Biosorption of pharmaceuticals from aqueous medium by *Luffa Cylindrica* Fibres: Application of the linear form of Redlich-Peterson isotherm equation

Amel Aloui[1, 2], Nouzha Bouziane[1], Hacene Bendjeffal[2,3*], Yacine Bouhedja[3], Abdennour Zertal[1]

[1] *Laboratory of Innovative Techniques for the Environment Preservation, University of Mentouri Brothers - Constantine 1, 25000, Algeria.*

[2] *Laboratory of physical chemistry anD biology of matrials, Higher Standard School of Technological Education –Skikda, Algeria.*

[3] *Laboratory of water treatment and recovery of industrial waste, Annaba University, Algeria.*

***** Corresponding author: Dr. Hacene Bendjeffal (drbendjeffal@gmail.com). *Laboratory of water treatment and recovery of industrial waste, Annaba University, Algeria.*

Abstract

This study is focused on the removal of Dextropropoxyphene (DPP) and Paracetamol (PAR) from aqueous solutions by sorption on *Luffa Cylindrica* fibres, as a low-cost biosorbent, that was initially characterized using BET, FTIR spectroscopy, and SEM analysis. The sorption study has been realized by the batch method with the effect of the biosorbent amount, initial concentration, solution pH and batch temperature. The modelling of the sorption phenomenon was based on the mathematical approach of the modified Redlich-Peterson isotherm equation (RP), where the dimensionless form of this isotherm, corresponding to the optimal curve, allows the α parameter evaluation. The same value of α was obtained for both pharmaceutical compounds, while the $b_{RP}C_e^{\alpha}$ values where 2 and 10 for DPP and PAR, respectively. The linear regression of the Redlich-Peterson isotherm equation was also confirmed by analysis of variance (ANOVA). The obtained results show that p-value is less than 0.05, with correlation coefficients (R_{adj}^2) equal to 0.9515 and 0.9283 for DPP and PAR, respectively. The kinetics modelling shows that the sorption mechanism obeys the pseudo-second-order and intraparticular diffusion. The adsorption process is exothermic, spontaneous and the molecules of the two pharmaceutical products have a random behaviour on the *Luffa Cylindrica* active sites.

Keywords: Dextropropoxyphene, Paracetamol, sorption, *Luffa Cylindrica*, Redlich-Peterson isotherm.

1 Introduction

In the last dictate, the removal of chemical, biochemical, and biological pollutants (heavy metals, dyes, and pharmaceutical products…) from natural aquatic mediums became a necessary operation to save the environment. The great dispersal of these hazards related

directly to the fast growth of the manufacturing activities in our cities [1,2]. Pharmaceutical pollution becomes an inevitable environmental problem of emerging concern; these kinds of compounds are persistent and they have incompletely degraded in sewage treatment stations [3-5] due to their resistance to biodegradation [6] and persistence in aquatic ecosystems. In addition, the presence of these products in aquatic media can produce serious damage to different microorganisms[7].

The consumption of pharmaceuticals is increasing in a dreadful way, which poses a great menace to life on earth[8]. Animals and humans in different levels of transformation emit these products[9]. Many of these pharmaceuticals degrade in nature and are transformed into by-products resulting from direct/indirect photolysis or hydrolysis[10]. In fact, some of them can be removed by adsorption techniques, under random environmental conditions. In another way, the physicochemical parameters and the mechanisms that serve for the best natural degradation are not controlled. However, many compounds persist in aqueous systems around the world[11]. The presence of these chemicals in surface water can be explained by the incomplete removal of these hazards during treatment processes of wastewater[12]. Unfortunately, there is a lack of research on the identification of by-products such as metabolites and products of transformation from pharmaceutical elimination and degradation that persist in all types of water[13,14].

Since 2001, the environmental risk assessment has been done first by determining an environmental predicted concentration (PEC) at the surface water level[15]. Below 0.01 $\mu g.L^{-1}$, the considered molecule does not present any environmental risk under normal conditions of prescription and use. However, if the 'PEC' exceeds this limit value, the requisition of deeper data on the physicochemical, pharmacological, and toxicological properties with a study of degradability, persistence or bioaccumulation capacity of the molecule is envisaged. The limit values corresponding to predicted environmental concentration (PEC) are for the soil of 100

$\mu g.kg^{-1}$. This threshold is directly related to veterinary drugs. In the case of the marine environment, the convention 92 considers about twenty molecules for pharmaceutical use as the most dangerous for the marine environment, such as clotrimazole.

Dextropropoxyphene (DPP) and Paracetamol (PAR) are considered among the pharmaceuticals widely used. However, the occurrence of these drugs in water sources with high amount can be dangerous to health. Recent studies revealed that the (DPP) has been detected with important concentrations in surface waters. In the estuary water, Roberts and Thomas (2005) recovered the DPP at concentrations varied between 0.008 $\mu g.L^{-1}$ and 0.033 $\mu g.L^{-1}$. The measured data in the sediments are almost non-existent, in particular, the studied molecule.

PAR is antipyretic and analgesic. It seems to inhibit cyclo-oxygenase (Cox_1-Cox_2) in the nervous system. It is frequently found in wastewater and its concentration at the inlet in different treatment plants is measured at 6 $\mu g.L^{-1}$[16]. The maximum concentration of PAR in surface waters is about 0.11 $\mu g.L^{-1}$[17]. Although it is a highly degradable compound, its highest concentration in seawater reached 250 $\mu g.L^{-1}$[18].

Protection of aquatic ecosystems and different water sources from the undesirable and toxic effects of pharmaceuticals and their transformation products has been the subject of several types of research works[13-7]. The chemical[19-23], biological[24], electrochemical[25], and bio-electrochemical[26] methods have proved their limitation towards the treatment of wastewater. That is why the adsorption remains the most preferred technique compared to the other processes[19]. The principal advantages of an adsorption phenomenon are a short-term investment of both cost and land, and it remains a simple and very efficient process in the elimination of toxic and harmful substances[27,28]. The pharmaceuticals removal using the activated carbon as an adsorbent is a promising process. This material is characterized by high porosity, an important surface area, and it has a good capacity in the elimination of toxic

pollutant in a short time; it can be found as granular or powdery black material[29], but it is too expensive[30]. The selection of highly efficient adsorbent is primordial for a successful adsorption process, essentially in the pharmaceutical elimination. However, the bio-sorption using natural adsorbents such as natural clays, marine algae, and plants fibres are among the most practical, green, and economical techniques used in pollutants removal. This study is undertaken to evaluate the use of *Luffa Cylindrica* (*LC*) for (DPP) and (PAR) sorptive removal from the aqueous medium at different temperature and pH values. The model analysis of the batch adsorption system is given by a graphical representation of the *Luffa cylindrica* residual amount in aqueous solution. This application is generally based on choosing an empirical relationship between experimental data and relevant dimensionless parameters using regression techniques[31]. Linear regression has been successfully employed to investigate the parameters of sorption isotherms[32]. Modelling of some adsorption system, by plotting solid-phase amount against the concentration of residual liquid using the two and three parameters of isotherm (Langmuir, Freundlich, and Redlich-Peterson) have shown some of the inaccuracies. The poor precision of these isotherms is due essentially to a poor linear fitting model. Feng-Chin-Wu has proposed a novel linear exponential form of Redlich-Peterson (RP) by estimating the three parameters isotherm using the characteristic line obtained from the dimensionless form of Redlich-Peterson equation[33]. To our knowledge, this study is first to its kind, which elucidates adsorptive properties of (*LC*) to removal pharmaceutical products from aqueous medium.

The aim of this work is the application of *Luffa cylindrica* (*LC*) in DPP and PAR removal from an aqueous medium in a batch system, firstly and the correlation of our experimental results using a mathematical approach. This approach is based on the linear form of Redlich-Peterson isotherm equation proposed by Feng, secondly. The exponential form has shown its superiority for fitting Redlich-Peterson isotherm to experimental data obtained from sorption

processes compared to the logarithmic form used currently by the selection of a suitable α value range, which was determined from the dimensionless form plot of Redlich-Peterson equation. Analysis of variance (ANOVA) was also employed to investigate the adequacy of the fitted model by determining the adjusted correlation coefficients (R^2_{adj}) and mean square of squares (SS). Statistical significance is judged by the Fisher value (F-value) and the probability value (p-value) which must be less than 0.05.

2 Materials and methodology

2.1 Reagents

The biosorbent *Luffa Cylindrica (LC)* was purchased from a local shop in Skikda, Algeria. Only, the *LC* fibres were used. The adsorption experiments were carried out with two pharmaceuticals: Dextropropoxyphene (Sigma Aldrich, 98.22%) and Paracetamol (Merck, 99.60%). Their main Physico-chemical characteristics are collected in Table 1. All the reagents were analytical grade chemicals and used without further purification. Deionized and distilled water were used throughout this study.

Table 1. Parameters of RP isotherm.

	α	q_{mon} (mg g^{-1})	b_{RP}	R^2_{adj}
DPP	0.8	33.8066	0.5898	0.9515
PAR	0.8	38.2895	3.4355	0.9265

2.2 Adsorbent pre-treatment and Characterization

100g of *luffa* fibres were soaked in 1L of hydrogen peroxide for a period of two days to remove adhering dirt. Thereafter, fibres were washed with distilled water and dried in an oven at 80 °C for 12 h. After, they were dipped in NaOH (0.1N) solution for about 1h to increase their hydrophilicity. Alkalized fibres were finally washed with distilled water and dried again at 80 °C for 12 h.

The Fourier transform infrared ray (FTIR) spectrum of the treated fibres was performed using

a Shimadzu Spectrometer (FTIR 8700, Japan) via KBr pellets method. The spectra were collected in the range of 400- 4000 cm^{-1} with a spectral resolution of $4cm^{-1}$. Their surface morphology was analysed using scanning electron microscopy (SEM) (JEOL, JSM-7600F, Japan). Their porosity was determined by nitrogen adsorption-desorption isotherms measured at 77 K using Cooltronic micro-meretics 2100E model surface area analyser. The N_2 isotherms were used to calculate the specific surface area using the BET equation.

2.3 pH of zero point charge (pH_{PZC})

The point of zero charges (pH_{pzc}) was carried out to determine the pH value for which the surface net charges of the *Luffa cylindrica* are zero. To quantify the pH at the point of zero charges, 0.1 g of *LC* has been added to 50 mL of distilled water, whose initial pH has been adjusted with NaOH or HCl in the range of 2 to 12. The containers are sealed and placed in a shaker for 24 h, after which the pH is measured. The PZC occurs when there is no change in the pH after contact with the carbon. The value of (pH_{PZC}) is illustrated in Fig 1.

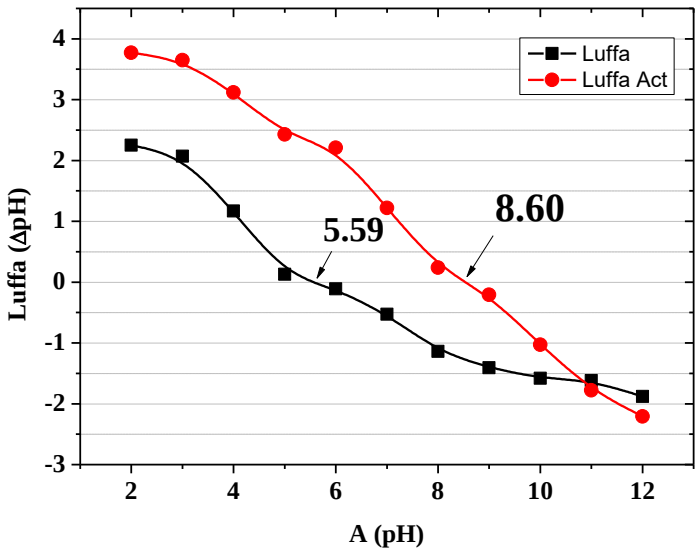

Figure S1: pH of zero charges of natural and modified *luffa*

2.4 Biosorption Experiments

The study of parameters affecting the biosorption process of DPP and PAR solutions onto *LC* allowed us to determine the optimal value of each parameter, which accords to the highest elimination rate. Thus, this study is done by changing the values of a studied parameter and fixing the other parameters.

2.5 Effect of different parameters of adsorption processes of DPP and PAR onto LC

The optimisation of the operating conditions has been studied by varying one parameter and setting the others constants. The study of the effect of pH solution is done in a range 2 to 12, at room temperature, 0.1 g of *Luffa* and 50 ppm of the solution of each pharmaceutical. For the temperature, the same condition was taken by varying the range of temperature between 10°C and 50°C and with the free value of solution pH. The optimal *Luffa* mass was obtained by changing the mass interval between 0.05 to 0.4 g of *Luffa fibres* (50 ppm of solution, free pH and ambient temperature).

The stock solution (200 mg L^{-1}) of DPP or PAR has been prepared by adding 50 mg of the solid pharmaceutical in 250 mL of deionized water and the different initial concentrations (20-120 mg L^{-1}) of an aqueous solution of each product were obtained by dilution. The contact of 100 mg of (*LC*) with each initial concentration was carried out at ambient temperature and pH value of the solution for 1h to reach equilibrium state. Separation of biosorbent from solution was carried out by filtration through a Whatman filter paper prior to analysis and the amount of uptake of each solution was analysed by UV-Vis spectrophotometer Shimadzu at 257 and 243 nm for DPP and PAR, respectively.

The DPP and PAR removal efficiencies (R%) have been determined at various experimental conditions. The R% was calculated according to the following equation:

$$R\ \% = (C_0 - C_t) \times 100 / C_0 \qquad (1)$$

where C_0 and C_t are respectively the concentration (mg L^{-1}) of adsorbat at initial and t timerespectively. Equation 2 was used to estimate the adsorption amount (q_e) of DPP and PAR as shown in the following formula:

$$q_e = (C_0 - C_e) \times V / W \qquad (2)$$

In which C_e is the equilibrium concentration of pharmaceutical compounds in aqueous media (mg/L), W the weight of the biosorbent (g) and V the solution volume (L).

2.6 Adsorption isotherms

The Redlich-Peterson (RP) isotherm model is more accurate than the Freundlich and Langmuir equations in describing the sorption system [33-34]. The RP isotherm equation is generally used to explain the formation of monolayer and multi-sites interactions phenomena at the same time[35]. It also describes homogeneous adsorption mechanism systems[36]. In addition, it integrates the isotherms of Freundlich and Langmuir into a single equation[37]. The non- linear Redlich-Peterson isotherm equation is presented as:

$$q_e = \frac{q_{mon} b_{RP}}{1 + b_{RP} C_e^{\alpha}} C_e \qquad (3)$$

where b_{RP} and q_{mon} are the parameters of Redlich-Peterson isotherm equation. The exponent, α, as it ranges from zero to 1, it has two limiting behaviors: Henry's law form for α equal to 0 and Langmuir forms for α equal to 1. At low concentrations, it is also similar to Henry isotherm and performs like Freundlich equation for high concentrations[38]. The linear, non-logarithmic, form of equation (3) is given by Eq.4:

$$\frac{C_e}{q_e} = \frac{1}{b_{RP}\, q_{mon}} + \left(\frac{1}{q_{mon}}\right) C_e^{\alpha} \qquad (4)$$

However, the dimensionless of RP equation form proposed by Feng is expressed as follows:

$$\frac{q_e}{q_{ref}} = \left(\frac{C_e}{C_{ref}}\right) \frac{\left(\frac{1}{b_{RP} C_e^{\alpha}}\right) + 1}{\left(\frac{1}{b_{RP} C_e^{\alpha}}\right) + \left(\frac{C_e}{C_{ref}}\right)^{\alpha}} \qquad (5)$$

Here, C_{ref} is the adsorption system highest equilibrium concentration and q_{ref} is the equilibrium adsorption quantity at C_{ref}. α is a parameter attained by trial and error for

$b_{RP}\ C_{ref}^{\alpha}$ = 2 and 10, respectively [33]. Its value must be less than 1. The plot of q_e/q_{ref} against C_e/C_{ref} of Eq. (5) gives an indication on the optimal line that corresponds to the appropriate α value. The data obtained from the batch concentration studies were fit into Redlich-Peterson expression, the linear regression lines have been realized by plotting C_e/q_e versus the C_e^{α} of Eq.(4), with different values of α. The values of C_e^{α} were calculated for each α value in the first, after that, the regression line associated with the specific value was plotted. The values of other parameters such as b_{RP} and q_{mon} were estimated from the slope and intercept of linear plot of Eq. (4). The ANOVA has been introduced to compare the mathematical model validity. The analysis of variance presents the statistical results and the diagnostic checking test, which allows the model to be evaluated[39]**.** If the p-value is inferior than 0.05, the studied model is significant. The low mean square sum of squares (SS) is also evident that the model is apparently the best.

3 Results and discussion

3.1 Characterization of the biomaterial

The fibres of (*LC)* are composed of 60 % cellulose, hemicelluloses 30% and 10% lignin a fact that makes it flexible and durable biosorbent. Scanning electron microscopy (SEM) analysis of (*LC*) brought us the presence of macropores in the structure of (*LC*) fiber. Fig 2 of *Luffa Cylindrica* SEM illustrates the fibrous nature with some fissures and small holes having about 1µm diameter, which facilitate the biosorption of DPP and PAR. The surface area of *(LC*), using BET method, is 123 $m^2\ g^{-1}$.

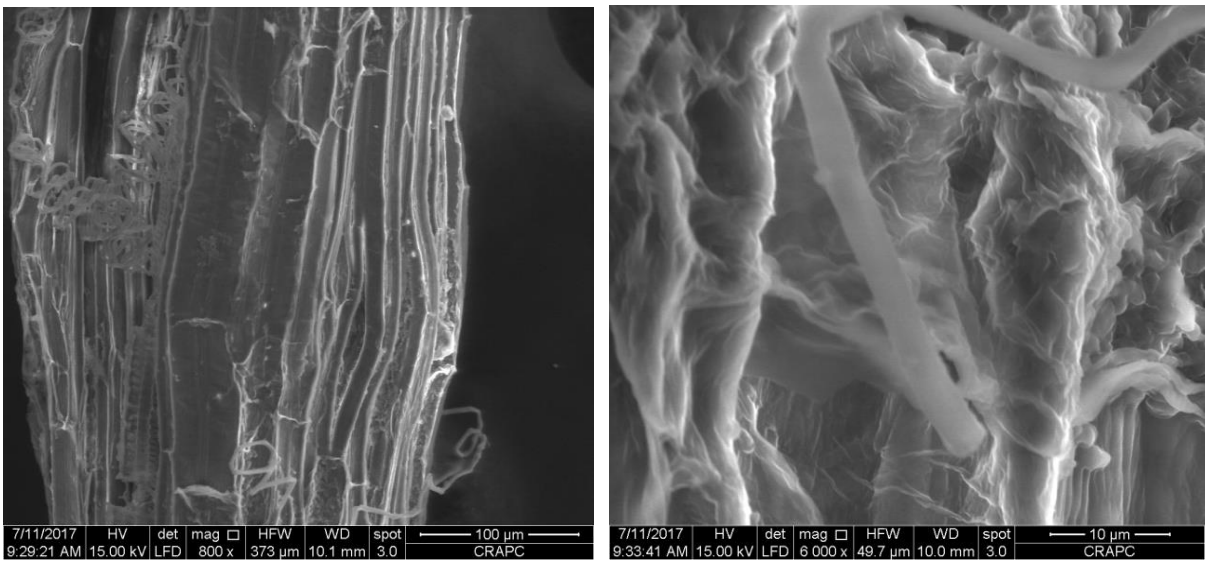

Fig 2. Scanning electron microscopy of *Luffa Cylindrica (LC)*

The point of zero charge (pzc) of LC and modified *LC* is about 5.59 and 8.60, respectively. This former value may be attributed to the alkaline treatment. Consequently, the surface of modified *LC* is predominantly positively charged below 8.60 and negatively charged above this value. As a consequence, adsorption of compounds could depend from pH.

Fig 3 shows the FTIR spectra of *Luffa*. The significant bands obtained and assigned to the functional groups found on the surface of alkalized *Luffa* are shown on the same Fig. The spectrum displays the following bands: The strong band located at 3444.63 cm^{-1} evidences the presence of O-H groups. The bands that are situated between 2858.31 and 2920.03 cm^{-1} are attributed to the symmetrical absorption in the bond –C-H. The band 2858.31 cm^{-1} appears as a shoulder. The peaks appeared at about 1762.82 cm^{-1} are assigned to C=O band (Pectin) [40].

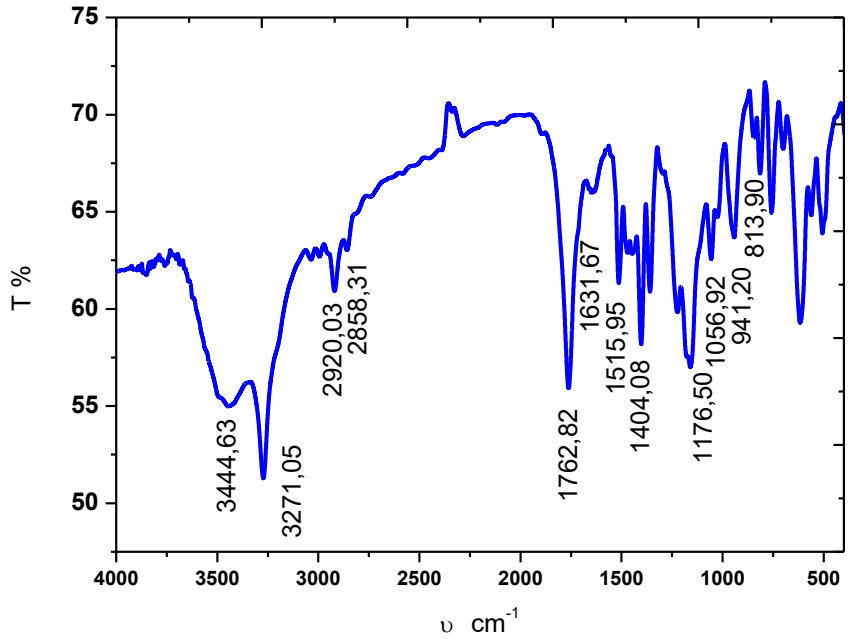

Fig 3. FTIR spectrum of alkalized *Luffa Cylindrica (LC)* biosorbent

The weak band at 1388.60 cm^{-1} is assigned to C–H, the shaper band at 1404.08 cm^{-1} corresponds to CH_2 and CH_3. The band located at 1515.93 cm^{-1} is due to benzene ring stretching (lignin) [30]. The peaks ranging between 1000 and 1300 cm^{-1} correspond to C–O (ketones), specially the clear peak at close to 1058.92 cm^{-1} represented C-O (cellulose)[40] and that's observed at 1176.50 cm^{-1} may correspond to C-O-C (cellulose and hemicellulose) [30]. Finally, the carbohydrate (C-C) peaks are located between 813.90 and 941.20 cm^{-1}.

3.2 Parameters affecting the DPP and PAR adsorption process

3.2.1 Effect of initial pH

It is well known that the sorptive uptake of the organic and inorganic pollutants can be significantly influenced by the initial pH of the aqueous medium. Indeed, the concentration of hydroxyl and hydrogen ions affects the adsorption process through the dissociation of functional groups on the adsorbent surface and/or the ionization degree of the adsorbed molecules [30]. The variations of DPP and PAR removal by *LC* at various pH values (2.0-12.0) were depicted in Fig 4a. It demonstrates that at all experimental pH values, except pH 10, the

adsorption process is more efficient with DPP than PAR. Moreover, the percentage of removal seems to exhibit dissimilar behaviour. Actually, the percentage removal of PAR slightly decreased from 81% to 66% with increasing pH from 2.0 to 10.0 and increased when the pH value was raised above 10.0 (72% at pH 12.0). Herein, it should be noted that the *LC* surface is positively or negatively charged when the solution pH is above or below the pH_{pzc} (8.52). So, the decrease of PAR adsorption with increasing pH from 2.0 to 10.0 and the increase of R% at pH 10.0 to 12.0 can be explained by the electrostatic interaction between the adsorbent surface and the paracetamol. Concerning DPP, the optimal efficiency of its removal (67.97%) is appropriate for the basic pH value (pH = 10.0). Thus, it can be explained by the occurrence of the great number of hydroxide function available on (*LC)* surface at pH in range (2.0-4.0), which is positively charged. The DPP molecules will be absorbed in an ionic form. The increase in pH leads to increase in the sorption of the DPP and on the negatively charged surface of the sorbent to pH = 10.10 and then a decrease in the adsorption is observed (pH = 12, for example). This decrease is attributed to the strong electrostatic repulsion between the *Luffa* particles and adsorbate molecules negatively charged (pKa (DPP) = 6.3). In addition, DPP tends towards the non-ionic form for higher pH values (pH> 10.10) and anions will be surrounded by water molecules and will not be significantly adsorbed.

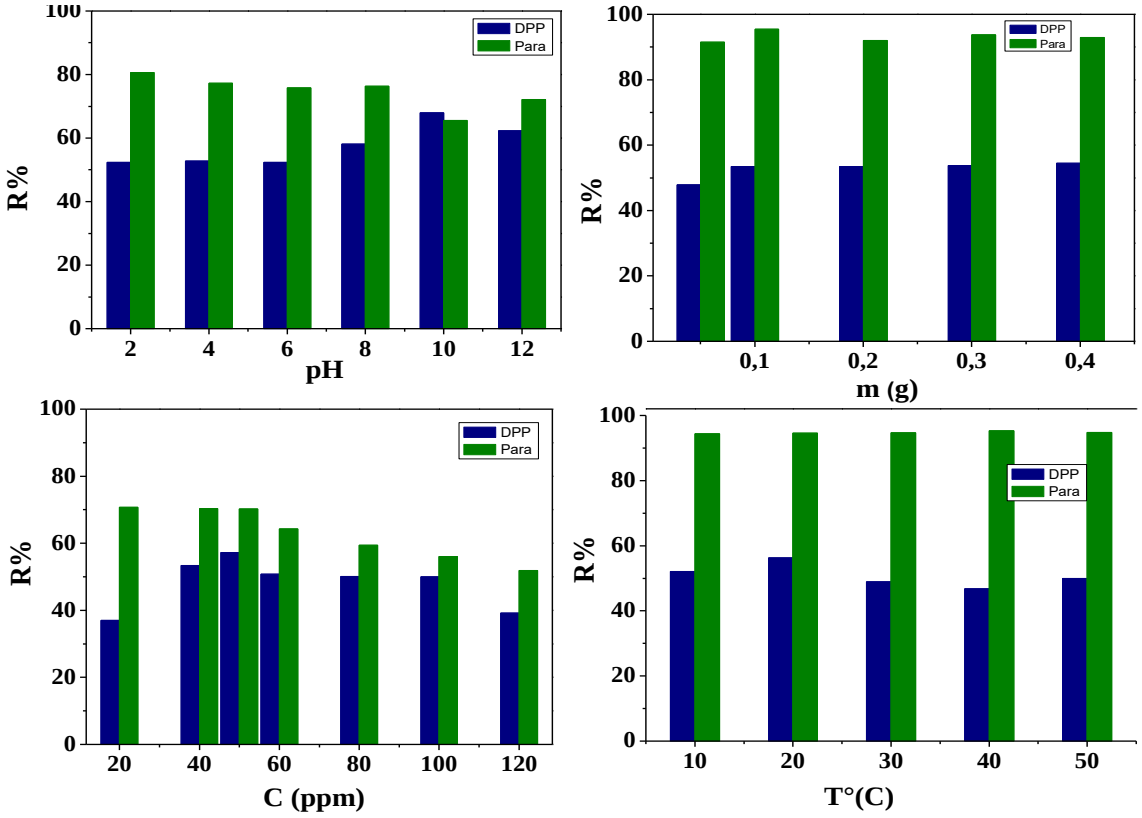

Fig 4. Histogram of different Parameters affecting DPP and PAR biosorption onto (*LC*).

3.2.2 Effect of LC masse

Regarding the used dose of *LC*, which range from 0.05 to 0.4 g, we note that 0.1 g is sufficient to eliminate 53.52% of DPP and 95.55% of PAR (Fig.4b). With this amount, the greater part of the molecules of each pharmaceutical can take place on sorbent sites.

3.2.3 Effect of pharmaceutical concentration

About the initial concentration for each pharmaceutical, the highest rate of DPP adsorption (54.29%) is attributed to 50 mg L^{-1} (Fig.4c). While, the optimal initial concentration of Paracetamol, appropriate for the highest elimination rate (R =70.70%), is equal to 20 $mg.L^{-1}$.

3.2.4 Effect Temperature

The media temperature effects on sorption onto (*LC*) is remarkable for the temperature 20°C and the adsorption efficiency (R %) is equal to 56.31% (Fig.4d), whereas for the optimal temperature for the highest elimination of PAR (R = 95.27 %) equals to 40 °C.

3.3 Adsorption Isotherms

The obtained results from the application of the new mathematical approach of RP isotherm equations are depicted in Fig 5 and are listed in Table1. Figs 5a and 5c represent the dimensionless RP form presented by Equation 5. Both Figs illustrate the presence of a single line that passes through experimental points and verifies the main condition of RP theorem, which is α value less than unity. This line corresponds to α value equal to 0.8 for both cases (DPP and PAR). Nevertheless, with a difference in the $b_{RP}\,C^{\alpha}_{e}$ value, of which $b_{RP}\,C^{\alpha}_{ref}$ is 2 for DPP and 10 for PAR. The data of DPP and PAR adsorption have been investigated according to the linear form of Langmuir isotherm of the Equation 3 (α equals to unity).

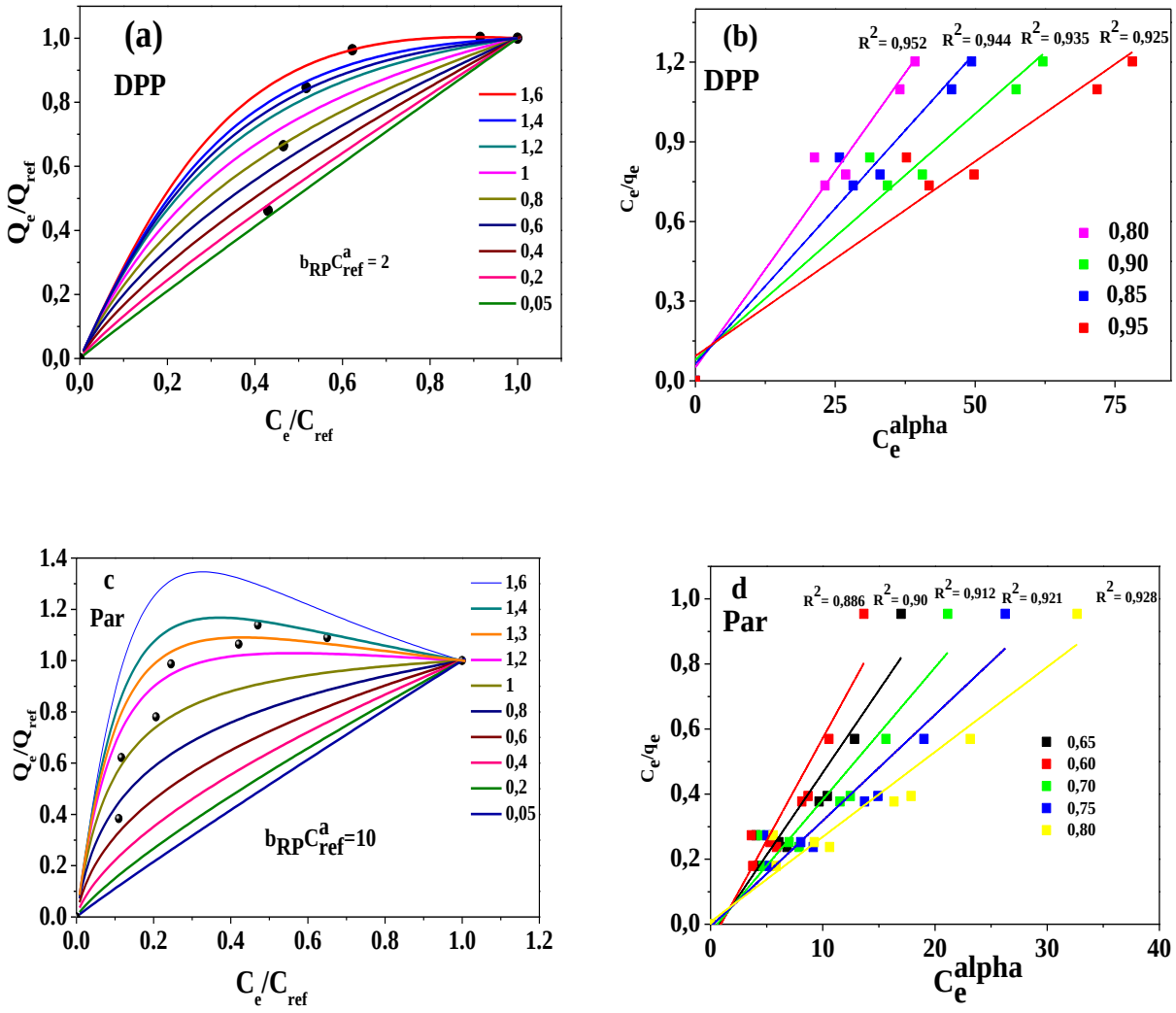

Fig 5. Dimensionless RP form (a, c) and exponential linear form of RP (b, d) of DPP and PAR

The retained results are collected in Table 2, where b_{RP} has become K_L and q_{mon} is taken q_m. These lines proved to be linear over the majority of the experimental points of the concentration range studied for DPP and PAR, with an extremely high value of R^2_{adj} for Par (R^2_{adj} = 0.9364). Tables 1 and 2 show that the biosorption model constants of DPP onto *luffa cylindrica* fibres can be well defined by RP equation since a higher adjusted linear regression correlation coefficient (0.95) was obtained for this model. Thus, the same constant of PAR adsorption isotherm onto (*LC*) was found equal to 0.93 for Langmuir model (obtained using the linear equation RP when α equals 1) (see Table2). The monolayer sorption capacity for PAR is considerably highest (q_m = 97.0873 mg g^{-1}). It can be given information that *luffa cylindrical* fibres have homogeneous surface energy [41].

Table 2. Parameters and ANOVA for adsorption of DPP and PAR for α = 1 (Langmuir Isotherm resulting from RP model)

	K_L	q_m(mg g^{-1})	R^2_{adj}	SS	F-value	p-value
DPP	4.4305	12.1951	0.8320	0.1499	20.8048	0.010
Par	7.7864	97.0873	0.9364	0.4246	104.0418	**5.1727×10^{-5}**

In the present research, the ANOVA has been introduced to guess the goodness of the studied model fit. If the model data forms are more significant, the sum of square (SS) or mean square (MS) will give small values, P-value must be smaller than 5% and F-value will be higher. From Table S2, we can conclude that the regression explains well the studied phenomenon since the meaning of the model risk is less than 0.05 ($p < 1.8411 \times 10^{-5}$ for PAR and $p < 5.7114 \times 10^{-4}$ for DPP). Of course, the calculations of F-value (99.1702 for DPP and 104.6546 for PAR) confirm that this model is extremely significant. The adequacy of the fitted model has been judged by the adjusted coefficient of correlation R^2_{adj}, which measures the total variation proportion in the average response clarified by the regression. In fact, it is the correlation between the experimental and adapted model. Furthermore, the adjusted correlation

coefficient R^2_{adj} is more than enough to give a concordance between the experimental results and the adapted model of the linear exponential form of RP isotherm Equation 4. Figs 4b and 4d show the goodness of the experimental results fitting. The value of R^2_{adj} mentioned in Table 1 showed that only 4.85 % and 7.45% of the total variation of DPP and PAR respectively could not be explained by adapted model.

3.4 Adsorption kinetic modeling

The nature of the adsorption process depends essentially on the chemical and physical properties of the adsorbent surface and the nature of sorbates. The obtained kinetic outcomes of DPP and PAR adsorption were correlated using various conventional methods, namely, the intraparticle diffusion, pseudo-first and pseudo-second-order kinetic methods, in order to study the mechanism and rate of DPP and PAR biosorption process onto *Luffa*. Table 3 collects the principal experimental adsorption data obtained using DPP and PAR initial concentrations 40 and 60 $mg.L^{-1}$, respectively, and 0.1g of adsorbent. In 1898, Lagergren proposed the kinetic model of pseudo-first-order[42] using an empiric equation (Table 3), which plots the $\ln (q_e - q_t)$ in terms of the contact time. Previous several studies indicated that this equation is a fruitful model, in which it can provide a good linear relationship between k_1 and q_e, which may be confirmed from its slope and intercept.

An analysis of the experimental q_e values shows that the distance of intercept is aptness and failed in describing the experimental outcomes. In addition, the adsorption rate does not obey to this equation. On the other hand, the adsorption kinetics is explained using the pseudo-second-order kinetic model[43]**.** This last produces a straight line and high values of R^2. The adsorption equilibrium capacity (q_e) and k_2, have been extracted respectively from the intercept and the slope curve and the plot of t/q_t versus t. The theoretical capacity of adsorption (q_e), the correlation coefficient values (R^2) and the experimental closeness values demonstrate that the second order model explain successfully our experimental data (Table 3).

The correlation coefficient (R^2) values reached 0.9999 and a strong similarity between the calculated values of adsorption equilibrium capacity (q_e) and the experimental values of adsorption capacity was obtained under different experimental conditions. Moreover, the process has been also studied using the intraparticle diffusion model[44], which is based on adsorbate mass transfer diffusion, where, the sorption rate is related to the square root ($t^{1/2}$). The K_{diff} and C values were determined respectively from the slope and the intercept of q_t versus $t^{1/2}$ plot. The C values related to the boundary layer thickness and the rate constant intraparticle diffusion K_{diff} are collected in Table 3. Since the curve of the intraparticle diffusion model does not pass through the origin, the diffusion kinetic model and the second-order model proceed controls the process of sorption mechanism.

Table 3. Kinetic model rate parameters obtained using the linear equations.

Model	Equation	Parameter	Value of parameters			
			40 mg L^{-1}		60 mg L^{-1}	
			DPP	PAR	DPP	PAR
First-order kinetic	$ln\,(q_e - q_t) = ln\,(q_e) - kt$ (42)	k_1	0.1274	0.2477	0.1432	_
		$q_{e\,(cal)}$	1.6538	0.7422	2.8352	_
		R^2	0.7622	0.8307	0.9687	_
Second-order kinetic	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t)$ (43)	k_2	0.3329	2.1595	0.1743	2.2050
		$q_{e\,(cal)}$	36.1402	39.2157	54.945	59.1366
		R^2	0.9999	0.9999	0.9999	0.9999
Intraparticle diffusion	$q_t = K_{dif} t^{\frac{1}{2}} + C$ (44)	K_{diff}	0.1584	0.8442	0.1403	0.8442
		C	36.1879	37.2284	53.8869	57.2289
		R^2	0.9190	0.9251	0.8974	0.9251
		$q_{e\,(exp)}$	36.0909	39.1414	54.7273	59.0995

3.5 Thermodynamic study

The thermodynamic parameters of DPP and PAR sorption such as Gibbs energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) have been determined by the following equations:

$$\Delta G° = -RT\ ln\ ln\ K_d \qquad (9)$$

$$ln\ ln\ K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (10)$$

Where, R is the gas universal constant, K_d the thermodynamic equilibrium constant and T the absolute temperature (Kelvin). The thermodynamic study (Table 4 and Fig 6) shows that all $\Delta G°$ *have* negative values, which indicate a spontaneous and feasible process. In addition, the $\Delta G°$ values decreased with increases in temperature. Thus, the $\Delta H°$ negative values indicate that an exothermic sorption process, which could be accredited to a physisorption process mechanism[45], characterized adsorption of DPP and PAR. At the same time, the negative values of ΔS° suggest that the decrease in the concentration of DPP and PAR in solid-liquid interface indicates thereby a rise in the concentration of DPP and Par on the surface of the solid phase

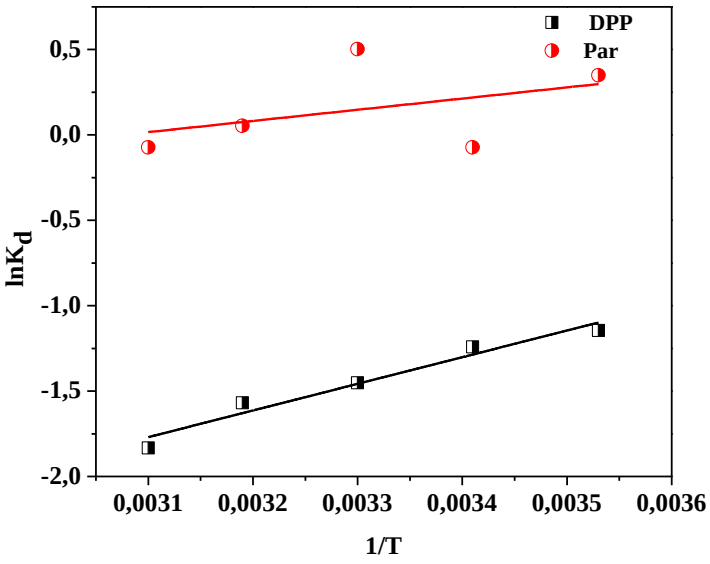

Fig 6. Thermodynamic parameters for DPP and Par adsorption on (*LC*) at different temperature**.**

Table 4. Thermodynamic parameters for biosorption of DPP and PAR onto (*LC)*.

	Parameters	Temperature (K)				
		283	293	303	313	323
DPP	ΔG° (kJ mol^{-1})	-10.9023	-12.8189	-17.5344	- 20.4570	-27.9211
	ΔH° (kJ mol^{-1})	- 12.9798				
	ΔS° (J mol^{-1} k)	- 54.9405				
Par	ΔG° (kJ mol^{-1})	-821.2689	- 178.6351	- 1265.7614	- 136.2763	- 196.9254
	ΔH° (kJ mol^{-1})	- 5.4453				
	ΔS° (J.mol^{-1} k)	- 16.7427				

4 Conclusion

This study demonstrates the suitability and the applicability of the novel dimensionless and exponential linear forms of RP isotherm proposed by Feng, which allowed us to determine easily the parameters of the RP model for DPP and PAR. α value was equal to 0.8 for each studied pharmaceutical, corresponding to an optimum line which gives the other parameters, mainly b_{RP} and q_{mon}. The RP equation involving adsorption on homogeneous active sites is definitely the most suitable modelling tool to describe satisfactorily the DPP biosorption and the Langmuir model showed strong adequacy to describe the adsorption experimental data of PAR onto (*LC)*, by providing the highest adjusted squared correlation coefficients R^2 and the lowest p-value. The kinetic and thermodynamic studies were investigated for the adsorption process. The kinetics curves are successfully characterized by the pseudo-second-order rate equation and the intra-particle diffusion was not the rate-limiting step. The thermodynamic parameters confirmed that the process is exothermic, spontaneous and that the molecules of studied drugs have random behaviour on the surface of (*LC*) used in this work.

Declarations

1. **Availability of data and materials :** Not applicable

2. **Funding** Not applicable

3. **Acknowledgments**

The authors gratefully acknowledge Laboratory of Innovative Techniques for the Environment Preservation, University of Mentouri Brothers - Constantine 1 for providing instrumental facilities for sample characterizations.

4. **Competing interests**

The authors declare that they have no competing interests

5. **Authors' contributions**

The manuscript was mainly based on a draft written by AA, and written through contributions of all authors. All authors read and and approved the final manuscript.

6. **Authors' information**

[1] Laboratory of Innovative Techniques for the Environment Preservation, University of Mentouri Brothers - Constantine 1, Algeria. [2] Laboratory of physical chemistry and biology of matrials, Higher Standard School of Technological Education –Skikda, Algeria.[3] Laboratory of water treatment and recovery of industrial waste, Annaba University, Algeria.

References

[1] Matsubara M E, Karin Helwig K, Hunter C, Roberts J, Subtil, E L, Helen, L. Ecotex Environ Safe. **2020**;192:110258.

[2]Ji Y, Zhang X, Gao J, Zhao S, Dou Y, Xue Y, Chen L. Ecotox Environ Safety. **2020**;188: 109887.

[3] Rúa-Gómez P C. Environ Sci Pollut Res. **2012;**19:689–699

[4] Rúa-Gómez P C. Chemosphere. **2013**;90 :1952–1959.

[5] Arriaga S, de Jonge N, Lund Nielsen M, Rasmus Andersen H, Borregaard V, Jewel K, Ternes T, Lund Nielsen J. Wa Res. **2016;**107: 37-46

[6] Golovko O, Kumar V, Fedorova G, Randak T, Grabic, R. Environ Sci Pollut Res. **2014**;21:7578–7585.

[7] Calisto V, Ferreira I.A.C, Oliveira, J.A.B.P, Otera M, Esteves, V I. J of Env Man. **2015**;152:83-90.

[8] Wahlberg C, Björlenius B, Paxéus N. Wa Sci and Tech. **2011**; 63:1772-1780.

[9] Vymazala J, Bˇrezinová D.T, Koˇzeluh M, Kule, L. Eco Eng. **2016**; 98: 354-364.

[10] Yu-Chen Lin A, Reinhard M. Env Tox and Chem. **2005**; 24:1303–1309.

[11] Zhang Y, Zhu H, Szewzyk U, Lübbecke S, Geissen SU. Chem Eng J. **2017**; 317:454-460.

[12] Sehonova P, Svobodova Z, Dolezelova P, Vosmerova P. Sci of Tot Env. **2018**; 631: 789-794 ·

[13] Mompelat, S., Bot, B.L., Thomas, O. Env Inte j. **2009**, 35, 803–814.

[14] Löffler D, Römbke J, Meller M, Ternes T.A. Environ Sci Technol. **2005 ;**39:5209–5218.

[15] Collette-Bregand M, Alice J, Catherine M, Gilles B. Contamination des milieux aquatiques par les substances pharmaceutiques et cosmétiques-Etat des lieux et perspectives. **2009**; 44.

[16] Roberts P H, Thomas K.V. Sci Total Environ. **2005**;356:143-153.

[17] Kolpin D W, Skopec M, Meyer M T, Furlong E T, Zaugg S.D. Sci Total Environ. **2004**; 328:119-130.

[18] Hari A, Paruchuri R, Sabatini D, Kibbey T.G. Environ Sci Technol. **2005**;39:2592–2598.

[19] Annadurai G. Biop Eng. **2000**;23:451-455.

[20] Kasprzyk-Hordern B, Dinsdale R.M, Guwy A.J. Envir Pollut. **2009**; 157:1778–1786.

[21] Javanbakht M, Attaran A M, Namjumanesh M H, Esfandyari-Manesh M, Akbari-adergani B. J of Chromat B. **2010**; 878:1700–1706.

[22] Roshanfekr R L, Irani M, Divsar F, Pourahmad H, Sayyafan M S, Haririan I. J of the Taiwan Insti of Chem Engin. **2015**;47:190–196.

[23] Cantwell M G, Katz D R, Sullivan J C, Shapley D, Lipscomb J, Epstein J, Juhl A R, Knudson C, O'Mullan G D. Wat Res. **2018**; 142:130-138.

[24] Rozman M, Acuna V, Petrovic M. Envir Pollut. **2018**; 233:1131-1137.

[25] Eversloh C L, Schulz M,Wagner M, Ternes T A. Wat Res . **2015**;72:293-304.

[26] Zhang L, Yin X,Yau LiSF. Chem Eng J. **2015**;276:185–192.

[27] Garg U.K, Kaur M P, Garg V K, Sud D. Biores Tech. **2008**;99:1325–1331.

[28] Thiebault T, Guégan R, Boussafir M. J of Coll and Inter Sci. **2015**;453:1–8

[29] Sahu J N, Acharya J, Meikap BC. J Haz Mat. **2009**;172:818–825.

[30] Altinisik A, Gur E, Seki Y. J Haz Mat. **2010**;179:658-664.

[31] Benmaamar Z, Bengueddache A. J of Appl Sci in Envi Sani. **2007**;2:43-56.

[32] Toprak F, Armagan B. J of Envi Stud. **2013**; 22:1007-1011.

[33] Feng C W, Liu B L, Wu K T, Tseng R L. Chem Eng J. **2010**;1162:21-27.

[34] Haimour N, ElBishtawi R, Ailwhbi A. Desalination. **2005;**181:145-152.

[35] Redlich O, Peterson D J. Phys. Chem. **1959**; 63:1024–1029

[36] Vilela P B, Dalalibera A, Duminelli E C, Becegato V A. Paulino A T. Envi Sci and Pollut Res. **2018** ; 1-9.

[37] Ncibi M C**,** Altenor S, Mahjoub B, Seffen M, Gaspard S. J Haz Mat. **2008**;153:207-212.

[38] Quesada-Peñatea I, Julcour-Lebiguea C, Jáuregui-Hazac U J, Wilhelma A M, Delmasa H. J Hazs Mat. **2012**; 221:131-138

[39] Malakahmad A H, and Chuan S Y. Desal and Wat Treat. **2013**;51:6729–6735.

[40] Jiang B, Shen Z, Shen J, Yu D, Sheng X, Lu H. Scientia Horticulturae. **2009**;122:638-644.

[41] Demir H, Top A, Balkose D, Ulku S. J Haz Mat. **2008**;153:389- 394.

[42] Lagergren S. Vetenskapsak. Handl. **1898**;24:1-39.

[43] Blanchard G, Maunaye M, Martin G. Wat Res. **1984**; 18:1501-1507.

[44] Weber W, Morris J. J Sanit Engi Divi. **1963**;89:31-60.

[45] Rouquerol F., Rouquerol J, Sing K S W., Llewellyn P, Maurin G. Second ed. United Kingdom; **2014**.