Kinetics and Equilibrium for Adsorption of Atenolol from Water using Moringa Oleifera and Nirmali Seeds

Archana Rao P, Mayuka S. Reddy, Yashwanth J, Lokeshwar Y, Satyanarayana S.V.

Abstract: Water is the principal element needed in the formation and progress of healthy life. Pharmaceutical products and their associated metabolites devoted for humans or animals, land up in the aquatic environment after use. Small concentrations of pharmaceuticals are noticed in civic wastewater, surface water, and even drinking water as per the present day research. Development of resistance by microorganisms, pharmacological effects and ecotoxicological effects are the inherent risks due to exposure to small concentrations of pharmaceutical pollutants. Out of all the methods for treatment of water, Adsorption, with biomaterials such as natural adsorbents is an economical process that is simple and easy to carry out. In the present study natural adsorbents such as Moringa Oleifera and Nirmali seeds were used to remove pharmaceuticals (Atenolol) from water. The adsorbents used in this study were characterized by FTIR. The experiments were carried out in batch system and parameters such as time of contact and adsorbent dosage were optimized. A good Atenolol removal percentage of 86% with Nirmali seed and 77% with Moringa Oleifera were obtained. Results obtained recommend that the proposed process represent noteworthy potential for degradation of pharmaceutical contaminant Atenolol.

Key words: Pharmaceutical contaminant; Adsorption; Moringa Oleifera seed; Nirmali seeds.

I. INTRODUCTION

In present days, major cause for water pollution is increasing population and growth of industries. Collection, treatment and disposal of domestic and industrial Wastewater are the major issues to be addressed for preventing destruction to the environment are collection and treatment of civic and industrial wastewater. [1]. One of the studies finds that untreated sewage water is main cause for the pollution of surface and ground water in our country. This polluted water might affect the life of living beings by causing diseases. Recent studies recognized that small concentrations of pharmaceutical pollutant are identified in water bodies and this extended exposure may be detrimental to life in water [2]. In the present study atenolol is selected as pharmaceutical contaminant.

Revised Manuscript Received on April 21, 2020.
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The human body does not fully metabolize Atenolol, one of the most consumed ß-blocker and hence is expelled mostly (about 90%) unchanged through urine [3,4,5]. Varying concentrations from about 0.78 µgL⁻¹ to 6.6 µgL⁻¹ of Atenolol has been noticed in hospital runoff [3,6,7,8,9]. Some of the methods used for treatment of water are incineration, bioremediation, thermal desorption, and adsorption with nano particles. Out of these techniques, adsorption a physical-chemical method is one of the simple and cost effective methods to treat the pharmaceuticals in water [10]. Currently there are efforts made to use inexpensive and available agricultural wastes and natural products as adsorbents to eliminate industrial pollutants from ground water and waste water [11]. In the present study, natural adsorbents used for the degradation of pharmaceutical waste from water are Nirmali seeds and Moringa Oleifera seeds.

II. MATERIALS AND METHODS

A. Materials

The adsorbent Moringa Oleifera and Nirmali seeds and sorbate drug Atenolol 25 mg were procured from local market in Hyderabad, Telangana. Ethanol was procured from Akshaya Chemicals Hyderabad, Telangana. Analytical reagent grade chemicals were used for the experiments. Purified water was used for preparation of all solutions. Solutions of the desired concentrations to be used in experiments were prepared by dilution of the stock solution.

B. Pre-Treatment Of Natural Adsorbents

Nirmali seeds were first soaked in water with 1% of Hydrochloric acid for 10-15 days [12]. These seeds were then ground, dried in hot air oven at 60°C and weighed. Moringa Oleifera seed powder was dried and weighed. The drying was continued till steady state was reached. Final moisture content of both seeds was estimated. Both the seeds were sieved in an electrical shaker and the powder with the mesh size of 44 (0.335mm) to 72 (0.212mm) was separated and stored in zip lock cover for further use. Moisture content was calculated using the equation

\[ \text{Moisture content} = (C_0 - C_i) * 100 \]  
(1)

Where \( C_0 \) and \( C_i \) are initial and final weight of powder in grams.
Kinetics and Equilibrium for Adsorption of Atenolol from Water using Moringa Oleifera and Nirmali Seeds

C. Instrumental Analysis

In order to determine the functional groups present Moringa Oleifera and Nirmali seeds were characterized by using FTIR (Fourier transform infrared spectroscopy). To analyse the concentration of atenolol UV-Visible spectroscopy was used at wavelength of 224 nm. Percentage degradation of atenolol drug and quantity of Atenolol uptake per unit of natural adsorbent used (q) were calculated using following (2) and (3).

\[ \text{% Degradation} = \left( \frac{C_0 - C_i}{C_0} \right) \times 100 \]  \hspace{1cm} (2)

\[ q = \frac{V}{W} \left( C_0 - C_i \right) \]  \hspace{1cm} (3)

Where \( C_0 \) is the initial Atenolol concentration (mgL\(^{-1}\)), \( C_i \) is the Atenolol concentration at adsorption equilibrium (mgL\(^{-1}\)), \( V \) is the volume of drug solution (ml), and \( W \) is the weight of natural adsorbent used (g) [13].

D. Preparation Of Synthetic Atenolol Solution

Atenolol stock solution was prepared by using 25 mg of atenolol tablets. 25mg of atenolol was powdered finely using mortar and pestle then added to 50 ml of ethanol stirred for 10 min and 50 ml of distilled water was added to this and stirred for about 45 min with temperature maintained around 37 degree Celsius [14]. Next the solution was filtered using Whatman filter paper and made up to 1000 ml by adding distilled water. The concentration of this solution is 25 ppm. 10-ppm solution was made from 25-ppm solution by adding calculated amount of distilled water.

E. Experimental Procedure

Adsorption process for both the seeds was carried out as batch process in a 250ml conical flask. To the 50 ml of 10 ppm atenolol stock solution required amount of absorbent was added the stirred for particular interval of time [13]. After this process time the solution was immediately filtered and centrifuged. Final concentration was analysed using UV visible spectrometer.

III. RESULTS AND DISCUSSIONS

A. FTIR Analysis Of In-House Developed Adsorbent

Chemical species present in Moringa Oleifera seeds and Nirmali seeds were analyzed by FTIR, as shown in Fig 3 and fig 4.

Fig. 3: FTIR of Moringa Oleifera

Fig. 4: FTIR of Nirmali

Fig. 3 shows the FTIR of Moringa Oleifera seeds. The broad band centered at 3,420 cm\(^{-1}\) assigned to O-H stretching appears predominantly due to the presence of protein and fatty acid structures in Moringa Oleifera seeds [15]. The N-H stretching of amide groups in this region is also due to the high content of protein. The peaks at 2,923 cm\(^{-1}\) and 2,852 cm\(^{-1}\) are assigned to symmetrical and asymmetrical stretching of the C-H of CH\(_2\) group present in fatty acids [15]. Three intense bands assigned to C=O bond stretching are seen in the region between 1800 and 1600cm\(^{-1}\), two bands at 1,740 and 1,715 cm\(^{-1}\) shown by the spectra are linked with fatty acids and a band at 1,658 cm\(^{-1}\) connected with the amide group in the protein [15]. Peak at 1,587cm\(^{-1}\) can be assigned to C-N stretching and/or N-H deformation.

Fig 4 shows the FTIR of Nirmali seeds. The broad band at 3506 cm\(^{-1}\) could be assigned to stretching vibration of hydrogen bonded hydroxyl group. The band at 2930 cm\(^{-1}\) could be linked to the stretching vibration of C-H [16]. The bands at 1636 and 1060 cm\(^{-1}\) could be connected to C=O stretching vibration of carboxylic acid and C-O stretching vibration of alcohol, respectively [16].

B. Contact Time Effect On Adsorption Of Atenolol

The outcome of contact time on the percentage degradation of Atenolol using Moringa Oleifera and Nirmali seeds as natural Adsorbents was investigated. In 50ml of 10ppm atenolol solution 0.25g of Moringa Oleifera adsorbent was added and time was varied from 15 min to 90 min till steady state was reached. Same process was done with Nirmali seed as adsorbent. Percentage degradation of atenolol by Moringa Oleifera and Nirmali seed as adsorbents are shown in table I.
IV. ADSORPTION KINETICS

A number of kinetic models have been applied to pharmaceutical pollutant adsorption from aqueous solution and the adsorption controlling mechanism has been examined. In this study pseudo-first-order and pseudo-second-order, were applied [13,20], Lagergren’s first order rate equation is employed to describe the adsorption kinetics [13,20]. Lagergren’s first order rate equation in linear form is [13, 18]:

\[ \ln(q_e - q_t) = \ln q_e - K_1 t \]  \hspace{1cm} (4)

where \( q_e \) is the amount of pollutant adsorbed onto the adsorbent at equilibrium (mg/g), \( q_t \) is the amount of pollutant adsorbed onto the adsorbent at any time \( t \) (mg/g), and \( K_1 \) (min\(^{-1}\)) is the rate constant of the pseudo-first-order adsorption which can be calculated from the slope of the linear plot of \( \ln(q_e - q_t) \) vs. \( t \) and \( q_e \) can be calculated from intercept. A second order model based on, adsorbent adsorption capacity is proposed by Ho [13, 21]. This model differentiates two types of kinetic models of a second-order rate expression, one that is based on the adsorbent concentration and the other that is based on the solute concentration. A pseudo-second-order rate expression is represented and the linearized form of the model [13, 21] as given by Ho is

\[ \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \]  \hspace{1cm} (5)

Where \( K_2 \) (gmg\(^{-1}\)min\(^{-1}\)) is the rate constant of the pseudo-second-order adsorption, \( q_e \) is the quantity of pollutant adsorbed at equilibrium (mg/g), and \( q_t \) is the quantity of pharmaceutical contaminant adsorbed at any time, \( t \) (mg/g). \( t/q_t \) against \( t \) is plotted and the slope and the intercept of this plot would give \( K_2 \) (gmg\(^{-1}\)min\(^{-1}\)).
Kinetics and Equilibrium for Adsorption of Atenolol from Water using Moringa Oleifera and Nirmali Seeds

A. Adsorption Isotherms

Experimental sorption equilibrium parameters can be studied by number of isotherm equations, Langmuir and Freundlich models, being the most frequent. The Langmuir isotherm model assumes that there are a finite number of active sites, which are uniformly distributed over the surface of the adsorbent. The affinity of these active sites for adsorption of monomolecular layer is the same and the adsorbed molecules do not interact with each other [13,17].

A linear recognized form of the Langmuir equation is

\[ \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b_L} \]  

In the equation 6, \( q_e \) is the amount of pollutant adsorbed (mg/g), \( C_e \) is the equilibrium concentration of the adsorbate (mg/L\(^{-1}\)), and \( q_m \) is the Langmuir constant related to maximum adsorption capacity (mg/g) and \( b_L \) is Langmuir constant related to energy of adsorption (L/mg) [13].

As per to Equation (6), the plot of \( C_e/q_e \) versus \( C_e \) should be a straight line with a slope of \( 1/q_m \) and intercept \( 1/q_m b_L \), when the adsorption obeys the Langmuir equation. A dimensionless factor, \( R_L \) [13,18] is defined as

\[ R_L = \frac{1}{1+bl_Ca} \]  

The type of adsorption can be stipulated by \( R_L \) values as \( (R_L > 1) \) unfavorable, \( (0 < R_L < 1) \) favorable, or \( (R_L = 0) \) irreversible. [13].

For the case of adsorption on heterogeneous surfaces with interaction between the adsorbed molecules, and the formation of a monolayer is not curbed, Freundlich isotherm model is applied. The assumption of this model is that as the adsorbate concentration increases, it would take up most of the active sites on the adsorbent that leads to emptying of sorption centers. Sorption energy also decreases due to depletion of active sites. The recognized equation for this model [13,19] is

\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]  

In the equation (8) \( q_e \) is the amount adsorbed at equilibrium (mg/g), \( K_f \) is the Freundlich constant, \( 1/n \) is the heterogeneity factor that is related to the capacity and intensity of the adsorption, and \( C_e \) is the equilibrium concentration (mgL\(^{-1}\)). The slope and intercept of the plot of \( \log q_e \) against \( \log C_e \) presents the values of \( K_f \) and \( 1/n \).

B. Kinetics of Adsorption of Atenolol

For both Moringa Oleifera and Nirmali seeds, kinetics was studied with pseudo first and second order.

| Time | \( q_t \) | \( \log (q_e - q_t) \) | \( t/q_t \) |
|------|------------|----------------|--------------|
| 15   | 500        | 2.146          | 0.03         |
| 30   | 540        | 2              | 0.055        |
| 45   | 580        | 1.778          | 0.077        |
| 60   | 600        | 1.602          | 0.10         |
| 75   | 620        | 1.301          | 0.120        |
| 90   | 640        | 1.010          | 0.140        |

Table -III: Adsorption kinetics for the adsorption of Atenolol on Moringa Oleifera seed

Fig. 7: Pseudo first order kinetics for Moringa Oleifera seed

![Fig. 7](image)

\[ y = -0.0139x + 2.3918 \]  
\[ R^2 = 0.9854 \]

Fig. 8: Pseudo Second order kinetics for Moringa Oleifera seed

![Fig. 8](image)

\[ y = 0.0015x + 0.0102 \]  
\[ R^2 = 0.9983 \]

Retrieval Number: A1748059120/2020©BEIESP
DOI:10.35940/ijrte.A1748.059120

Published By:
Blue Eyes Intelligence Engineering & Sciences Publication

1657
Table -IV: Kinetics for the adsorption of Atenolol on Nirmali seed

| Time (min) | q_t | \(\log(q_e - q_t)\) | t/q_t |
|-----------|-----|---------------------|-------|
| 30        | 157.333 | 1.823               | 0.190 |
| 60        | 178.666 | 1.656               | 0.335 |
| 90        | 197.333 | 1.425               | 0.456 |
| 120       | 213.333 | 1.028               | 0.562 |
| 150       | 221.333 | 0.426               | 0.677 |
| 180       | 224    |                      | 0.803 |

The log (q_e - q_t) and t/q_t versus time for the pseudo-first order reaction, and pseudo-second-order reaction for Atenolol-Nirmali seed systems are the straight line plots that are shown in fig 7, 8, 9, 10 respectively. The correlation coefficients values \(R^2\) are nearer to one for pseudo-second-order kinetics and hence this model is more suitable for the present adsorption system.

C. Adsorption Isotherms

Isotherms of Adsorption were interpreted with Langmuir and Freundlich isotherms.

Table -V: Adsorption isotherm for the adsorption of Atenolol on Moringa Oleifera seeds

| \(C_o\) | \(C_e\) | \(q_e\) | \(\log q_e\) | \(\log C_e\) | \(C_e/q_e\) |
|--------|--------|--------|-------------|-------------|------------|
| 10     | 2.3    | 7700   | 3.8864      | 0.3617      | 0.0002     |
| 10     | 3.3    | 3350   | 3.5250      | 0.5185      | 0.0009     |
| 10     | 4.9    | 1700   | 3.2304      | 0.6901      | 0.0028     |
| 10     | 5.0    | 1250   | 3.0969      | 0.6989      | 0.0040     |
| 10     | 6.8    | 640    | 2.8061      | 0.8325      | 0.0106     |
| 10     | 7.5    | 416.66 | 2.619       | 0.8750      | 0.0180     |

The Langmuir and Freundlich isotherms for the adsorption of Atenolol on Moringa Oleifera seed system are presented in Fig 11 and 12. Atenolol –Moringa Oleifera seed system adsorption data is fitted to both Langmuir and Freundlich isotherms; correlation coefficients are calculated and presented in Table VII. As per the results obtained the adsorption of Atenolol on Moringa Oleifera seed is befitting with the Freundlich model. This suggests physical adsorption and heterogeneous distribution of active sites on the Moringa Oleifera seed.
Kinetics and Equilibrium for Adsorption of Atenolol from Water using Moringa Oleifera and Nirmali Seeds

The Langmuir and Freundlich isotherms for the Atenolol adsorption on Nirmali seed system are shown in figure 13 and 14. These results prominently indicate Atenolol adsorption on Nirmali seed fits well with the Langmuir model. The active sites on the Nirmali seed surface have the same compatibility for adsorption of monomolecular layer and there is no interaction between adsorbed molecules.

V. CONCLUSION

Present study represents the performance of natural adsorbents Moringa Oleifera and Nirmali seeds for removal of Atenolol drug from water. Different adsorption characteristics, which may result due to different features of these natural adsorbents, were shown by FTIR characterization. 86% removal of pharmaceutical contaminant atenolol was observed with Nirmali seed for a time period of 60 min with the adsorbent dosage of 0.05g. 77% removal of pharmaceutical contaminant atenolol was observed with Moringa Oleifera seed for a time period of 60 min with the adsorbent dosage of 0.05g. Adsorption profiles of these 2 adsorbents followed Pseudo second order model as shown by the kinetic studies. The best-described adsorption isotherm for Moringa Oleifera seed was the Freundlich isotherm and Langmuir isotherm model was well fitted to adsorption with Nirmali seeds.

ACKNOWLEDGEMENT:

The authors convey their regard to B V Raju Institute of Technology, Narsapur, Telangana, for providing the necessary facilities for the above studies.

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