three widely used equilibrium isotherms the Langmuir, Freundlich and Temkin which were compared in an experiment, examining Rifampicin adsorption onto Amberlite IRA-420 by continuous variation of 3 operational parameters (initial sorbate concentration, sorbent dosage and pH). In order to describe the phenomenon, the adsorption rate was kinetically evaluated using pseudo second-order and Temkin kinetic models.

II. Materials and methods

II.1 Adsorbent

In our study we have used as an adsorbent, a commercial ion exchanger gel-type strongly basic AmberliteIRA-420. It is an amine quaternary cross-linked styrene/divinylbenzene copolymer. Table 1 includes all the properties of the AmberliteIRA-420 resin. [21].

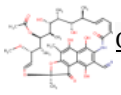
Table 1. *Properties of the resin Amberlite IRA-420*

Producer	**Rohm and Haas**
Functionality	**$-N^+-(CH_3)_3$**
Matrix type	**Polystyrene-DVB**
Standard ionic form	**Cl^-**
Total exchange capacity (m_{eq}/g)	**3.80**
Bed Porosity	**0.32**
Wet resin density (g/cm^3)	**1.15**
Bed density	**0.68**
pH operating range	**0 – 14**
Maximum operating temperature	**77°C**
Mean wet particle radius (mm)	**0.30 – 0.70**

II.2 Adsorbate

Stock solutions were prepared by dissolving accurately weighted samples of Rifampicin; an antibiotic used specifically as anti-tuberculosis, in distilled water to give a concentration of 30mg.L^{-1} and diluted with distilled water when necessary.
Some properties of this pharmaceutical are presented on table 2.

Table 2. *Molecular structure and some physic-chemical properties of Rifampicin.*

Pharmaceutical trade name	Structure	Chemical formula	Molecular mass (g mol^{-1})	pk$_a$
Rifampicine		$C_{43}H_{58}N_4O_{12}$	822,9402	1.7 7.9

II.3 Kinetic studies

Batch adsorption experiments were conducted by shaking 1g of Amberlite IRA 420 with 1L aqueous solution of Rifampicin at different concentrations values.
The adsorbent was removed by centrifugation and the concentration of drug in the supernatant liquid was analyzed by using the UV-Visible at λ=475 nm.

II.4 Equilibrium studies

II.4.1 Sorption isotherms

The removal efficiency (E) of Rifampicin on Amberlite IRA 420 and the sorption capacity (q) were calculated from Eqs. (1) and (2)

$$E(\%) = \frac{Ci - Cf}{Ci} * 100 \qquad (1)$$

$$q = \frac{(Ci - Cf) * V}{m} \qquad (2)$$

Where C_i and C_f are the initial and final concentrations of Rifampicin (mg/L), in aqueous solution respectively, V is the volume of the solution (L) and m represents the weight of the adsorbent (g).

III. Results and discussion

III.1 Effect of contact time

The adsorption efficiency of Rifampicin on the Amberlite IRA-420 was evaluated as function of contact time, ambient temperature (295K), free pH (pH=6), adsorbent dose (1g/L) and rifampicin concentration.

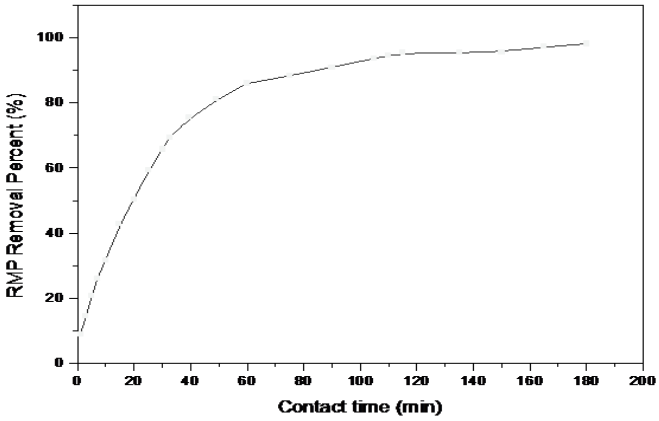


Figure 1. *Effect of contact time on the removal of Rifampicin with the Amberlite IRA-420 ([Rifampicin] = 10 mg L^{-1}, 295 K and pH $_{free}$).*

It is obvious from Fig.1 that the adsorption amount increases in the first and attains the equilibrium after 115 min. From the same figure, it is observed that the percentage removal of Rifampicin remains constant above 115 min to 180 min of adsorption process. The percentage removal of Rifampicin reaches about 98% at equilibrium time.

III.2 Effect of pH

The pH is one of the most significant factors, affecting the performance of adsorption's process. The effect of pH on pharmaceutical uptake by the adsorbent was investigated at 295K at various pH levels 4, 7, 9.5, 10.5 and natural pH solution (between 5.9 and 6.4), as illustrated in Fig.2.
Adsorption tests were conducted by adding 1g of adsorbent to the pharmaceutical solutions prepared to a concentration equal to 10 mg/L. The pH of

solutions was adjusted with either HCl (1M) or NaOH (1M).

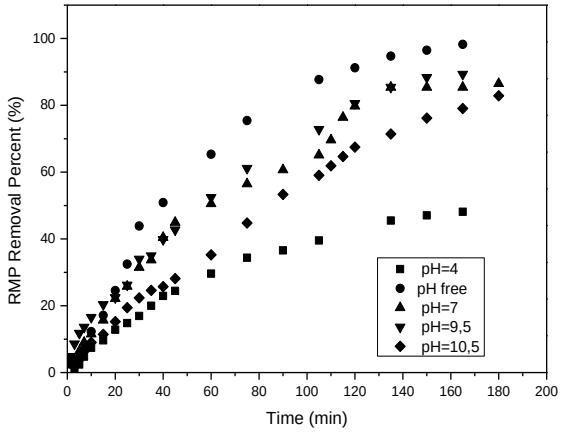


Figure 2. *Effect of equilibrium pH on the removal of Rifampicin with the Amberlite IRA-420 ([Rifampicin]= 10 mg L^{-1}, 295 K and [IRA-420]=1g/L).*

As shown in Fig.3, it is observed that an increase in the pH of the solution from 4 to the natural pH solution causes an increase in per cent adsorption of Rifampicin from 48.15 to 98.25%, due to the ionic form of Rifampicin (aromatic structure, polar groups) in solution and the electrical charge of amberlite IRA-420. Also, the presence of hydroxyl complexes can compete with Rifampicin molecules to reach the adsorption sites.

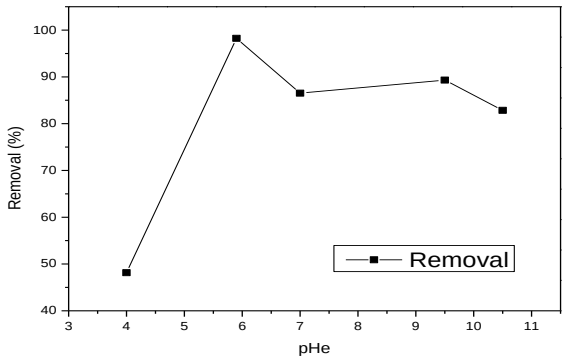


Figure 3. *Effect of equilibrium pH on the removal of RMP with the Amberlite IRA-420 ([Rifampicin]= 10 mg L^{-1}, 295 K and [IRA-420]=1g/L).*

III.3 Effect of adsorbent dose

In order to study the effect of the initial adsorbent dosage on adsorption, we have operated in an interval of sorbent concentration between (1 to 3 g/L) for a concentration of 10 mg/L and a free pH. During the adsorption, the temperature of system was kept constant at 295K.

The effect of sorbent dosages on the percentage removal of drug has been shown in Fig.4.

From Fig.4. We can observe that the adsorption of Rifampicin reached equilibrium at variable time according to the initial Amberlite IRA-420 dosage.

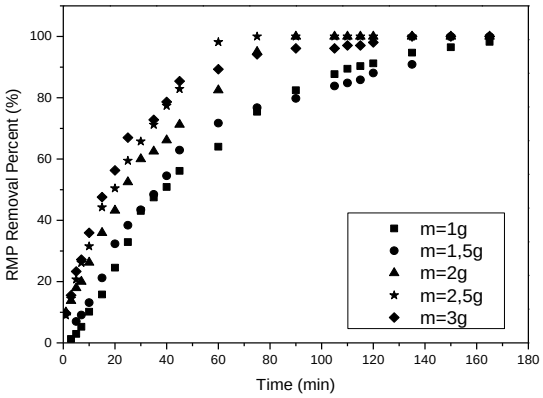


Figure 4. *Effect of adsorbent dosage on the removal of Rifampicin with the Amberlite IRA-420 ([Rifampicin]= 10 mg L^{-1}, 295 K and pH_{free}).*

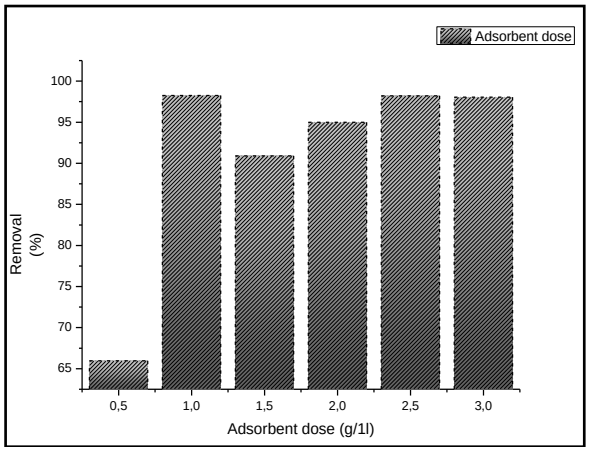


Figure 5. *Removal efficiency obtained for different initial Amberlite IRA-420 dosage at ([Rifampicin] = 10 mg L^{-1}, 295 K and pH_{free}).*

As shown in the Fig.5, it is expected that an increase in the dosage of adsorbent should conduct to a clear decrease in equilibrium time and a slight increase in the removal of drug adsorbed due to the presence of more sites onto the surface of the adsorbent.

It can be observed from the figure 5 that the % uptake increased from 66 to 98 % when adsorbent dose is increased from 0.5 to 1 g/ L, respectively. This may be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increasing dose of the adsorbent. For a given Rifampicin concentration (10 mg/L), 1 g/L of adsorbent is observed to be the

upper limit for the removal of rifampicin. This is probably due to the drug resistance tomass transfer from bulk liquid to the surface of the solid, which becomes important at high adsorbent loading. Moreover, the percentage removal is slightly decreased with the higher dosage (> 1g/L). It might have happened that the higher dosage causes particles aggregates and repulsive forces between binding sites.

III.4 Effect of initial pharmaceutical concentration

The effect of initial pharmaceutical concentration on the efficiency of adsorption of Rifampicin on the Amberlite IRA-420 was evaluated using batch agitation in 1 L beaker containing Rifampicin solution of initial concentration ranging from 10 to 30 mg L^{-1} and keeping the other control parameters at their optimum conditions. Results are shown in fig.6.

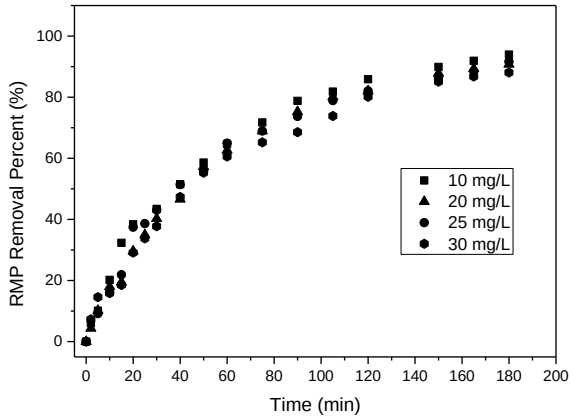


Figure 6. *Effect of [RMP] on the removal efficiency ([IRA-420] =1 g /L, 295 K and pH_{free}).*

From results shown in Fig.6, it can be seen that the amount of Rifampicin adsorbed decreased slightly with the increasing initial pharmaceutical concentration. This may be due to the saturation of the adsorption sites at higher Rifampicin concentrations.

IV. Adsorption isotherms

Three isotherm models related to adsorption equilibrium have been tested in the present study, i.e. Freundlich, Langmuir and Temkin isotherm models.

The mathematical expressions are given by Eqs. (3)- (5), respectively, as follows:

$$\frac{1}{q_e} = \frac{1}{q_{\max} k_L} \frac{1}{C_e} + \frac{1}{q_{\max}} \qquad (3)$$

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \qquad (4)$$

$$q_e = B \ln k_T + B \ln C_e \qquad (5)$$

Where q_m and k_L are Langmuir constants related to the adsorption capacity (maximum amount adsorbent per gram of adsorbent (mg/g)) and energy of sorption (L/mg), respectively. Values of q_m and k_L can be calculated from the slope and intercept of the linear plot of $1/q_e$ against $1/C_e$.

k_F and n are Freundlich constants related to an approximate indicator of adsorption capacity and adsorption intensity, respectively. The Freundlich coefficients n and k_F are obtained from the plots of Inq_e versus InC_e.

In the Temkin isotherm model k_T (L/g) is the equilibrium binding constant corresponding to the maximum binding energy, and constant B is related to the heat of adsorption. A plot of q_e versus lnC_e enables the determination of the isotherm constants B and k_T.

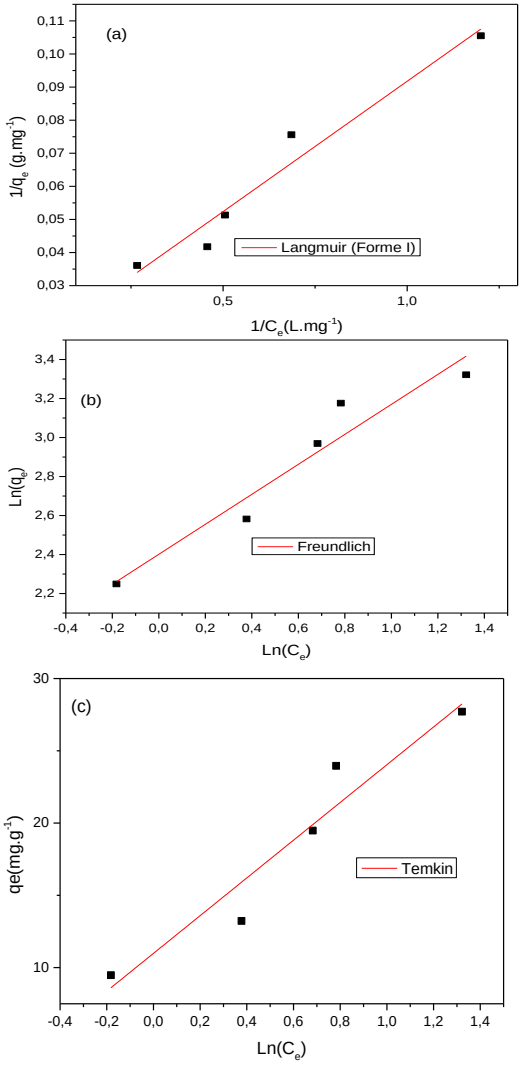


Figure 7. *Langmuir (a), Freundlich (b) and Temkin (c) linear isotherm models for the rifampicin adsorption on IRA-420.*

Investigation of the equilibrium sorption was carried out for five different concentrations, at 295K and free pH. The comparison of the applicability of each model was made essentially on the basis of the linear coefficient correlation R^2 values. The calculated constants of the three

isotherm equations along with R^2 values are presented in Table 3. This table shows that the Langmuir adsorption isotherm model, is the most suitable for describing the adsorption of Rifampicin on Amberlite IRA-420 (R^2= 0.944).

Table 3. *Parameters of Freundlich, Langmuir and Temkin linear isotherm models for the rifampicin adsorption on IRA-420.*

	ISOTHERM MODELS
	FREUNDLICH
n	1.30
k_F ($mg\ L^{-1/n}\ g^{-1}\ L^{1/n}$)	11.03
R^2	0.908
	LANGMUIR
q_{max}($mg\ g^{-1}$)	77.04
k_L($L\ mg^{-1}$)	0.16
R^2	**0,944**
	TEMKIN
k_T	2.32
B	13.05
R^2	*0,904*

V. Kinetic models

Kinetics of adsorption is an inevitable characteristic to be responsible for the efficiency of adsorption. Various kinetic models such us Pseudo second-order, intra-particle diffusion and Elovich have been applied to the experimental data to predict the adsorption kinetics. The applicability of the kinetic model is compared by judging the correlation coefficients R^2.

V.1 Pseudo-second-order model

The pseudo second-order model can be applied for the entire adsorption process. The rate limiting-step may result from chemical adsorption. The model may also suggest that two active sites participate in uptake of contaminant(s). [22]
Pseudo-second-order model in the linear form is expressed by Eq.(7).

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \qquad (7)$$

Where the term q_e has the same meaning previously mentioned and is expressed in mg/g and k_2 is the rate constant of pseudo second-order adsorption expressed in (g/mg min).

The initial constant h is defined as:

$$h = k_2 q_e^2 \qquad (8)$$

Thus, a plot of t/qt against t of Eq. (7) should give a linear relationship with a slope of $1/q_e$ and an intercept of $1/kq^2_e$.

All Pseudo second-order parameters are listed in Table 4. From this table we observe that the maximum adsorption capacities calculated increase from (12,01 to 35,86) when the concentration of Rifampicin increased from 10 to 30 mg/L due to large number of Rifampicin ions which are adsorbed at the available adsorption sites, while the k_2 decreased with increasing initial pharmaceutical concentration.

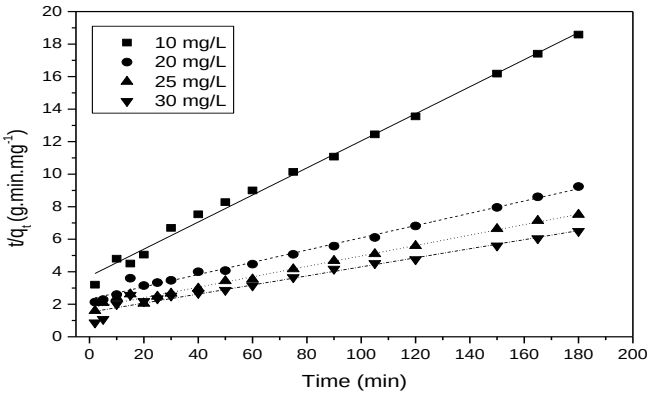


Figure 8. *Pseudo-second-order adsorption kinetic of Rifampicin on the Amberlite IRA-420 at various initial concentrations.*

Table 4. *Parameters for Pseudo-second- order equation*

	$k_2 10^3$ (g/mg min)	$q_{e\ Cal}$ (mg/g)	h (mg/g min)	R^2
C_i(mg/L)				
10	1.85	12.01	0.268	0,994
20	0.61	26.53	0.431	0,989
25	0.58	31.17	0.566	0,990
30	0.51	35.86	0.660	0,966

V.2 Elovich equation

The Elovich equation is one of the most useful models for describing chemisorption [23] and is given as follows:

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln t \qquad (9)$$

Where a is the initial adsorption rate ($mg\ g^{-1}min^{-1}$) and b is the desorption constant ($g\ mg^{-1}$) related to the extent of surface coverage and activation energy for chemisorption.

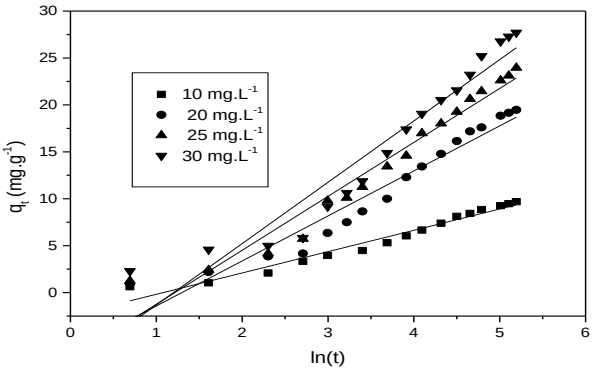


***Figure 9**. Plot of Elovich equation for sorption of the Rifampicin on the Amberlite IRA-420 at various concentrations.*

***Table 5.** Parameters for Elovich equation*

	a (mg/g min)	b (g/mg)	R^2
C_i (mg/L)			
10	0,77	0,43	0,961
20	1,31	0,20	0,936
25	1,70	0,17	0,952
30	1,96	0,15	0,920

Table 5 lists the kinetic constants obtained from the Elovich equation. From this table we can observe that the values of a and b varied as a function of the rifampicin concentration, the value of b decreased from 0,43 to 0,15g/mg due to the less available surface for the Rifampicin ions. On the other hand, an increase in the solution initial concentration from 10 to 30 mg/L leads to an increase in the value of a from 0,77 to 1,96 mg/g min. This means that adsorption increased while desorption decreased during increasing solution concentration.

VI. Conclusion

Based on the experimental results, the following conclusions can be drawn:
The Amberlite IRA-420 resin showed an excellent affinity in the adsorption of the rifampicin. The parametric study showed that the uptake efficiency and the adsorption capacity reach 98% and 9,8 mg /g respectively, under optimized conditions (pH of 6) adsorbent dose of 1g/L, rifampicin concentration of 10 mg/ L and temperature of 295K. The Langmuir isotherm model is found to be the best fitting. Batch studies showed that the pseudo-second-order kinetic model can adequately predict the adsorption of rifampicin on IRA-420 resin.

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