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ADSORPTION OF PHARMACEUTICAL CONTAMINANTS FROM AQUEOUS SOLUTIONS BY USING NATURAL PLANTS AS ADSORBENTS ASSISTED BY ULTRASOUND PROCESS

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Abstract

Activated carbon (AC) as a source of natural plants (apricot stones) were using as a good adsorbent for removal of pollutants Ranitidine drug from aqueous solutions by assisted of sonicated. The results of different experiments showed that a (AC) that considered a friendly of the environment have ability to adsorb Ranitidine drug from aqueous solution. The sorption process dependent of the pH and was found the best result at pH 6.5, and the adsorption process has nearly reached equilibrium in 60 min. The experimental data are fitted well to Langmuir isotherm model, and the maximum adsorptive quantity of Ranitidine was 96.071 mg/g according to Langmuir model.

Key words : Pharmaceuticals, Ranitidine drug, Adsorption, Ultrasound, Activated carbon.

Introduction

Ranitidine is a histamine H2-receptor antagonist which differs in chemical structure from both histamine and cimetidine (Rakesh Pahwa1 2016) Some selected physicochemical properties of amoxicillin are shown in table 1. Ranitidine is commonly employed in the management and treatment of acute duodenal ulcer disease, Zollinger-Ellison syndrome and systemic mastocytosis with gastric hypersecretion (J. G. M I L L S 1997; Aljeboree and Alshirifi 2018). Ranitidine is the drug of choice in the treatment of the Zollinger-Ellison syndrome because of its increased potency and lesser effect on endocrine function compared to cimetidine. This drug is a selective, competitive histamine H2-receptor antagonist and is utilized in the short-term treatment of active duodenal ulcers and gastric hypersecretory conditions (Rakesh Pahwa1 2016; Alkaim 2017; Aljeboree 2019). activated carbon (AC) take to be among the adsorbents that have been utilize for the effective removal of drug from aqueous effluents (M. Ghaedi 2011; Enas M Alrobayi 2017; Louis Lefebvre 2018). Activated carbon, also called, carob activates, activated coal, or activated charcoal, is a form of carbon processed to have minor, little-volume pores that increase the surface area obtainable for adsorption or chemical reactions. (Aljeboree, Alkaim *et al*. 2019; Hoppen, Carvalho *et al*. 2019). In this study, preparation activated carbon to removal/adsorption of drug Ranitidine from an aqueous water. The effects of different factors, for example amount of the activated carbon, pH solution, and concentration of the drug Ranitidine.

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Materials and Methods

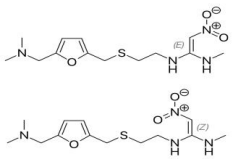
Determinations of Calibration Curves of ranitidine Drug

The calibration curve of different concentration of ranitidine drug were prepared in serial dilutions (10-100 mg/L). Absorbance was measured at the ëmax for drug and plotted against the concentration values of ranitidine (Fig. 1).

Adsorption Equilibrium Experiments

Stock solutions of the drug (1g/1000 mL) were prepared, and the range of required concentrations was made by dilutions with distilled water. The initial tested concentrations of drug were (10, 20, 30, 40, 50, 60, 70, 80,90 and 100 mg/L), The effect of initial solution pH on the drug adsorption by AC was studied at a concentration

Table 1: Physicochemical properties of Ranitidine.

Ranitidine	Physicochemical properties
$C_{13}H_{22}N_4O_3SHCl$	Molecular Formula
350.87	Molecular weight(g/mole)
Ranitidine hydrochloride	Proper name
(n-methyl)thio]ethyl}- n-methyl-2-nitro-1,1-ethenediamine, hydrochloride	Chemical name
Ranitidine hydrochloride is a practically odourless white to pale yellow granular substance. At room temperature, ranitidine hydrochloride is soluble in water, methanol, ethanol, and chloroform.	Physicochemical properties
	Structural formula

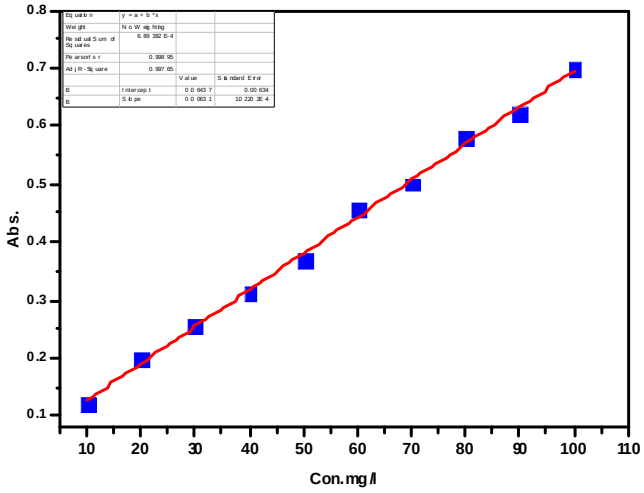


Fig. 1: Calibration curve for Ranitidine drug.

Table 2: Statistics data of calibration for different concentrations of Ranitidine drug.

Parameters	Proposed Method Ranitidine
λ_{max} (nm)	330
Beer's law limit (µg/ml)	10-100
Regression equation	(Y = mX + C) 0.0063X+ 0.0644
Slope (m)	0.0063
Intercept (C)	0.0644
Correlation coefficient (r^2)	0.9979
Color	Colorless

of 40 mg/L. and the pH was adjusted using 0.1 N KOH and 0.1 N HCl solutions by using an Orion 920A pH-meter with a combined pH electrode. pH-meter was standardized with NBS buffers before every measurement. The effect of mass dosage was studied by agitating in different masses (0.01, 0.03, 0.05, 0.08, 0.1 and 0.15 g) of AC, at 25 °C of 40 mg /L.

Ultrasound adsorption experiment was undertaken as follows: 100ml of 40 mg/L ranitidine drug was mixed thoroughly with 0.08g of AC at pH =6 at room temperature for 1hr under sonicated effect "ultrasound" assuming that the equilibrium has reached.. Finally, the sample was centrifuged and then analyzed for residual drug concentration by UV–vis spectrophotometer (Shimadzu UV/ Vis 1650 spectrophotometer, Japan) at 330 nm. The amount of drug uptake by AC in each flask was calculated using the mass balance equation (Yang, Li *et al.*)

$$qe = \frac{Co - Ce}{W} * V \quad (1)$$

Where q_e is the amount of drug adsorbed by (AC) at equilibrium, C_o and C_e are the initial and final drug concentrations (M), respectively, V is the volume of solution (L), and W is the adsorbent weight (g). The drug percent removal (%) was calculated using the following equation:(Yang, Li *et al.*)

$$E\% = \frac{Co - Ce}{Co} * 100 \quad (2)$$

Results and Discussion

Effect of Solution pH on Drug Adsorption

Solution of pH play an important role in adsorption through is effect on the target compounds, the charge species and density on the surface of sorbent (Aljeboree, Alkaim *et al.*, 2019; del Mar Orta, Martn *et al.*, 2019). In this work, the effect of pH is investigated at pH range from 3-10.2. The removal of Ranitidine from aqueous solution by AC is highly pH dependent. The optimum solution pH was found to be 6.5 (Ruwaida A Raheem 2016). The percentage removal was minimum at pH 3 (44.44mg/g) and increased up to pH10.2, reached maximum (99.12 mg/g) over the initial pH show in Fig 2. At higher pH, the surface may get positively charged, which enhances the negatively charged drugs anion through electrostatic forces of attraction (Aljeboree, Alkaim *et al.*, 2019).

Effect of Adsorbent Dose

Effect of the Adsorbent Dose (AC) was needing in arranging to the minutest probable quantity, which appear the maximum adsorption stoichiometric. The several quantity from 0.01 to 0.15 gm /100 ml of (AC). The results

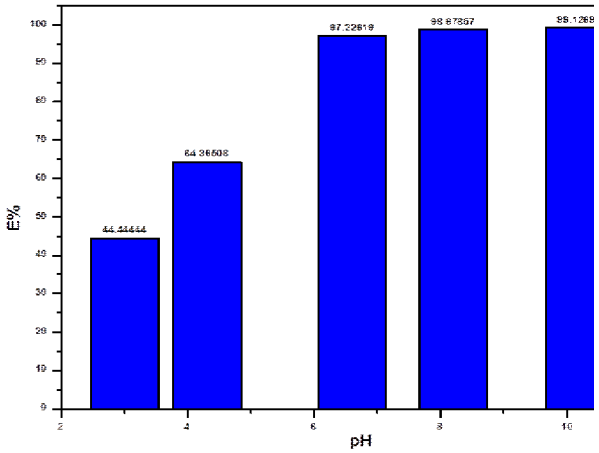


Fig. 2: Effect of solution pH on the percent removal Raniti drug onto (AC) initial concentration = 40 mg/L, Tem 25°C, contact time 2 h, and mass of adsorbent 0.08 g).

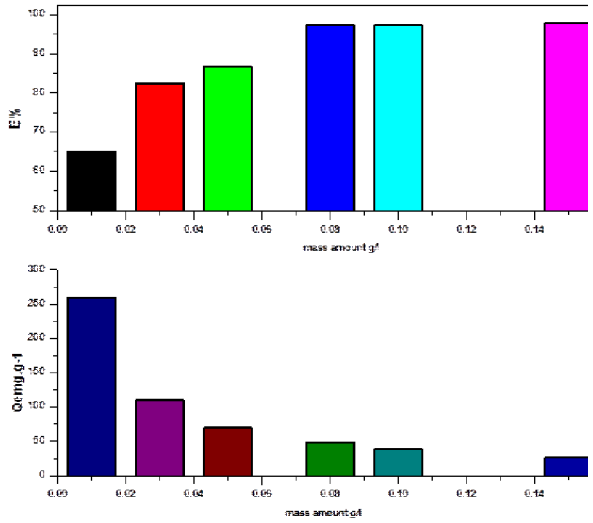


Fig. 3: Effect of mass amount of adsorbent (AC) on the percent removal and amount of adsorbed Ranitidine drug , initial concentration = 40 mg/L, Temp. = 25°C, contact time 2 h.

show in Fig. 3. percentage removal (E%) of Ranitidine drug against the mass of AC adsorbent. From Fig. 3, it is observed that the E% of adsorption is increases with increasing in the adsorbent. This might be reflected to surface area increase of the AC, that increases the binding sites. (Aljeboree and Abbas 2019; Yazidi, Atrous *et al*., 2020; Aljeboree, Al-Gubury *et al*., 2019).

Effect of initial dye concentration

The plot of the quantities of drug adsorbed (Qe) and (E%) drug removal versus primary concentration at several experimental conditions Fig. 4, Fig. 5. The adsorption capacity (Qe) increase with increasing initial drug concentration, while the percentage of removal decreasing with initial drug concentrations. The removal of drug by adsorption on *AC* was found to be rapid low

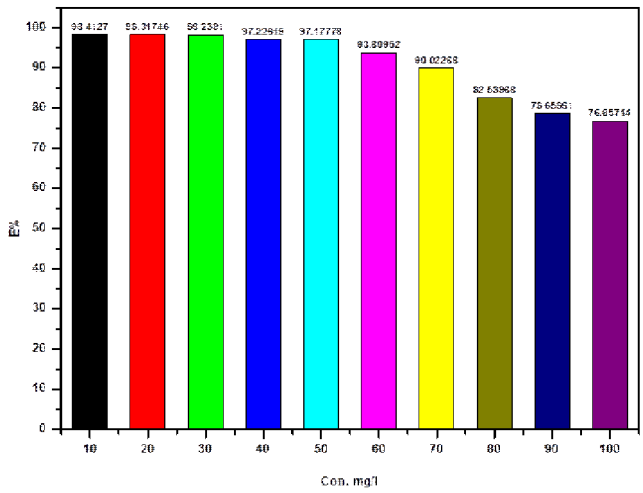


Fig. 4: Effect of initial concentration on the percent removal Ranitidine drug onto (AC) Temp. = 25°C, contact time

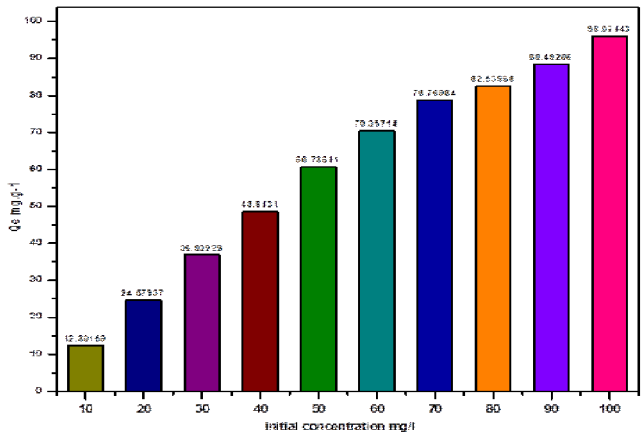


Fig. 5: Effect of initial concentration on the amount of adsorbed Ranitidine drug onto (AC) Temp. = 25°C, contact time 2 h, and mass of adsorbent 0.08 g).

concentrations of drug and then to slow down with increasing in dye concentration. the color removal of drug solution onto AC by adsorption rose rapidly at the beginning and then gradually slowed down until equilibrium was reached. It might be explained that a large number of vacant surface sites were available for adsorption during the initial stage (Fabryanty, Valencia *et al*., 2017; Aljeboree 2019; Aljeboree, Al-Gubury *et al*., 2019).

Effect of acid treatment on the adsorbent surfaces

The study of the effect of acid treatment on the surface was necessary to show the maximum adsorption. The adsorbent was treated by different acids such as (HNO_3, HCl, H2SO4). The results are illustrated in fig. 6.

It was obvious from the results shown in figures 6 the best adsorption capacity when the adsorbent treated by HNO_3, this is may be due to the increased in acid

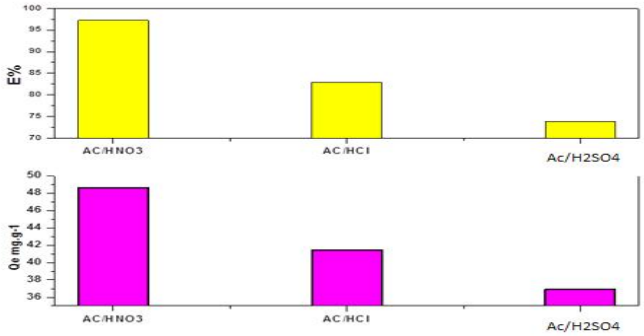


Fig. 6: Effect of different treatment on the activity of AC surface for the adsorption of drug (pH 6.5, mass adsorbent 0.08 gm).

acidity caused to re-activated the active sites for adsorbent surface (Alkaim, Zainab *et al*., 2015).

Models of Adsorption Isotherms

Isotherm Freundlich

the isotherm Freundlich is known as equation 3 (Y.S. Ho 2002; M. Özacar 2003)

$$q_e = K_f C_e^{\frac{1}{n}} \quad (3)$$

q_e: adsorbent Amount adsorbed / unit mass at equilibrium (mol/g),(mg/g), Ce : the adsorbate Equilibrium scam solution next adsorption (mg/L), (mol/L), Kf : capacity factor ($L.g^{-1}$), 1/n heterogeneity factor, n is a deviation measured of the deviation from adsorption linearity.

Its value indicates nonlinearity unit among adsorption and solution concentration as follows: adsorption route is chemical if value under to unity or it is linear if the n value equal to unity, finally the favorable physical route when value is above unity adsorption (P. Senthil Kumar 2010).

A plot of qe versus Ce (Fig. 7) where the values of KF and 1/n are optained from the intercept and slope of the linear regressions (Table 3).

Isotherm Langmuir: it is used for the adsorption of contaminants from liquid solutions (I. Langmuir 1916; I. Langmuir 1918). Langmuir derived Other equation on the definite case of the adsorption rout nature from solution. The Langmuir adsorption isotherm was developed based that (G. Crini 2007) All accessible sites fixed number has same energy and it is available on the adsorbent surface, There was reversible Adsorption. Occurring of Monolayer adsorption. And no side communications among the adsorbates. thus Lang. adsorption isotherm is clarified in equation 4 (I. Langmuir 1916; I. Langmuir 1918)

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

Where qe: adsorbed amount per unit weight at equilibrium (mg/g), Ce: con. Of adsorbent equilibrium in solution after adsorption (mg/L), qm: the constant of Empirical Langmuir represents maximum qe (mg/g), KL: empirical Langmuir constant (L/mg).

The Results of this model are shown in Fig. 7, and the Langmuir constants are illustrated in table 3.

Table 3: Model of Freundlich and Langmuir isotherms parameters for Ranitidine drug adsorbed on Activated carbon (AC) at 25 °C.

Ranitidine drug	Parameters	Isotherm models
92.2319± 2.412	qm ($mg.g^{-1}$)	Langmuir
1.10903 ± 0.125	K_L ($L.mg^{-1}$)	
0.98009	R^2	
44.096 ± 3.6479	K_F	Freundlich
0.2548 ± 0.03381	1/n	
0.9003	R^2	

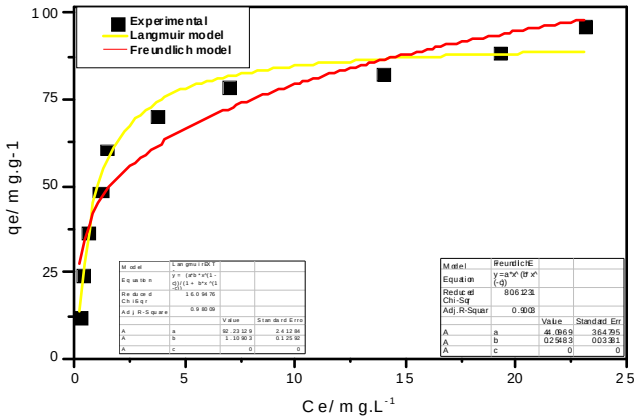


Fig. 7: Ranitidine drug adsorption model of Different adsorption isotherm nonlinear fit . on AC at mass dosage 0.08 gm, pH 6.5, 25 °C initial conc. 40mg/L.

Conclusion

1. The adsorption capacity and percentage removed increase with increasing contact time, surface area, and decreasing with increasing of adsorbent dosage
2. Optimum contact time for equilibrium to be achieved is found to be 1 hours. It is basically due to saturation of the active site which do not allow further adsorption to take place.
3. The best result have been found in pH 6.5, adsorbent dosage 0.08 gm of $ACHNO_3$.

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