

**A SUSTAINABLE RAW RICE HUSK ADSORBENT FOR EFFECTIVE LEVOFLOXACIN REMOVAL FROM AQUEOUS SOLUTION: KINETIC, THERMODYNAMIC AND ISOTHERM STUDIES**

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**ABSTRACT**

Levofloxacin (LEV) is an important and widely used antibiotic. It is used to treat many bacterial infections. It may be found in water sources as a result of incomplete metabolism in humans and other sources. In this study, the adsorption of Levofloxacin by raw rice husk (RRH) was investigated. The effect of pH, time, temperature, RRH weight, and initial Levofloxacin concentration on the adsorption process were determined. Kinetic, isotherm and thermodynamic models were studied to explain the Levofloxacin adsorption mechanism on raw rice husk. The results of adsorption kinetics and isotherms revealed that the adsorption of LEV by RRH was better fitted with the Intraparticle model with coefficient of determination ( $R^2=96\%$ ), while the Langmuir model represents the best isotherm model to describe the adsorption process with ( $R^2=95\%$ ). The removal efficiency reached 99% , the monolayer maximum uptake  $q_{max}$  is 2.47 mg/g and the adsorption intensity parameter ( $1/n$ ) value is 0.763, which means that the adsorption is favorable. According to the thermodynamic coefficients, the adsorption process was spontaneous and feasible for the temperatures under investigation; the sorption efficiency was more favorable at higher temperatures, and the adsorption process is endothermic.

**KEYWORDS:** adsorption, Freundlich model, optimization

عطا وآخرون

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استخدام قشور الرز كمادة مازة مستديمة للإزالة الفعالة لدواء الليفوفلوكساسين من محلول مائي: دراسة حركية، ديناميكية

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المستخلص

يعتبر الليفوفلوكساسين كمضاد حيوي مهم وشائع الاستخدام إذ يتم استخدامه لعلاج العديد من الالتهابات البكتيرية و يمكن العثور عليه في بعض مصادر المياه نتيجة التمثيل الغذائي غير المكتمل في البشر والمصادر الأخرى. في هذه الدراسة، تم فحص امتزاز الليفوفلوكساسين بواسطة قشور الرز الخام. تم تحديد تأثيرات الأس الهيدروجيني، وزن القشور، الوقت، درجة الحرارة وتركيز الليفوفلوكساسين الأولي على عملية الامتزاز. تم استخدام النماذج الحركية والديناميكية والاتزان الحراري للتعبير عن آلية امتصاص الليفوفلوكساسين على قشور الأرز الخام. أوضحت نتائج حركية الامتزاز والاتزان الحراري أن امتزاز الليفوفلوكساسين بواسطة قشور الرز الخام كانت متطابقة بشكل أفضل مع نموذج **Intraparticle** بمعامل ارتباط يساوي 96% ، بينما يمثل نموذج **Langmuir** أفضل نموذج اتزان حراري لوصف عملية الامتزاز بمعامل ارتباط يساوي 95%. وصلت كفاءة الإزالة إلى 99% وأقصى قابلية امتصاص  $q_{max}$  هو 2.47 مجم / جم. كانت قيمة قيمة  $1/n$  تساوي 0.763 وتشير إلى أن الامتزاز مفضل. تشير المعاملات الديناميكية الحرارية إلى أن عملية الامتزاز كانت تلقائية ومجدية لدرجات الحرارة قيد التحقيق وكانت كفاءة الامتصاص اعلى في درجات الحرارة المرتفعة، وعملية الامتزاز ماصة للحرارة.

الكلمات المفتاحية: الامتزاز، نموذج فريندلج، الأمثلية

## INTRODUCTION

The spread usage of antibiotics to treat bacterial infections for humans and animals in the past decades resulted in releasing these compounds to water bodies. The antibiotics found in wastewater have recently emerged as a matter of concern for their probable adverse impact on human health and for preservation of the environment as well (39, 27, 22). As a result of their incomplete metabolism by the body, the fraction of 30% – 90% is excreted to the wastewater (41, 48). Several studies showed that traditional wastewater treatment plants are not designed to remove antibiotics compounds, and eventually, they will find their way to water bodies (22, 38). The main impact of the antibiotics presence in water bodies is the potential biological action on microorganisms, that will generates antimicrobial-resistant bacteria (ARB). Antibiotics' presence in aqueous solution shapes the microbial community and decreases the microbial diversity significantly (22, 39). Several studies showed that different types of antibiotics were found in water bodies (51, 57) and fluoroquinolone antibiotics are one of the antibiotics types that have been extensively deployed to treat different pathogens and it could be genotoxic (10); thus it is important to develop an efficient and cost-effective methods to remove it from water (58). Many treating technologies were invented to study their efficiency in removing antibiotics, such as sedimentation (56), electrochemical techniques (20, 39), coagulation–flocculation (56), flotation (37), filtration (18), membrane processes (31, 57) precipitation (50), biological (45), advance oxidation (28), ion exchange and adsorption (27, 51, 53) Despite that some of these technologies /methods have a high efficiency in removing antibiotics, many of these methods may require addition of chemicals and radiation which might be harmful to the ecosystem and this will decrease their usage economic feasibility (43) Adsorption is considered as one of the most suitable and effective method to remove antibiotics in developing countries by using low-cost adsorbents (6) The adsorption process is a surface mass transfer phenomenon that when a multi-component fluid mixture is attached to the surface of a solid adsorbent by

physical or chemical bonds (30). Various materials are used in these processes, such as resins (43) activated carbon (15) and Nano-materials (38). Adsorption process are consists of several stages; at the beginning the solute is transported in the bulk of the solution (convection) and disperse through interstices of the sorbent, after that the solute transports across the liquid thin film around the sorbent particles, then the solute is diffused in the quiescent fluid contained in the adsorbate particle pores and along the pore walls; and finally surface diffusion of solute molecules on the sorbent surface. Adsorption overall rate could be managed by any of these steps; or a combined effect of a few steps (21). Recently, raw rice husk (RRH), which is considered a waste biomass material with the world production of approximately of 150 million ton each year (46) gains a major attention as abundant, low-cost and effective adsorbent for environmental pollutants (13, 58). Rice husk effectively removed different pollutants, such as beta-lactam cefixime (43), tetracycline (16), heavy metal (7), 17 $\alpha$ -ethinylestradiol (13) meropenem (31), dyes (3) and heavy metals (24). The objectives of this study are i) to utilize raw rice husk (RRH) as a low cost agricultural waste adsorbent to remove Levofloxacin from aqueous solution, ii) to determine the effect of solution pH, LEV concentration, contact time, RRH dosage, and particle size and iii) to interpret the kinetics, isotherms models and thermodynamics parameters of Levofloxacin adsorption on the RRH.

## MATERIALS AND METHODS

Levofloxacin (LEV), the empirical formula is  $C_{18}H_{20}FN_3O_4 \cdot \frac{1}{2} H_2O$  and its molecular weight is 370.38 (40). Raw Rice Husk (RRH) was collected from Al-Mishkhab district – Najaf Governorate, Iraq. RRH was washed with deionized water (DI) several times to remove any dirt or impurities and then let to dry at room temperature for 24 hours. After dried, the RRH was sieved through a 2-1 mm mesh sieve to obtain a uniform size and kept in an enclosed container. HCL and NaOH with 1N were used for pH adjustment. Characteristics of raw rice husk are shown in Table 1.

**Table 1. Physical Characteristics of RRH**

Color	Light to dark Yellow
Oder	Essentially non
Surface area (m <sup>2</sup> /g)	0.328
Real Density (g/cm <sup>3</sup> )	1.48
Bulk Density (g/cm <sup>3</sup> )	0.11

**Raw rice husk characterization**

The microstructure of the RRH was examined by scanning electron microscopy SEM (Tescan Vega II- Czech Republic). Fourier transform infrared spectroscopy (FTIR) (IRAffinity-1, Shimadzu – Japan) absorption spectrums using the potassium bromide disc method for the adsorbent pre and post adsorption were performed in the range 4000-400 cm<sup>-1</sup> with a resolution of 0.1 cm<sup>-1</sup>. Point of zero charge for the RRH was calculated using salt addition method (12, 13).

**ADSORPTION EXPERIMENTS**

5000 Hatch UV-Visible spectrophotometer with wavelength range (190–1100 nm) was used to detect the LEV wavelength and the maximum absorption wavelength (λ<sub>max</sub>) was 290 nm. A 100 mg/L stock solution was prepared, and then the stock solution was diluted to synthesize the other concentrations of LEV. The removal percentage (R%) was calculated by Equation 1 (34)

$$R\% = \frac{C_0 - C_e}{C_0} * 100 \dots\dots\dots(1)$$

Where: C<sub>0</sub> and C<sub>e</sub> refer to the initial and final concentrations of antibiotic, respectively. With exception of the experiment for studying temperature effect, which was conducted in (298, 303, 308 and 313 K) with other parameters kept constant, other adsorption experiments were performed at room temperature with 150 rpm mixing speed, different pH range of (2-8), LEV concentration of (25- 100 mg/L) and RH weights (0.5-12 g.) and three RH particle sizes (0.25-2 mm Mesh). All experiments were performed in duplicate. HCL and NaOH were used to reach the desired pH value.

**Adsorption isotherm models**

The isotherms model experiments were performed with LEV concentrations of 25, 50, 75 and 100 mg/L, pH value of 5 and RRH dosage of 9g was mixed with 100mL of each concentration. The solution was shaken with 150 rpm and after three hours, the filtered samples were tested to get the removal percentage of LEV by using the UV–Visible

spectrophotometer and it was calculated by Equation1. Langmuir and Freundlich were used to fit the isotherm models.

**Langmuir model**

The Langmuir isotherm model assumes that the adsorbent forms a monolayer on the adsorbent surface and the adsorption occurs at a specific uniform location on the adsorbent surface (4, 42). Langmuir model can be represented by Equation 2 (8, 12).

$$q_e = \frac{q_{max}bC_e}{(1+bC_e)} \dots\dots\dots(2)$$

Where: q<sub>e</sub> ; is the amount of adsorbed molecules on the surface of the adsorbent at any time(mg /g)

q<sub>max</sub> ; is the maximum adsorption capacity(mg /g)

b ; represents the Langmuir constant (L /mg)

**Freundlich model**

In contrast to Langmuir assumptions, Freundlich assumes that the adsorption is multilayer adsorption takes place and the surfaces are heterogeneous with different adsorption characteristics and energies, Non normalized form is Equation 3. (1, 51)

$$q_e = K_f C_e^{1/n} \dots\dots\dots(3)$$

Where; K<sub>f</sub> = Freundlich coefficient and 1/n is adsorption intensity parameter.

**Adsorption kinetics**

Kinetics is an important factor in understanding the removal process, and measuring the rate adsorption and developing an effective cleaning method for polluted environments (35). Different kinetic models have been developed to describe the adsorption process, such as the pseudo-first-order (PFO) model, the pseudo-second-order (PSO) model, Intraparticle and the Elovich model. Pseudo-first-order (PFO) model (27, 33).

$$q_t = q_e (1 - e^{-k_1 t}) \dots\dots\dots(4)$$

Pseudo-second-order (PSO) model ( 27, 44)

$$q_t = q_e^2 K_2 / (1 + q_e K_2 t) \dots\dots(5)$$

Intraparticle diffusion model (23)

$$q_t = K_{id} t^{0.5} + C_i \dots\dots(6)$$

Elovich model (25)

$$1/\beta \ln(\alpha\beta t) \dots\dots(7)$$

Where q<sub>e</sub> and q<sub>t</sub> are the amount of LEV adsorbed at equilibrium and at time t respectively (mg/g), k<sub>1</sub> ,K<sub>2</sub> , K<sub>id</sub> is the rate constant of the first-order, second order and Intraparticle diffusion respectively (min<sup>-1</sup>), β

is desorption constant (g/mg) and  $\alpha$  is initial sorption rate constant (mg/g. min).

**Models validation**

In order to validate the most accurate model , mathematically analyze the adsorption system and to confirm the consistency and theoretical assumptions of kinetic and isotherm models (19), CHI square , Sum of the squares of errors (ERRSQ) and average relative error functions were used.

**Adsorption thermodynamics**

Establishing the adsorption mechanism (both physical and chemical) is highly important. Both types can be recognized through the thermodynamic parameters such as Gibbs free energy ( $\Delta G^\circ$ ) KJ/mol, entropy change ( $\Delta S^\circ$ ) J/mol/K and enthalpy change ( $\Delta H^\circ$ ) KJ/mol . The equilibrium equation is (2, 8, 12)

$$\Delta G^\circ = -RT \ln(K_l) \dots\dots\dots(8)$$

Where

$$K_l = \frac{C_a}{C_e} \dots\dots (9)$$

$$\text{And } \Delta G^\circ = \Delta H^\circ - \Delta S^\circ T \dots\dots(10)$$

Therefor the equation can be rewritten as the following

$$\ln K_l = -(\Delta H^\circ/RT) + (\Delta S^\circ/R) \dots\dots(11)$$

Where:  $K_l$  is the equilibrium constant or the linear adsorption distribution coefficient

$C_a$ ; the amount of pollutant adsorbed at equilibrium (mg/l),

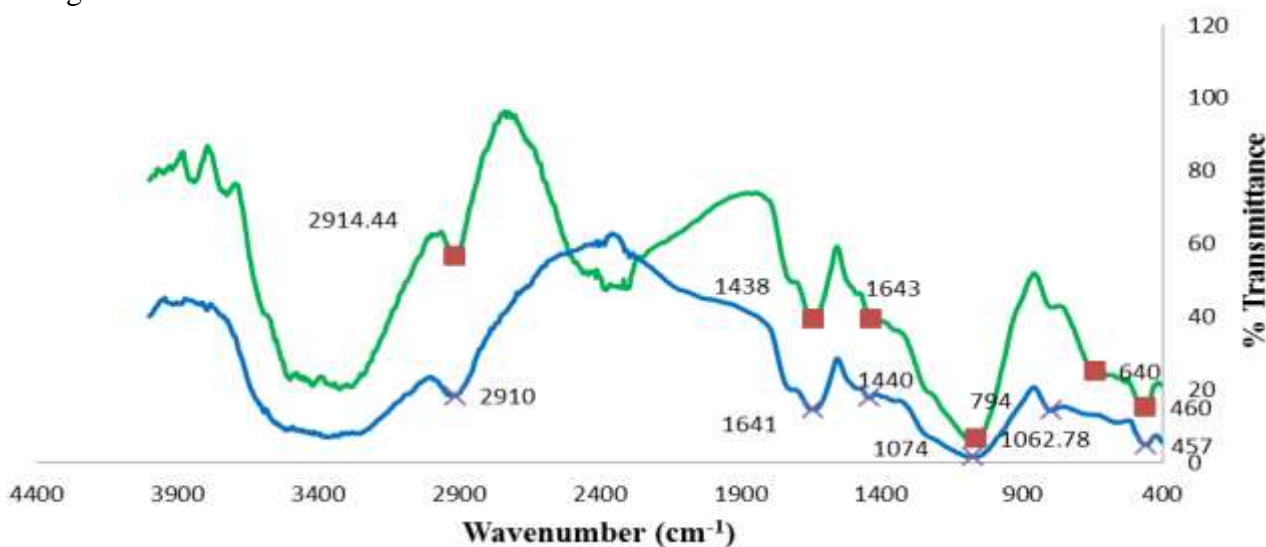
$C_e$ : the equilibrium concentration of the pollutant in the solution (mg/l),

R: the universal gas constant (8.314 J/mol K),

T: is absolute temperature (K),

**RESULTS AND DISCUSSION**

**Rice husk characterization:** The wide peak **Fig.1** at 3242.34 in RRH and 3221  $\text{cm}^{-1}$  in RH-LEV is representing the hydroxyl functional groups O-H (47).The peak at 2914.44  $\text{cm}^{-1}$  indicates the C-H stretching vibration of alkyl functional groups and this peak was changed to 2910  $\text{cm}^{-1}$  (29) .The 1643 and 1438  $\text{cm}^{-1}$  peaks at the unloaded RRH and 1641 and 1440  $\text{cm}^{-1}$  of LEV loaded RH represent the presence of Carbonyl [C=O] group (11).The peak at 1062.78 in RRH and 1074  $\text{cm}^{-1}$  in LEV loaded RH is mainly attributed to the Carboxylic acids and alcohols [C-O] (2) .



**Figure1. IR Spectrum of RRH ( green line) and LEV loaded RH (blue line) samples**

The peak at 640 and 460 $\text{cm}^{-1}$  in RRH and 794 and 457 in RH-LEV is probably for the presence of aromatic compounds in RH (47). The FTIR results showed the presence of different functional groups on RRH before and after the sorption of LEV. Some FTIR peaks were disappeared or shifted and some new peaks were emerged. In the sorption of LEV on RH mainly aliphatic C–H groups, Hydroxyl [-OH], Carboxylic [C-O] and aromatic compounds functional groups played the major

role in biosorption of LEV. SEM images are shown in Fig.2. These images reveal that RRH had a coarse highly porous surface; and it consists of several non-uniforms and separated aggregates. Moreover, there are many long grooves and big ravines in the outer surface of RRH. The RRH surface morphology provided a high surface area and active sites for antibiotics molecules adsorption. On comparing the SEM image of RRH and RH-LEV, it is clear that the RRH surface

morphology were altered significantly during the process of antibiotic adsorption. Furthermore, the RH-LEV surface becomes smoother, and some previously separated aggregates are enclosed which might be a result of adsorption of the antibiotics on active sites of the RH. The point of zero charge ( $pH_{PZC}$ ) is a crucial analysis to characterize different adsorbents. RRH point of zero charge

of was calculated by using the salt addition method (59). Conical flasks with 250 mL capacity were filled with 100 mL of 0.1 mol /L NaCl solution. Solution pH was ranged between 2 and 8 with HCl or NaOH. RH of 1 gram weight was added to different conical flasks, shake for 24 hours. Initial and final solutions pH was calculated and their difference was recorded.

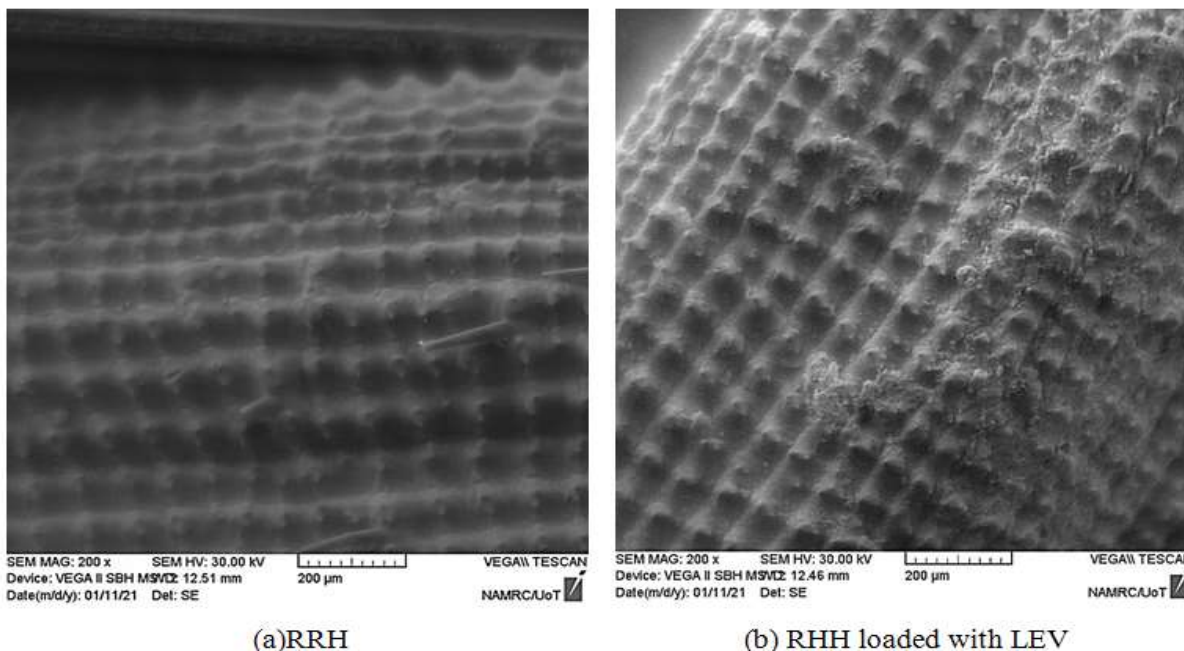


Figure 2. SEM for RRH and RH Loaded with LEV

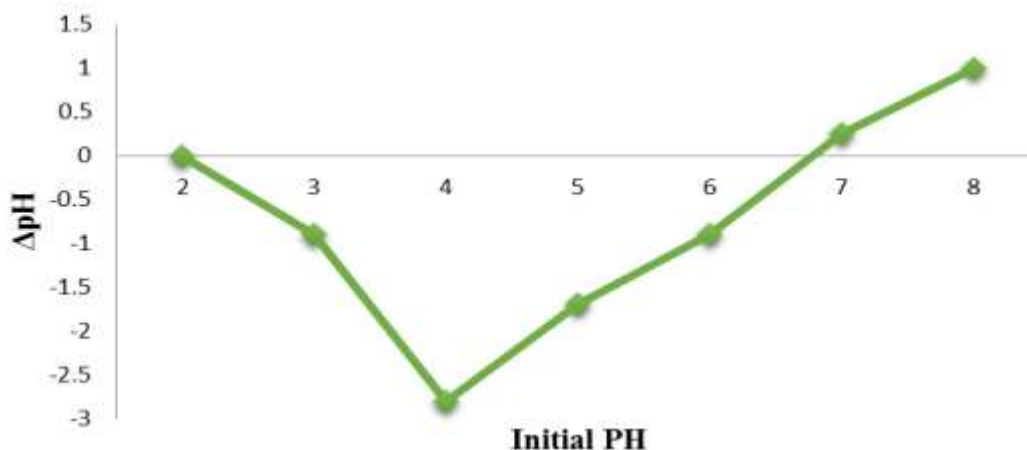


Figure 3. Estimation of Point of Zero charge

**Optimization factors influencing Adsorption process**

**Effect of particle size:** Particle size effect on the adsorption process was studied by using different sizes of 2, 1 and 0.25 mm mesh as shown in Fig.4. Experiment was conducted with solution of 50 ppm, at 5 pH for three hours with 150 rpm and 3g of husk in 100 mL solution .It was noticed that the reduction of the particle size of rice husk lead to increase

the removal efficiency from 56% to87%. This might be a result of greater accessibility to pores increasing the diffusion paths (9),

**The Effect of RRH Dosage**

The removal efficiency increased largely from 27.8% to 93.8 % when the RH dosage increased from 5 to 120 gm./L as shown in Fig.5. The removal efficiency increment with increasing RH dose is probably due to the larger surface area, increased pore volume, and

unsaturated sites available on RH surface at higher dose (9), which leads to provide more active adsorption sites that resulted in higher removal percentages (43).

**Effect of time and initial concentration**

The impact of time and initial concentration on the removal efficiency was studied by different concentrations 25, 50, 75, 100 ppm for three hours, while other factors kept constant. The LEV removal was increased with increased time Fig.6. Analysis indicated that the rate of adsorption was high in the first 10 minutes; thereafter the rate of adsorption decreased gradually and remained constant till equilibrium was established. It took 120 minutes to reaches equilibrium and subsequently, the saturation of active sites at equilibrium lead to that the rate of adsorption

became constant (52).The adsorption rate was found to decrease with increase in time. From Fig.7, the removal efficiency decreased as the concentration of LEV increased from 25 ppm to 100 ppm by 9% from 99% to 90%. At lower concentrations, the LEV-RH interaction is greater since the ratio of available active sites to initial LEV concentration is greater, while in higher initial concentration the ratio is lower as result of active site saturation which will decrease the available surface area to accommodate LEV molecules abundant in the solution (14) which eventually decreases the removal efficiency (9). Even though the removal efficiency decreased with concentration increment, the change is limited and still above 90%.

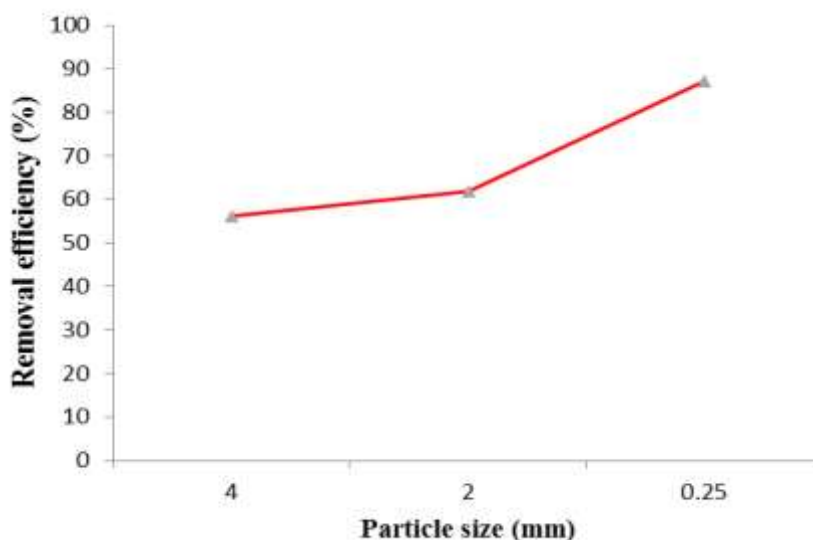


Figure 4.Effect of particle size on removal efficiency

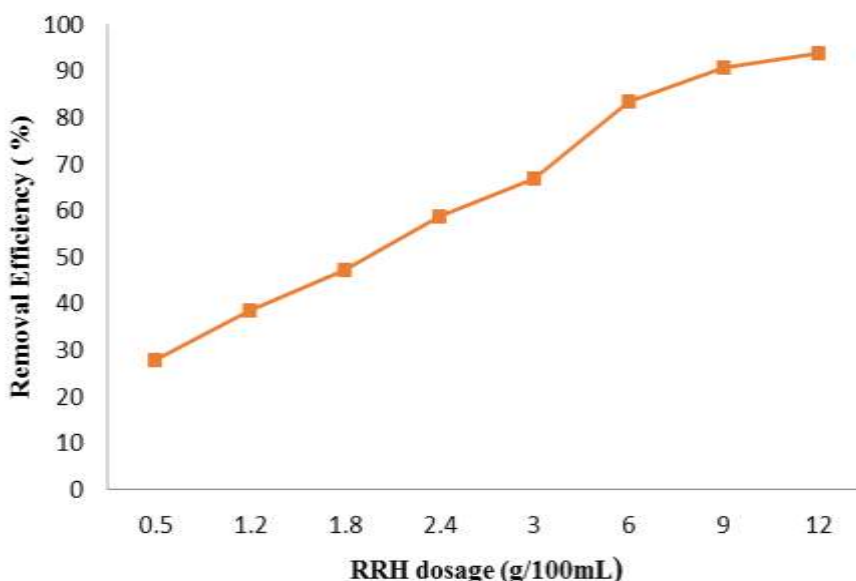


Figure 5. Effect of RH dosage on removal efficiency

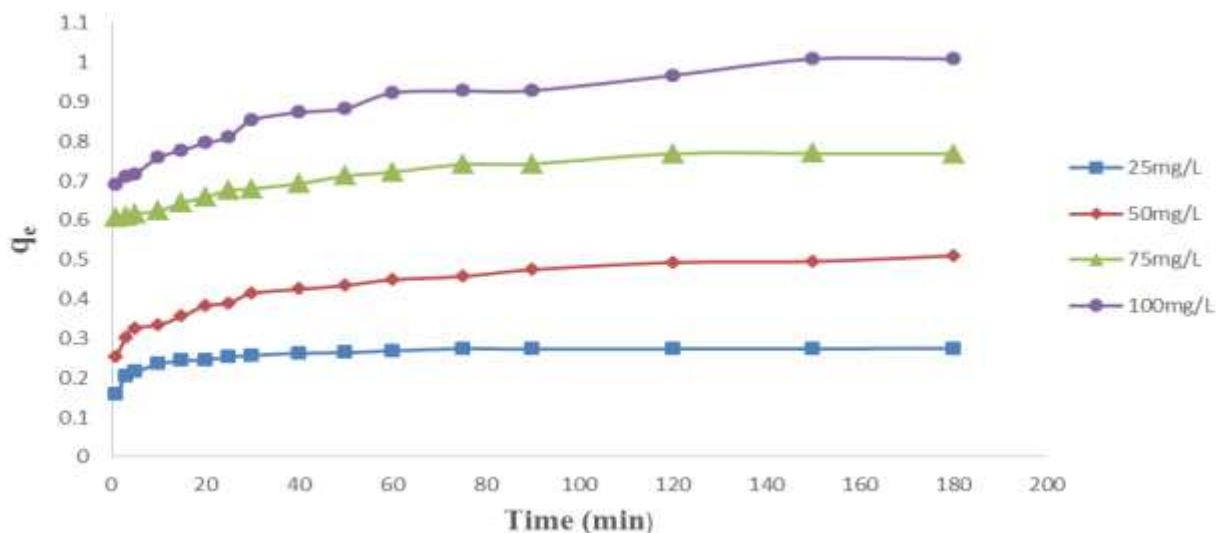


Figure 6. Effect of Experiment time on removal efficiency

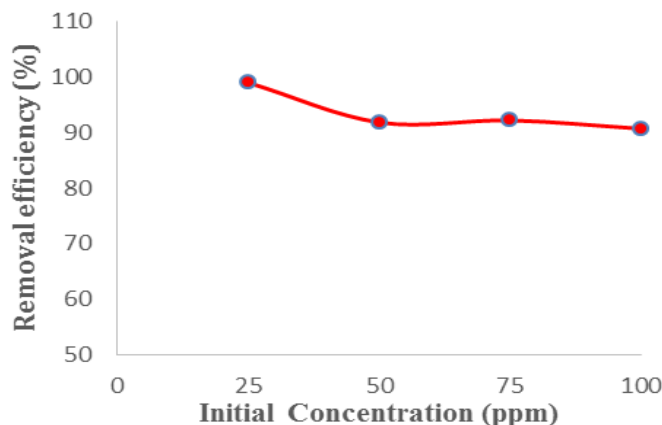


Figure 7. Effect of Levofloxacin initial concentration on removal efficiency

**Effect of initial pH**

LEV have three species, zwitterion species around neutral 6.0–7.5, cationic species at lower pH (below 5.33), and anionic species at higher pH values (higher than 7.94) (4). At pH less than 5 ( $pH < pK_{a1}$ ), the adsorption of LEV onto RH increased with increasing pH Fig.8. This was probably a result of the electrostatic repulsion decreasing between the protonated amine groups on LEV molecules and the positive charge on the RH (36). Another reason might be that the relatively low protonation of functional groups on the surfaces, which competed with the polar attraction of LEV in aqueous solution. The removal efficiency varied very little when pH ranges from 5–8, probably because the RH showed strong buffering effect to solution pH which might result from its higher silicon contents (surface silicon hydroxyls) (32,58). (17) Revealed that the electrostatic interaction between NCZM surface and LEV molecules do not play an important role in LEV

adsorption. (54) Found that pH of wastewater influence on the adsorption of different fluoroquinolone antibiotics by bamboo biochar can be neglected in most cases and only extreme pH values may influence the adsorption of fluoroquinolone antibiotics. Researchers found that optimum pH for LEV on Positive charge adsorbents was between 5–6 (36,55).

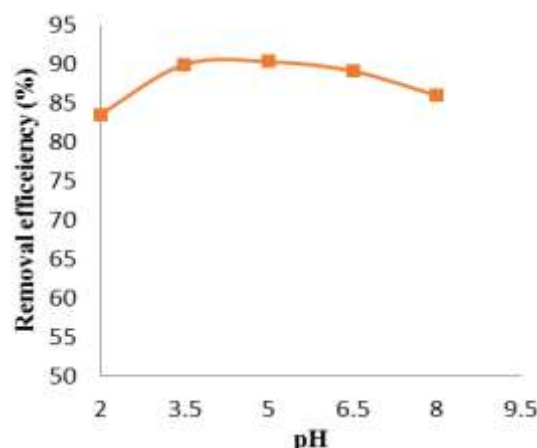
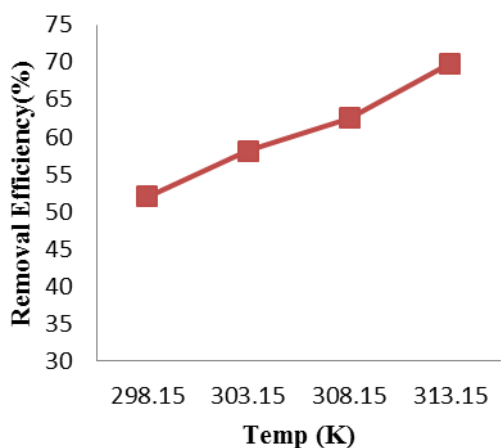


Figure 8. Effect of pH on removal efficiency

**Effect of temperature**

The temperature effect on the adsorption process is shown in Fig.9. As shown in Figure 11, Removal efficiency increased from 52% to 70% when the temperature increased from 25 to 40°C. The higher temperature may generated higher energy that is required by LEV to overcome activation barrier thus more LEV was able to penetrate the RH (26) .This might be resulted from higher mobility of LEV molecule with the increased temperature, more molecules across the external boundary layer and the internal pores of the adsorbent particles (14). Moreover, increasing temperature may produce a swelling effect within the internal structure of adsorbent, lead to penetrating the large LEV molecule further (14).



**Figure 9. Temperature effect on removal efficiency**

**Isotherm models**

Two isotherm models were studied for the removal of Levofloxacin; the parameters of each model are displayed in table 1 and Fig.10. langmuir model has the best correlation

Coefficient ( $R^2$ ) with 95% followed by Freundlich 93%. These results suggest that the monolayer adsorption plays a great role in the removal process. The monolayer maximum uptake  $q_{max}$  is 2.47 mg/g and the  $1/n$  value is 0.763 which indicates that the adsorption is favorable (10).

**Adsorption thermodynamics**

In order to examine the thermodynamic parameters (free energy change, enthalpy change and entropy change) four experimental temperatures were used (298, 303, 308 and 313 K) .From table 2, negative values of  $\Delta G$  for LEV sorption at the various temperatures, indicates the feasibility and spontaneous nature of the process (26). The decreased values of  $\Delta G$ . with the increasing temperature indicate that LEV sorption efficiency was more favorable at higher temperature (49). Positive  $\Delta H$  value indicates that the adsorption process is endothermic and positive value of  $\Delta S$  confirms randomness increasing and the disorder of the solid- solute interface at RRH surface during the process (26).

**Adsorption Kinetics**

The results shown in table 3 shows that low CHI Square, Sum of the squares of errors (ERRSQ) and Average relative error (ARE) values characterized the Intraparticle and the removal of all concentrations were in the first hour, which indicate the rapid adsorption rate of adsorption process . The PFO cannot be used due to its very low  $R^2$ . Fig.11 shows that more than 80% percent equilibrium at 120 min and after that the removal efficiency fluctuates insignificantly.

**Table 1. Isotherm models**

Isotherm model	Parameters			Sum of square errors (ERRSQ)	Average relative error (ARE)	CHI Square
Langmuir	$q_{max}(mg/g)$	<b>b</b>	$R^2$	0.05	0.99	0.20
	2.47	0.073	0.95			
Freundlich	<b>K</b>	$1/n$	$R^2$	0.04	0.90	0.16
	0.18	0.763	0.93			



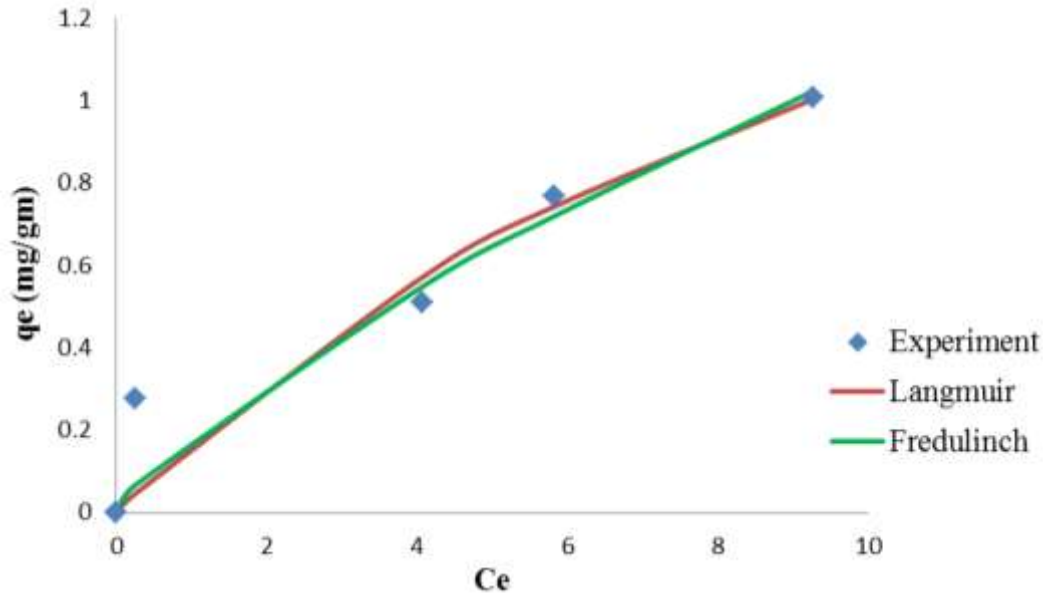


Figure 10 . Isotherm models  
Table 2. Thermodynamic parameter

		$(\Delta G^\circ)$ KJ/mol			
$(\Delta H^\circ)$ KJ/mol	$(\Delta S^\circ)$ J/mol/K	298	303	308	313
37.117	125.134	-0.197	-0.823	-1.312	-2.188

**CONCLUSION**

Different adsorption models were used to investigate the adsorption mechanism of LEV onto RRH. The adsorption kinetics results revealed that the adsorption of LEV by RRH was better fitted with Intraparticle model with more than 80% percent removal of all concentrations were in the first hour, which indicate the rapid adsorption rate of adsorption process. The Langmuir model represents the

best isotherm model to describe the adsorption and the monolayer maximum uptake  $q_{max}$  is 2.47 mg/g and the  $n$  value is larger than 1 indicate that the adsorption is favorable. Thermodynamic coefficients indicate the feasibility and spontaneous nature of the process; the sorption efficiency was more favorable at higher temperature and the adsorption process is endothermic.

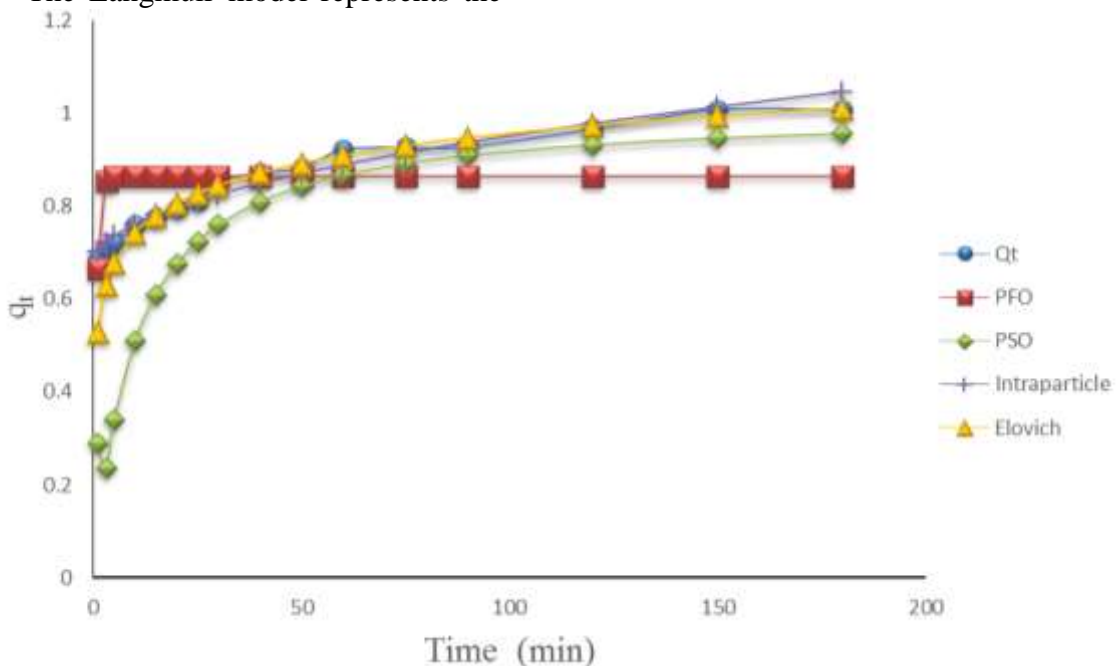


Figure 11. Kinetic models

**Table 3. Kinetic models parameters**

Method	Parameters	R <sup>2</sup>	Sum of the squares of errors (ERRSQ)	Average relative error (ARE)	CHI	
Pseudo first order	K <sub>1</sub> 1.45	q <sub>e</sub> 0.86	0.19	0.13	1.48	0.15
Pseudo Second order	K <sub>2</sub> 0.10	q <sub>e</sub> 1.84	0.89	0.66	3.07	0.92
Intraparticle	K <sub>p</sub> 0.027	C <sub>i</sub> 0.67	0.96	0.01	0.25	0.00
Elovich	Alpha 624.07	Beta 14.57	0.92	0.01	0.42	0.01

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