Adsorption of Levofloxacine Antibacterial from Contaminated Water by Non – Conventional Low Cost Natural Waste Materials

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ABSTRACT

An experimental study was conducted with low cost natural waste adsorbent materials, barley husks and eggshells, for the removal of Levofloxacine (LEVX) antibacterial from synthetic waste water. Batch sorption tests were conducted to study their isothermal adsorption capacity and compared with conventional activated carbon which were, activated carbon > barley husks > eggshells with removal efficiencies 74, 71 and 42 % with adsorbents doses of 5, 5 and 50 g/L of activated carbon, barley husks, and eggshells respectively. The equilibrium sorption isotherms had been analyzed by Langmuir, Freundlich, and Sips models, and their parameters were evaluated. The experimental data were correlated well with the Langmuir model which gives the best fit for LEVX adsorption / biosorption on to activated carbon, barley husks, and eggshells respectively.

The adsorption capacity was almost dependent on temperature. The thermodynamic parameters associated with the adsorption process, ΔG^o , ΔH^o and ΔS^o were reported and it is suggested to be physisorption, and of exothermic nature.

Keywords: adsorption, biosorption, levofloxacine, activated carbon barley husks, eggshells

إمتصاص المضادالحيوي ليفوفلوكساسين (LEVX) من الماء الملوث باستخدام مواد غير تقليدية من مخلفات طبيعية رخيصة

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الخلاصة

تم دراسة الإمدصاص / الامدصاص البيولوجي للمضادالحيوي الليفوفلوكساسين (LEVX) لأزالته من الماء الملوث على مجموعة مختارة من الممتزات غير التقليدية من مخلفات طبيعية رخيصة هي:قشور الشعير وقشور البيض ومقارنتها مع الكربون المنشط بطريقة الوجبة .هذه الدراسة تناولت تأثير عدة عوامل على عملية الإمدصاص مثل : درجة الحموضة ,الرقم الهيدروجيني ,وقت الاتصال بين الدواء والمادة الممتزة ,تركيز الدواء ,كمية المادة الممتزة ودرجة الحرارة. تم تحديد الإمدصاص عن طريق قياس تركيز الدواء قبل وبعد الاتزان باستخدام مطياف من خلال قياس الأشعة فوق البنفسجية والمرئية (Spectrophotometer) Spectrophotometer –Visible عند طول الموجة المناسبة للدواء,واستخدمت النتائج لتحديد الامدصاص (Adsorbance) ومنحنى الإمدصاص . حيث تبين ان الكربون المنشط > قشور الشعير> قشور البيض. حيث وجد ان كفائة الازالة 74، 71، 42% عندما يكون تركيز المادة الممدصة 5، 5، 50 g/L لكل من الكربون المنشط ، قشور الشعير و قشور البيض على التوالي. تم تطبيق علاقات الإمدصاص على النتائج (Adsorption isotherms) وكذلك عدة موديلات رياضية للأمدصاص / الإمدصاص البيولوجي حيث وجد انها ذات ارتباط قوي مع موديل لانكماير لجميع الممتزات اعلاه. كما تم حساب المتغيرات الثرموديناميكية ΔG^o, ΔH^o, ΔS^o , وتبين ان الإمدصاص / الإمدصاص البيولوجي ذو طبيعة فيزياوية وباعث للحرارة.

1. INTRODUCTION

The occurrence of pharmaceutical products in the aquatic environment has become crucial topic in the last few years. The investigation efforts focused in an initial phase mainly on the environmental risk assessment and extensive data have been gathered to document the contamination of the aquatic environment by these pollutants**, Nikolaou, et al., 2007; Farré, et al., 2008** and **Kümmerer, 2009a**. The studies point out the continuous introduction to sewage waters of these compounds along with their metabolites and the inefficiency of many conventional wastewater treatment plants (WWTPs) in their removal**, Jones, et al., 2005; Batt, et al., 2006** and **Kümmerer, 2009a**. Antibiotics are among the most commonly detected pharmaceutical compounds in the aquatic environmental. Several classes of antibiotics have been detected in different environmental waters such as groundwater, surface, and in a few cases even in drinking water**, Batt, et al., 2006** and **Farré, et al., 2008**. Some of the major concerns about the presence of these drugs in the environment include possible ecotoxicological effects to non-target organisms human pharmaceuticals pollute aquatic environments and there is considerable scientific uncertainty about the effects that this may have on aquatic organisms. Human drug target proteins can be highly conserved in non-target species**, Farré, et al., 2008; Kümmerer, 2009a** and **Santos, et al., 2010**. Ecotoxicological assessment of pharmaceuticals has been based on acute toxicity experiments performed by standard tests according to existing guidelines (i.e. OECD) using laboratory organisms belonging to different trophic levels such as algae, zooplankton, other invertebrates and fish. There is very little information about the chronic toxicity, or the bioaccumulation potential of pharmaceuticals in biota and food chains. An exception represents diclofenac, which is accumulated in prey of vultures**, Oaks, et al., 2004**, and the development of antibiotic-resistant bacteria**, Baquero, et al., 2008,** and **Kümmerer, 2009b**.

Due to the high public and health concern about the presence of these compounds in the environment and there cognizance of the WWTPs as the major source of pharmaceutical contamination, a number of conventional and innovative treatment methods, such as activated carbon, oxidation via chlorination, zonation, Fenton and photo-Fenton, biological process (activated sludge treatment), and membrane bioreactor and filtration, have been evaluated**, Homem,** and **Santos, 2011**. Each option of treatment has its own limitation and benefit in removing trace contaminants.

Adsorption is a well-established technique to remove pollutants, and it has been considered superior to other techniques in terms of initial cost, flexibility and simplicity of design, ease of operation, and insensitivity to toxic pollutants**, Crini, 2006**. One of the main advantages of the adsorption processes is that no byproducts are generated**, Homem,** and **Santos, 2011**.

Although activated carbon is probably one of the most effective methods for the removal of organic pollutants from water, its comparably high cost typically prohibits the treatment of large amounts of wastewaters; hence, alternative sorbent materials have been proposed that rely on low cost and readily available natural material, **Crini, 2006, Ngah,** and **Hanafiah, 2008, Gupta,** and **Suhas, 2009** and **Gupta, et al., 2009**. Several waste materials from industry or agriculture have been studied as non-conventional sorbents for inorganic**, Gupta, and Rastogi, 2008a; Freitas, et al., 2008** and **Gupta, et al., 2010.** As well as organic substances**, Crini, 2006;** and **Gupta, and Ali, 2008.** Most frequently, these materials are chemically modified to increase their sorption capacities or to remove nonstructural constituents such as tannins, terpenes, or phenolic compounds**, Crini, 2006**.

LEVAQUIN® is a synthetic broad-spectrum antibacterial agent for oral and intravenous administration. Chemically, levofloxacin, a chiral fluorinated carboxyquinolone, is the pure (-) (S)-enantiomer of the racemic drug substance ofloxacin. The chemical name is (-)-(S)-9-fluoro2,3-dihydro-3-methyl-10-(4-methyl-1-piperazinyl)-7-oxo-7H-pyrido[1,2,3-de]-nzoxazine-6-carboxylic acid hemihydrate. The chemical formula is $C_{18}H_{20}FN_3O_4 \bullet ½\ H_2O$ and the molecular weight is 370.38 as in **Fig. 1, RxList, 2013.**

Levofloxacin is a light yellowish-white to yellow-white crystal or crystalline powder. The molecule exists as a zwitterion at the pH conditions in the small intestine. The data demonstrate that from pH 0.6 to 5.8, the solubility of levofloxacin is essentially constant (approximately100 mg/mL). Levofloxacin is considered soluble to freely soluble in this pH range, as defined by USP nomenclature. Above pH 5.8, the solubility increases rapidly to its maximum at pH 6.7 (272 mg/mL) and is considered freely soluble in this range. Above pH 6.7, the solubility decreases and reaches a minimum value (about 50 mg/mL) at a pH of approximately 6.9. Levofloxacin has the potential to form stable coordination compounds with many metal ions. This in vitro chelation potential has the following formation order: $Al^{+3}>Cu^{+2}>Zn^{+2}>Mg^{+2}>Ca^{+2}$**, RxList, 2013**. Binding and chelation of the Levofloxacin and metal ions will result in decreased adsorption of bioavalability of Levofloxacin and potential increase the risk for treatment failure of the infection. Although they can be beneficial in cases of heavy metal poisoning, chelating agents can also be dangerous. Use of disodium Ethylenediaminetetraacetic acid (EDTA) instead of calcium EDTA has resulted in fatalities due to hypocalcemia**, RxList, 2013**.

The aim of this study is to compare and analyze the adsorptive behavior and the potential application of some adsorbents such as: activated carbon, and raw natural waste materials like barley husks and eggshells for the uptake of Levofloxacin Hemihydrate from aqueous solutions. The effect of the following parameters on adsorption process will be evaluated: Concentration of the drug used, amount of adsorbent used, contact time between adsorbent and drug (equilibrium time), particle size of adsorbent, pH value of the drug's solution, and temperature.

2. THEORY

2.1 Adsorption Mechanism, Isotherms, and Kinetics

Adsorption isotherms or known as equilibrium data are the fundamental concept in adsorption science that is the correct explanation of experimental adsorption in mathematical equations or functions.

Isotherm's parameters (q_e, C_e, K_f, n_f, q_m, b, K_s, a_s, and β_s) express the surface properties and affinity of the adsorbent at known temperature and pH. The most frequently isotherms used in describing the non-linear equilibrium are: Langmuir isotherm model assumes that the adsorption is limited to a monolayer, Freundlich isotherm model assumes that the adsorption is a multilayer, originally empirical in nature, but later was interpreted as the sorption to heterogeneous surfaces or surfaces supporting sites with various affinities, and Sips isotherm model represent combination of Langmuir and Freundlich isotherm models.

Adsorbents must have high abrasion resistance, high thermal stability and small pore diameters, those results in higher exposed surface area and hence high surface capacity for adsorption. The adsorbents must also have a distinct pore structure, which enables fast transport of the pollutants, **Gupta, and Rastogi, 2008a**.

The study of sorption kinetics of pharmaceutical products removal from wastewater is significant as it provides valuable insights into the reaction pathways and into the mechanism of sorption reactions. It describes the solute uptake rate which in turn controls the residence time of sorbate uptake at the solid–solution interface**, Gupta, et al., 2009**.

2. 1.1 External mass transfer coefficient (k_f)

The external mass transfer coefficient k_f in meters per second, in a batch adsorber was determined from the concentration decay curves at optimum speed and the initial rate data, using Eq. (1)**, Ziagova, et al., 2007**.

$$k_f = -\frac{R_P \rho_P V_L}{3 w_a t} \ln\left(\frac{C_t}{C_0}\right) \qquad 0 < {}^{C_t}\!/_{C_0} < 1 \tag{1}$$

2.1. 2 Pseudo-first-order kinetic model

The Lagergren rate equation was the first rate equation for the sorption of liquid/solid system based on solid capacity and this model represents physical adsorption for pollutants onto sorbent/biosorbent surface Eq. (2)**, Sulaymon, et al., 2013** and **Gupta,** and **Rastogi, 2008b:**

$$q_t = q_e(1 - \exp(-k_1 t)) \tag{2}$$

2. 3 Pseudo-second-order kinetic model

If the sorption rate of system is a Pseudo-second-order mechanism, the rate-limiting step may be chemisorption involving valence forces through sharing or the exchange of electrons between sorbent and sorbate as covalent forces Eq. (3)**, Gupta, and Rastogi, 2008b;** and **Holan, and Volesky, 1995:**

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} + \frac{t}{q_e}\right) \tag{3}$$

The initial sorption rate is $h = k_2 q_e^2$, and K_2 Pseudo second-order coefficient.

2.2 Sorption Thermodynamics

Based on fundamental thermodynamic concepts, it is assumed that in an isolated system, energy cannot be gained or lost and the entropy change is the only driving force. The apparent equilibrium constant for the process has been shown to be as shown in Eq. (4)**, Gupta, and Rastogi, 2008b**:

$$\Delta G^0 = -RT \ln \pi (K_c) \tag{4}$$

Also, enthalpy changes (ΔH) and entropy changes (ΔS) can be estimated by Eq. (5):

$$\Delta G^0 = \Delta H^0 - \Delta S^0 T \tag{5}$$

The negative values of ΔH° reveal the adsorption is exothermic and physical in nature. Generally, the change in adsorption enthalpy for physisorption is in the range of −20 to 40 kJ mol^{-1}, but chemisorptions are between −400 and −80 kJ mol^{-1}**, Tuzun, et al., 2005**.

3. EXPERIMENTAL PROCEDURE AND METHOD

3.1 Levofloxacin Hemihydrate (LEVX) Adsorbate

Levofloxacin Hemihydrate (LEVX) 500 mg tablets were obtained from the commercial Iraqi market. For this study LEVAQUIN®500mg tablets are available as film-coated tablets and contain the following inactive ingredients: 500 mg (as expressed in the anhydrous form) crospovidone, hypromellose, magnesium stearate, microcrystalline cellulose, polyethylene glycol, polysorbate 80, synthetic red and yellow iron oxides and titanium dioxide**, RxList, 2013**.

Fresh stock solutions of 500 mg/L LEVX were prepared daily by dissolving one tablet of LEVX in 1000 mL distilled water, 0.1M HCl was added to the solution to control the pH to 7,and then vigorously shacked on a mechanical gyratory shaker (HV-2 ORBTAL, Germany), 200 rpm for 1h. Absorbance was measured at 280 nm by (T80 Spectrophotometer /VIS spectrometer PG Instrument Ltd.) against blank at 30 ±3^{o}C. The stock solution was protected from light exposure by aluminum foil and kept at room temperature**, Sarkozy, 2001**. Stock solutions showed stability at room temperature with time.

Activated carbon, barley husks, and eggshells were used as adsorbents. Their characteristics were examined at the (Ministry of Oil, Petroleum Development and Research Center, Baghdad, Iraq) as shown in Table1 and according to **APHA, 1995.**

3.2 Determination of the Optimum Contact Time and pH

The optimum contact time was found by measuring the time to reach equilibrium conditions when the uptake q_e was constant with time for the three adsorbents. 0.5 g of activated carbon, and barley husk, while 5 g of eggshells were mixed with 100 mL of LEVX solution concentration of 150 mg/L, 200 rpm, normal pH, and 30 °C. The optimum time was used for the next experiments.

The effect of pH on sorption LEVX onto activated carbon, barley husk and eggshells were studied; 0.5 g of activated carbon, and barley husk, while 5 g of eggshells were mixed with 100 mL of LEVX solution concentration of 150 mg/L. These were maintained at different pH values ranging from 4 to 9 by using 0.1 M HCl or NaOH solution, the flasks were placed on the shaker at an agitation speed of 200 rpm for a period of 3 h (as found experimentally in **Fig.2** and at temperature of 30°C. Samples of 10 mL were taken from each volumetric flask and measured by the Spectrophotometer.

3.3 Isotherms

Different sorbate concentrations (25, 50, 75,100,125, and 150 mg/L) of 100 ml LEVX solution were used. 0.5 g of activated carbon, and barley husk, while 5 g of eggshells using (electronic balance Sartorius BL 210S) were placed separately in 250 mL volumetric flasks because of its low uptake of LEVX, respectively. pH of the solutions were adjusted to the desired value pH=7 using 0.1 M NaOH or 0.1 M HCl. The flasks were then placed on the shaker, and agitated continuously for 3 h at 200 rpm and 30°C. The samples were filtered by no. 42 Whatman filter paper. The final equilibrium concentrations of LEVX were measured by the Spectrophotometer, the adsorbed amount is then calculated by Eq. (6)**, Gupta, et al., 2010**.

$$q_e = \frac{V_L(C_0 - C_e)}{W_a} \tag{6}$$

3.4. Kinetics and Thermodynamics

Reaction pathways were found using 2 L pyrex beaker fitted with a variable speed mixer. The beaker was filled with 1 L of 150 mg/L concentration of LEVX and the agitation was started before adding the Activated carbon, barley husk, or eggshells as adsorbents separately. At time zero, the accurate weight of sorbent was added and the samples were taken at specified time intervals. The necessary dosage of sorbents, to reach equilibrium related concentration of C_e/C_o equals to 0.05, were calculated from better isotherm model and mass balance Eq. (6). For accurate estimation of k_f, samples were taken after 3, 6, 9, and 12 min and analyzed.

The principle parameter required for solving the batch model is the external mass transfer coefficient (k_f) which was obtained using the concentration decay curve obtained from experimental data at optimum agitation speed and Eq.(1).

The effect of temperature on LEVX sorption onto each of activated carbon, barley husk and eggshells were determined using 0.5 g of activated carbon, barley husks, and 5 g of eggshells respectively, mixed with 100mL of 150 mg/L of LEVX solution. These were maintained at different temperatures ranging from 20 to 50 °C for a period of 3 h, and agitation speed was 200 rpm. Samples of 10 mL were taken from each volumetric flask and the absorbency was measured by the Spectrophotometer.

4. RESULTS AND DISCUSSION

4.1 Effect of Contact Time and pH

Barley husks show a constant uptake rate (50 min),while activated carbon uptake (about 110 min) for the same adsorbent dose, but eggshells show lower uptake (40 min) in spite of increasing the biomass dose (about 10 times more than activated carbon and barley husks), considering same operating experimental conditions as shown in **Fig. 2**. These are due to that the eggshells that have been measured by the Spectrophotometer; there was a high percentage of LEVX concentration in the raw material due to the use of the antibiotic in vaccines for the chickens.

The pH of the LEVX solution usually plays an important role in the sorption of LEVX, RxList, 2013. **Fig. 3**, shows that the sorption capacities were enhanced significantly from 3.8 to 5.2 mg/g for activated carbon, from 2.1 to 3.7 mg/g for barley husk, and from 1.1 to 1.5 mg/g for eggshells, respectively, when pH value was raised from 4 to 7. The s effect of pH influences on adsorption of LEVX onto biomass adsorption capacities were increased with attractive interaction at pH 7 and decreased with repulsive interaction at pH 9. It could be indicated that combination of electrostatic interaction and hydrophobic force might effect on adsorption capacity of the biomass and activated carbon, same results were obtained by**, Hattab, 2010,** at pH of 7 the sorption capacity of LEVX onto charcoal was 5.5 mg/g.

4.2 Adsorption/Biosorption Isotherms

At equilibrium point adsorption/biosorption isotherms reflected the molecular distribution between the liquid and solid phases. At that point, adsorption quantity q_e of LEVX onto activated carbon, barely husks, and eggshells, at initial concentrations, 25 to 150 mg/ L for LEVX, are shown in Table (2). The amounts of adsorbed/ biosorbed LEVEX increased with the increasing of the concentration of LEVX in the equilibrium solution**, Hattab, 2010**.

The analysis of experimental results of equilibrium adsorption isotherms is important in developing accurate data that could be used for adsorption design purpose. The adsorption isotherm curves for adsorption of LEVX onto activated carbon, barley husks, and eggshells, were obtained by plotting the equilibrium concentration C_e of the LEVX solute with the experimental uptake (q_e) as shown in **Fig. 4**.

The adsorption/biosorption capacity (q_e) and LEVX removal rate were related to the amount of sorbent/ biosorbent added **Fig. 5**; the greater adsorption/ biosorption capacity was obtained at lower sorbent/ biosorbent dose, these results agreed with**, Gupta, and Ali, 2008** and **Ziagova, et al., 2007**. The higher removal rate was achieved at higher sorbent / biosorbent dose. The Langmuir model gives the best fit for the experimental data for LEVX adsorption / biosorption on to activated carbon, barley husks, and eggshells respectively, compared with Freundlich, and Sips models recognized by the highest values of (R^2). These models have been used successfully to describe equilibrium sorption/biosorption, with results agreed with**, Hattab, 2010**. Results were compared for the three adsorbants in term of adsorption/biosorption capacities: Activated carbon > Barley husks > Eggshells. This is due to increase the saturation of adsorbent surface with increase in initial LEVX concentrations. The activated carbon has greater surface area for adsorption.

4.3 Adsorption / Biosorption Kinetics

The amount of activated carbon, barley husks, and eggshells, used for the adsorption of LEVX were calculated for final equilibrium related concentration of $C/C_0 = 0.05$, the Langmuir model constants were used with the mass balance in 1 L of solution. The initial concentration was 150 mg/L with doses 20.745, 30.722, and 720 g of activated carbon, barley husks, and eggshells respectively as shown in **Figs. 6-8**. The average calculated values of k_f for each adsorbent were found to be 4.7×10^{-6}, 1.3×10^{-5} and 1.33×10^{-7} m/s for activated carbon, barely husks, and eggshells respectively. These indicate that the rate of surface mass transfer of barely husks is higher than the other adsorbents. In other words, LEVX is absorbed by barely husks at higher rate than others. Pseudo-first-order and Pseudo-second-order. Table 3 show the Pseudo second-order model for LVEX, the correlation coefficient values for the linear plots being higher than 0.98 as shown in **Figs. 9-10**.

4.4 Adsorption / Biosorption Thermodynamic

Table 4 shows the thermodynamic constants of adsorption / biosorption for LEVEX onto activated carbon, barley husks, and eggshells respectively. The value of enthalpy ΔH° was 7.478, 26.3 and 20.91 kJ/mole for activated carbon, barley husks, and eggshells respectively, suggested the physisorption and exothermic nature of adsorption **Fig. 11**. This is also supported by the decrease in the values of uptake capacity of adsorbent / biosorbents with the rise in temperature**, Sulaymon, et al., 2013**. The values of entropy ΔS° were –0.0327, -0.095 and -0.0735 J/mole K, reflect the affinity of LEVX to be adsorbed onto activated carbon, barley husks, and eggshells respectively.

The increase in the value of the free energy ΔG◦ with the increase in temperature indicates that the adsorption / biosorption process is exothermic and it is thereby favored with decrease in temperature, thus, the process is better carried out at low temperature**, Sulaymon, and Ahmed, 2008**.

5. CONCLUSIONS

The equilibrium isotherm for single component is of a favorable type and Langmuir isotherm gives the best fit model for the experimental data , and adsorption capacity parameters for LEVX onto activated carbon > barley husks > eggshells. Optimum pH was 7. Van der Wall's electrophoresis force play the major role in adsorption / biosorption of LEVX. There was a good matching between experimental and predicted data in batch experiments using second order kinetic model for all sorbent / biosorbents, sorption / biosorption of LEVX were exothermic and physical in nature.

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NOMENCLATURE

a_s	sips constant, dimensionless
b	langmuir adsorption constant related to the affinity to binding sites, l/mg
C_{ad}	adsorbed on adsorbents surface concentration, mg/l
C_e	equilibrium concentration of LEVX, mg/l
C_o	initial LEVX concentration, mg/l
C_s	saturation concentration of the adsorbed component, mg/l
C_t	concentration of LEVX at time t, mg/l
K_1	pseudo-first order coefficient, s^{-1}
K_2	second order kinetics, l mol^{-1} s^{-1}
K_c	C_{ad}/C_e constant used in Eq. (4), dimensionless
k_f	fluid to particle mass transfer coefficient, m/s
K_F	freundlich adsorption constant, related to adsorption intensity, $(mg/g)(mg/l)^{1/nf}$
K_s	sips constant, dimensionless
n_F	freundlich adsorption constant, related to the affinity to binding sites, dimensionless
q_e	amount of adsorbate adsorbed per mass of adsorbent of component, mg/g
q_{eq}	adsorbed LEVX quantity per gram of activated carbon, barley husk and eggshells at

	equilibrium, mg/g
q_m	langmuir adsorption constant of the pollutants shows the maximum amount of pollutants bound to the activated carbon, barley husk and eggshells, mg/g
qt	uptake amount at time t, mg/g
R	universal gas constant (=8.314), kj/mol.k
Rp	radius of adsorbent/ biosorbent particles, m
T	absolute temperature, k
t	time, s
V_L	volume of solution, l
W_a	weight of adsorbent/ biosorbent (activated carbon, barley husk, and eggshells), g
$\Delta G°$	standard Gibbs free energy change, kj mol^{-1}
$\Delta H°$	change in enthalpy (heat of adsorption/sorption), kj mol^{-1}
$\Delta S°$	change in entropy, kj mol^{-1}
β_s	Sips constant, dimensionless
ρ_p	bulk density of adsorbent/ biosorbent, kg/m^3

Table 1. Physical characteristics of the adsorbents (Ministry of oil, petroleum development and research center, Baghdad, Iraq).

Physical Property	**Barley Husk**	**Egg Shells**	**Activated Carbon**
Particle size range, (mm)	0.6 – 1	0.6 - 1	0.6 - 1
Equivalent diameter, (mm)	0.775	0.775	0.775
Apparent density,(kg/m^3)	332	640	480-490
Bulk density,(kg/m^3)	1011	1600	450
Solid density base dry, (kg/m^3)	1480	2350	770
BET Surface area, (m^2/g)	0.302	0.163	1100
Porosity	0.5	0.32	0.55
Ash %	19.6	84	5

Table 2. Parameters of single solute isotherm for Levofloxacin onto activated carbon barley husks, and eggshells at initial concentrations 25 to 150 mg/L of LEVX.

Model		Parameters	AC	BH	ES	Reference
Freundlich	$q_e = K_F C_e^{1/nF}$	K_F	2.059	o.468	0.0093	Gupta and Rastogi 2008
		n_F	1.625	0.958	0.775	
		R^2	0.970	0.982	0.986	
Langmuir	$q_e = \frac{q_m b C_e}{(1 + b C_e)}$	q_m	34.211	125.735	5.6423	Sulaymon et al. 2013
		b	0.0335	0.00498	0.00435	
		R_L	0.421	0.834	0.816	
		R^2	**0.995**	**0.988**	**0.995**	
Sips	$q_e = \frac{K_s C_e^{\beta_s}}{1 + a_s C_e^{\beta_s}}$	k_s	1.334	0.120	0.052	Sulaymon et al. 2013
		$ß_s$	0.9116	1.604	0.622	
		a_s	0.033	0.0029	-0.050	
		R^2	0.973	0.986	0.970	

Table 3. Kinetic parameters for activated carbon, barely husks, and eggshells.

Kinetic Model	Parameter	Activated Carbon	Barley Husk	Eggshells
Pseudo-first-order (Equation 2.24)	q_e(mg/g)	30.66	23.81	17.12
	K_1(min^{-1})	4.6× 10^{-4}	1.4× 10^{-4}	1.15× 10^{-4}
	Correlation coefficient	0.7224	0.7022	0.8099
Pseudo-second-order (Equation 2.28)	qe cal. (mg/g)	4.71	6.87	0.21
	K_2(mg/g.min)	0.0355	0.0108	0.1438
	h_0	28.174	92.388	6.955
	Correlation coefficient	0.9988	0.9966	0.9846

Table 4. Thermodynamic parameters for activated carbon, barley husk and eggshells.

Adsorbents	Temperature, K	ΔG° ($kJ.mol^{-1}$)	ΔH° ($kJ.mo1^{-1}$)	ΔS° ($J.mol^{-1}K^{-1}$)	R^2
Activated Carbon	293	-0.91	7.478	-0.0327	0.9778
	303	-2.418			
	313	-3.424			
	232	-4.503			
Barley Husks	293	-1.769	26.3	-0.095	0.989
	303	-2.524			
	313	-3.448			
	323	-4.653			
Eggshells	293	-0.719	20.98	-0.0735	0.966
	303	-1.049			
	313	-1.986			
	323	-2.856			

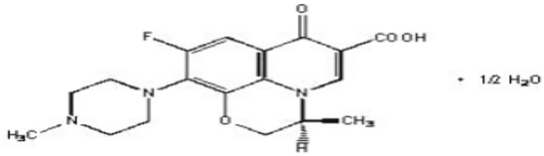

Figure 1. The chemical structure of Levofloxacin.

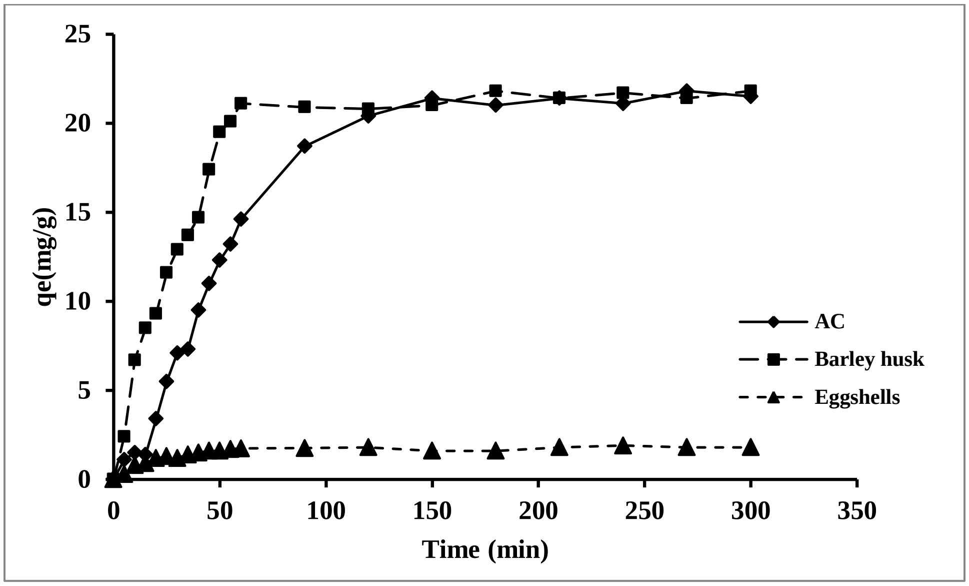

Figure 2. Effect of contact time on the uptake of Levofloxacin onto activated carbon, barley husk and eggshells, $C_{biomass}$= 0.5 g/L, $C_{0Levofloxacin}$= 150 mg/L, pH= 7 and agitation speed= 200 rpm.

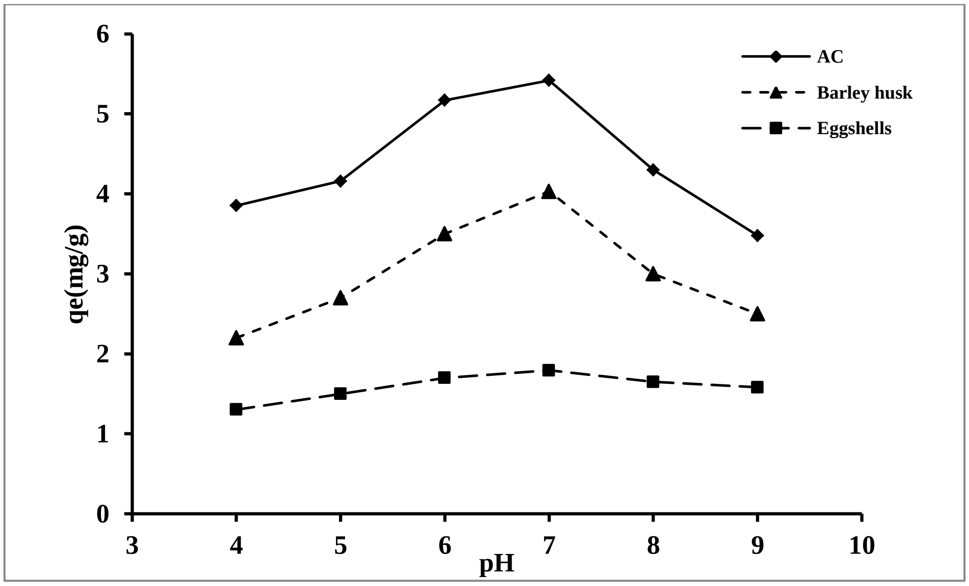

Figure 3. Effect of pH on the uptake of Levofloxacin onto activated carbon, barley husk, $C_{biomass}$= 5 g/L, and eggshells $C_{biomass}$= 50 g/L, $C_{0Levofloxacin}$= 150 mg/L, contact time = 3 h, and agitation speed= 200 rpm, temperature= 30°C.

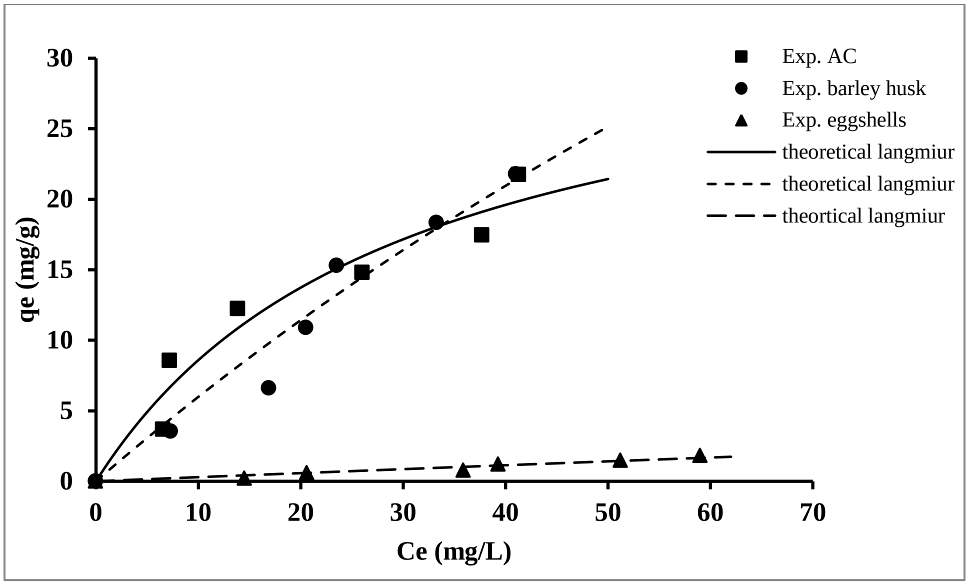

Figure 4. Adsorption isotherms of Levofloxacin as single solutes onto activated carbon, barley husk, $C_{biomass}$= 5 g/L and eggshells, $C_{biomass}$= 50 g/L, pH= 7 and agitation speed= 200 rpm.

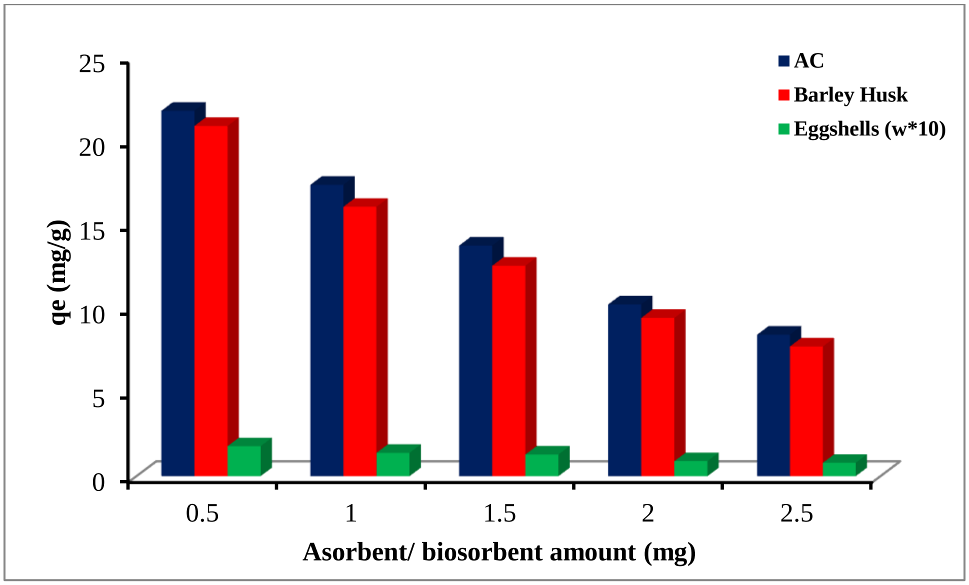

Figure 5. Effect of adsorbent/biosorbent amount on to the uptake capacity of Levofloxacin as single solutes, pH= 7, C_0=150 mg/L, and agitation speed= 200 rpm.

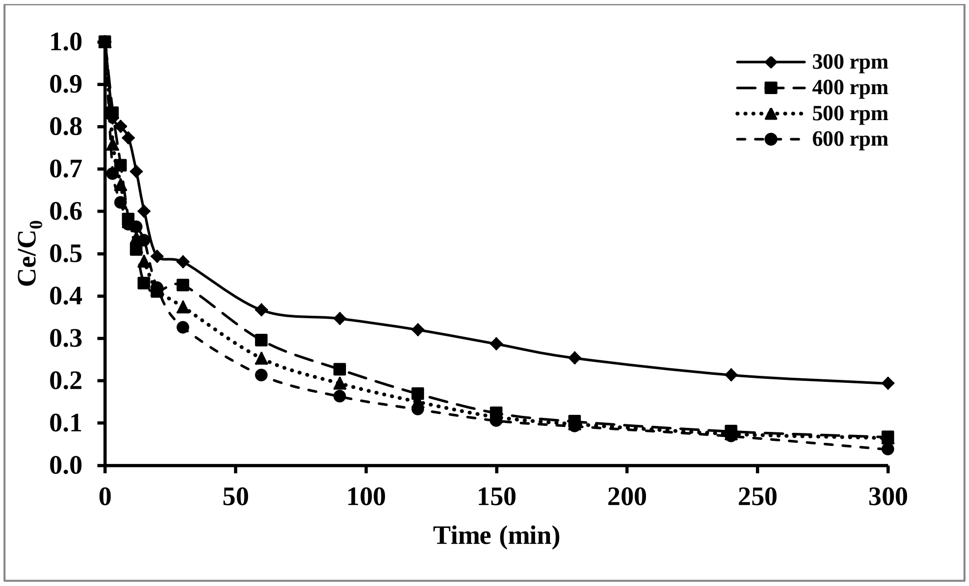

Figure 6. Concentration-time decay data for Levofloxacin onto activated carbon, $C_{absorbent}$= 20.744 g/L, $C_{0Levofloxacin}$ = 150 mg/L, pH= 7 at different agitation speeds.

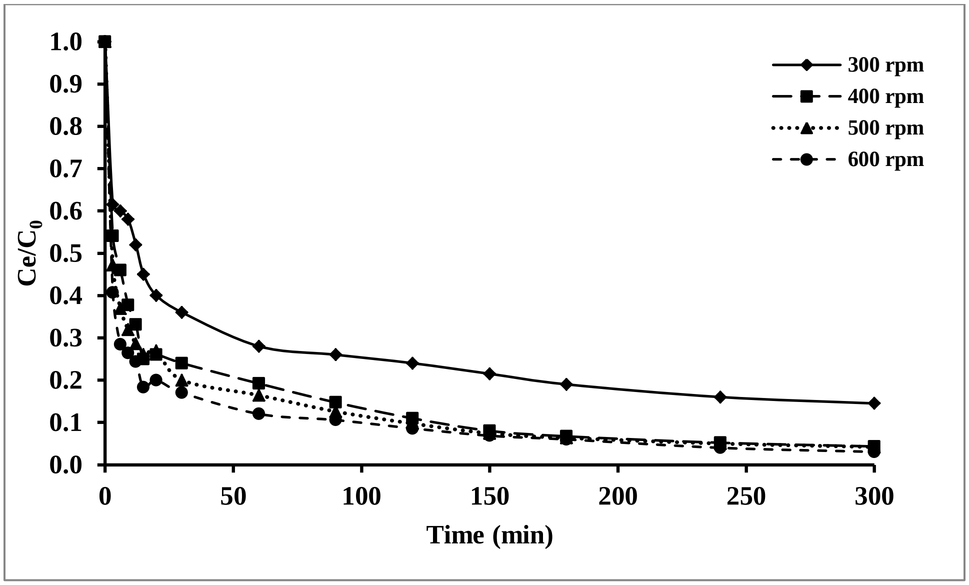

Figure 7. Concentration-time decay data for Levofloxacin onto barley husk, $C_{absorbent}$= 30.722 g/L, $C_{0Levofloxacin}$ = 150 mg/L, pH= 7 at different agitation speeds.

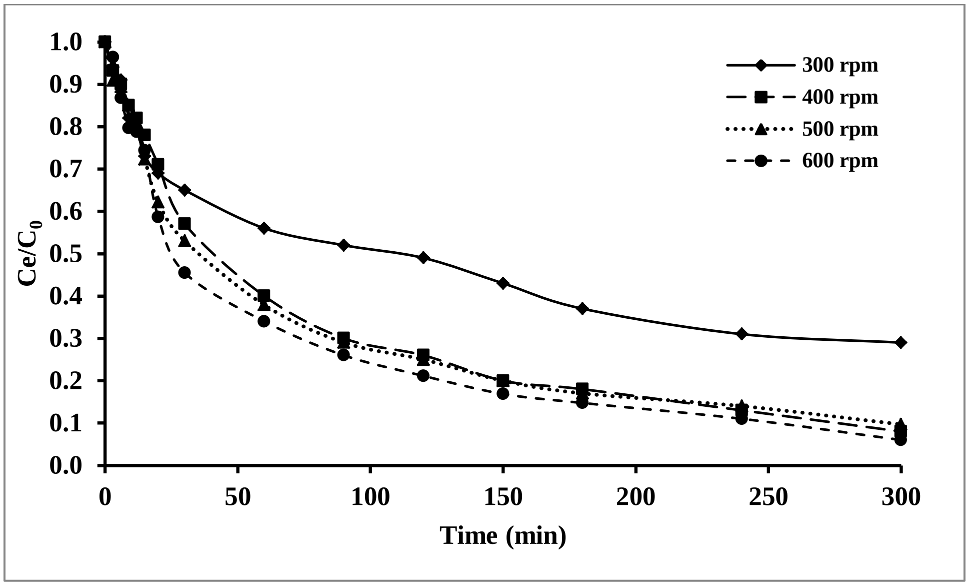

Figure 8. Concentration-time decay data for Levofloxacin onto Eggshells, $C_{absorbent}$= 720.3 g/L, $C_{0Levofloxacin}$ = 150 mg/L, pH= 7at different agitation speeds.

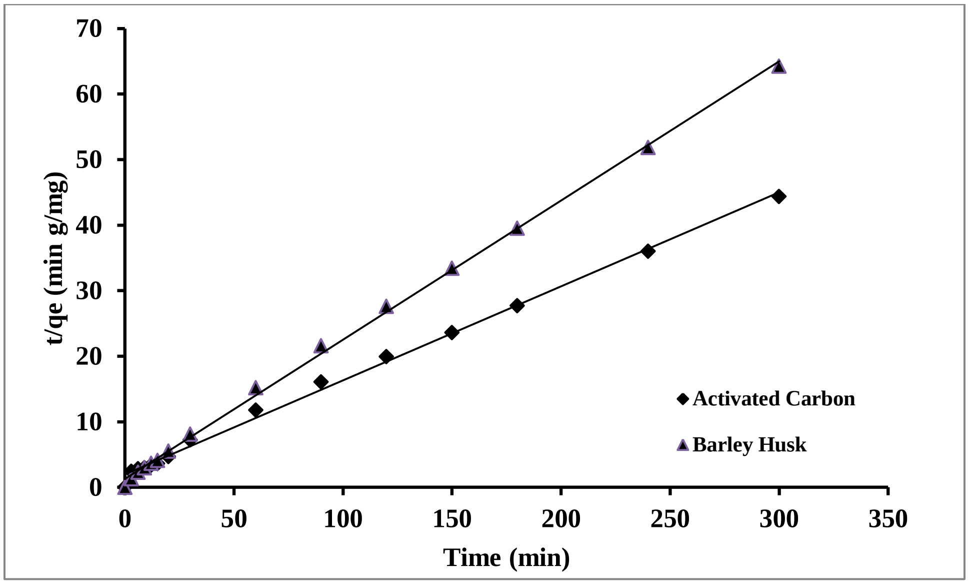

Figure 9. Pseudo-second-order model for Levofloxacin onto activated carbon and barley husk; $C_{0Levofloxacin}$ = 150 mg/L, pH= 7.

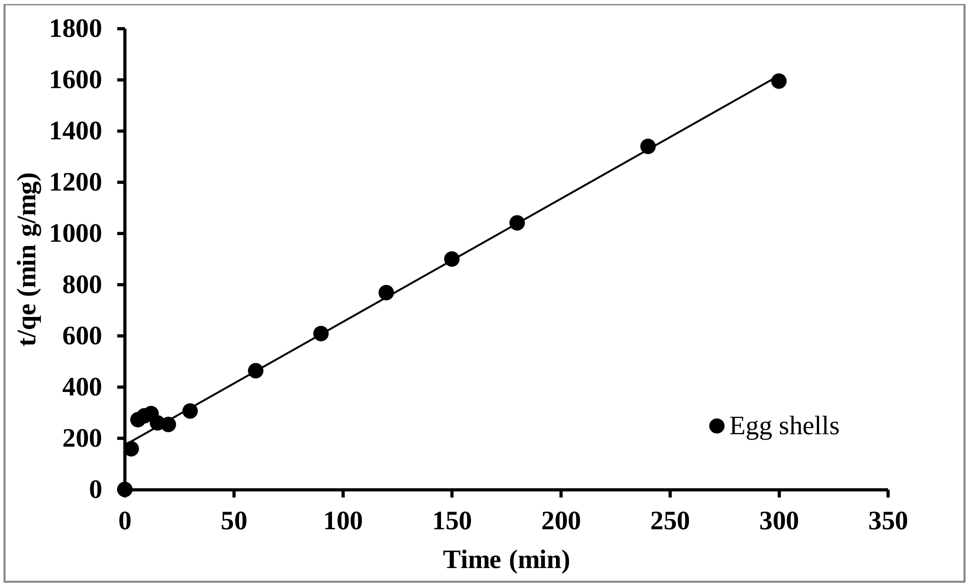

Figure 10. Pseudo-second-order model for Levofloxacin onto egg shells; $C_{0Levofloxacin}$ = 150 mg/L, pH= 7.

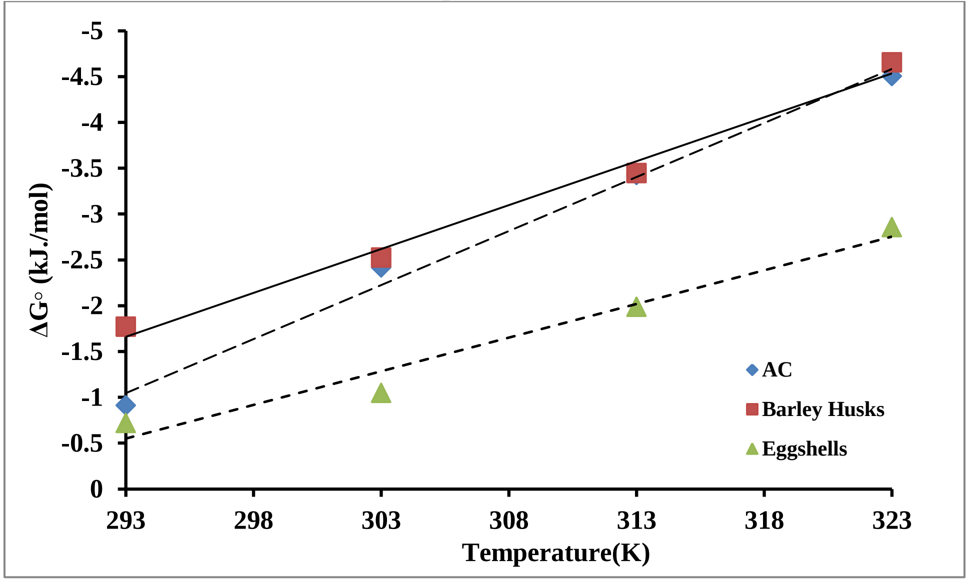

Figure 11. Change in free energy with temperature for the adsorption/biosorption of Levofloxacin onto activated carbon, barley husks and eggshells, at initial concentration of 150 mg/l, pH 7.