British Journal of Pharmaceutical Research
10(4): 1-8, 2016, Article no.BJPR.24083
ISSN: 2231-2919, NLM ID: 101631759

SCIENCEDOMAIN *international*
www.sciencedomain.org

Adsorption – Desorption and Theoretical Study of Propranolol Hydrochloride Drug on Chitosan and Cellulose Acetate Surfaces

Duaa J. Ali[1*], Reem A. Al-Bayati[1] and Ramzie R. Alani[1]

[1]Department of Chemistry, College of Science, University of Al-Mustansiriyah, Baghdad, Iraq.

Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/BJPR/2016/24083
Editor(s):
(1) Wenbin Zeng, School of Pharmaceutical Sciences, Central South University, Hunan, China.
Reviewers:
(1) Lorna T. Enerva, Polytechnic University of the Philippines, Philippines.
(2) Monika Waksmundzka-Hajnos, Medical University of Lublin, Poland.
Complete Peer review History: http://sciencedomain.org/review-history/13469

Original Research Article

Received 2nd January 2016
Accepted 1st February 2016
Published 26th February 2016

ABSTRACT

The research is concerned with the study of adsorption of propranolol hydrochloride drug on the surface of chitosan and cellulose acetate polymers.
Adsorption isotherms of propranolol hydrochloride on the two surfaces used from aqueous solution were specified. These adsorption isotherms were seen to be in agreement with Freundlish adsorption isotherm. Temperature, pH, and ionic strength parameters were studied which affected the adsorption process of the drug and desorption of the drug from the surface was studied to determine the efficiency of the surfaces as drug carrier. Chitosan and cellulose acetate were used as a model adsorbent in the experiments. Hyperchem 8.08 program was conducted using semiempirical (PM3, AM1) method to compare between experimental and theoretical results, both results were pointed to cellulose acetate as better absorbent for the drug.

Keywords: Propranolol hydrochloride; adsorption; chitosan; cellulose acetate; desorption.

**Corresponding author: E-mail: duaajamal87@gmail.com;*

1. INTRODUCTION

Drug toxicity is any substance which, when ingested, breathed in or consumed in moderately little quantities, by its chemical activity may damaging to structure or unsettling influence of function [1]. The clinical problem accompanied drug poisoning is that, most drugs do not have specific antidote for the management accidental poisoning caused by them. The immediate treatment of acute poisoning by overdose of drugs is directed toward reducing the absorption by removal of the toxic product from gastrointestinal tract. Several modalities are available to prevent absorption of poison from the gastrointestinal tract such as emetics, gastric lavage, cathartics and adsorbents [2,3]. The adsorbents ought to reply number of condition to benefit from adsorption system, to be active, steady, cheap, and, more importantly is that the exchange ions would be not hurtful. To Prevent further adsorption of drug been used chitosan and cellulose acetate polymers as a natural absorbent it has high specific surface and safety [4,5].

Chitosan has been used as a safe excipient in drug formulations over the last two decades [6] In clinical practice in the treatment of fatness, is based on supporting the low weight as adsorbent for some drug, also it's nonpoisonous.

Because of its properties cellulose acetate was used in the technology of sustainable release coating of solid dose forms [7]. Propranolol is a non-selective beta-adrenergic receptor blocking drug. (propranolol hydrochloride) Inderal is used for treating high blood pressure or atrial fibrillation, angina (chest pain). Also, It is used to treat tremors and used to prevent migraine [8]. The overdoses of propranolol can be toxic and even fatal. Several symptoms have been described: a) Neurological: fatigue, sleepiness, weakness, headache, visual disturbance, hallucinations. b) Cardiovascular: bradycardia, hypotension, ventricular dysrhythmias, heart failure and cardiac arrest; c) Gastrointestinal: nausea and vomiting. This search reports the results of experimental to adsorption and desorption of propranolol hydrochloride. In this study tested Freundlish and Langmuir isotherm equations. Also, this study give us to envisage adsorption pattern of propranolol hydrochloride on chitosan and cellulose acetate to different cases such as ionic strength, pH, temperature and desorption.

2. Experimental

2.1 Materials

Propranolol hydrochloride was obtained from the Drug Industries and Medical Appliances in Samarra, Iraq (SDI). The U.V-Vis spectra showed λ max for this drug is = 290 nm, molecular weight is equal to 295.8 g/mole, melting point (161℃ –163℃) and the chemical structure is shown in (Fig. 1).

The chitosan polymer used in this study was obtained from Sigma-Aldrich. While the cellulose acetate polymer used from BDH Chemicals, Ltd, UK.

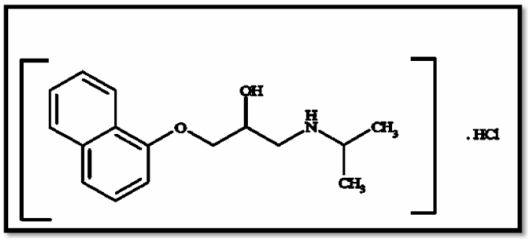


Fig. 1. The Propranolol hydrochloride structure

2.2 Methods

Adsorption – desorption experiences of propranolol hydrochloride drug on two surfaces, was utilized. Adsorption experiments were executed by shaking (0.1 g) of both of the adsorbents used in separate container with (12.5 mL) aqueous solution of propranolol hydrochloride drug of required concentration at different temperatures (7, 27, 37.5, 47℃), pH range (1.2-8), and ionic strengths (0.15 and 0.3 M NaCl solutions in water) for 1.5 hours and 1 hours (the required time for chitosan and cellulose acetate polymer respectively to reach the equilibrium concentration). A thermostatic shaker bath (BS.II digital, JEI. TECH, Korea), was used to keep the temperature constant. The initial concentration of drug solution, Co, were in extent of (1×10-4 – 3.5×10-4 mol•L- 1). All adsorption experiments were conducted at 37.5℃ and neutral pH except those in which the influence of temperature and pH of the solution were examined. The pH of the solution was modified with HCl solution by using (HM-73, TDA Electronics Ltd.) pH meter. At last of the adsorption interval, solution was filtered by using double filter papers (Whatman No. 42,

Germany), Then the concentration of the remaining drug, Ce, was determined with the aid of ultraviolet visible recording spectrophotometer (PG Instruments Limited U.V- T80). The adsorbed quantity of the drug was calculated from the concentration in solutions before and after adsorption based on the equation (1):

$$Qe = (Co - Ce)\ V/W \quad (1)$$

Qe: the equilibrium drug concentration on adsorbent (mg/g).
Co: the initial concentration (mg/L).
Ce: the equilibrium concentration (mg/L).
V: the volume of drug solution (L).
W: the weight of adsorbent (g).

For desorption experiments, The elution amplitude of the adsorbed drug has determined by distilled water as a solvent. Solution of each drug (12.5ml) of recognized concentrations, (1 x 10-4– 3.5 x 10-4 M) in distilled water must added to flasks containing (0.1 g) of the adsorbents. The flask was placed in a fixed temperature bath at 37.5℃. After equilibration, the suspensions were replaced by have and the supernatant was poured carefully. A (12.5 ml) portion of the eluent added; after shaking, the suspensions were filtered. The clear supernatant was assayed [9]. The quantity of drug desorbed was calculated according to the following equation

$$\text{The amount desorbed (mg/g)} = \frac{C_e \cdot V}{m} \quad (2)$$

Where

Ce: The concentration of drug desorbed at equilibrium (mg/L).
V: Volume of eluent (L), m: weight of adsorbent (g), The percent of desorption was obtained from the following equation:

percent desorption = [(amount of drug desorbed)/(amount of drug adsorbed)]×100

3. RESULTS AND DISCUSSION

3.1 Adsorption of Drug by Chitosan and Cellulose Acetate

Adsorption of propranolol hydrochloride by chitosan and cellulose acetate was studied. The applicability of Langmuir and Freundlich adsorption isotherms has been examined for these adsorption systems utilizing the equations (3) and (4)

$$Ce/Qe = 1/ab + Ce/a \quad (3)$$

$$Q_e = k_f C_e^{1/n} \quad (4)$$

(Ce): the concentration of drug at equilibrium (mg/L).
(Qe): amount of adsorbed at equilibrium (mg/g).

The a and b are Langmuir constants which agreed to the maximum adsorption capacity (mg/g) of adsorbent and intensity of adsorption (L/mg), respectively. (kf) and (n) are Freundlish experimental constants, then from the slope and the intercept we can get the value of them. Plotting log Qe versus log Ce values gives straight line and according to the results found correspond with Freundlich isotherm (Figs. 2 and 3).

Table 1. Value of best fitted Freundlish and Langmuir isotherm

Adsorbents isotherm	Freundlich isotherm	Langmuir
Chitosan	0.972	0.40
Cellulose acetate	0.902	0.83

3.2 Influence of Temperature

The influence of temperature on the adsorption rang of propranolol hydrochloride on chitosan and cellulose acetate surface has been studied at four different temperatures (7, 27, 37.5, 47). The general shapes of the drug adsorption are given in (Figs. 4 and 5). Variable temperatures will help in evaluating the basic thermo dynamical functions (ΔH, ΔG, ΔS) of the adsorption process.

Adsorption of propranolol hydrochloride on the two surfaces used in this work were increasing with increasing temperature.

The thermodynamic parameters were determined as following:

ln kads =(-ΔH)/RT+ΔS/R ,where R is the gas constant (8.314 J.mol-1.K-1) and T is the absolute temperature. The adsorption equilibrium constant [10], kads ($L.g^{-1}$), were calculated at different temperatures which is given by the following equation: kads =Qe/Ce*m(g)/v(L),

Where (Qe) is the maximum uptake of adsorption at a certain value of equilibrium concentration (Ce) that was fixed for all temperatures of the study. The values of ΔH and ΔS were determined from the slope and intercept of lines respectively. The value of the Gibbs free energy ΔG) of a reaction or ΔG has calculated from equation: ΔG= ΔH-TΔS.

Table 2 show thermodynamic parameters of drug adsorption on the adsorbent surfaces. Thermodynamic function appeared endothermic heat of adsorption accompanied with an increase in entropies suggesting the positive entropy changes could be viewed the formation of less ordered adsorbed species on the surface. The change in free energy (ΔG) of the adsorption process was found to possess positive values indicating a nonspontaneous adsorption process.

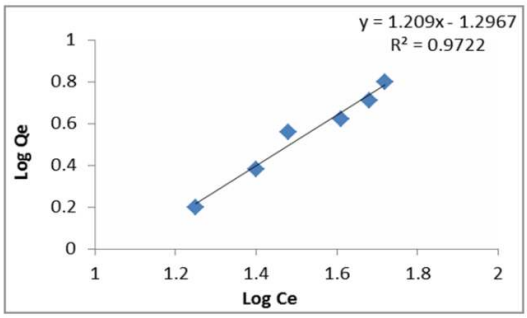


Fig. 2. Freundlich lines of the adsorption of propranolol hydrochloride on chitosan

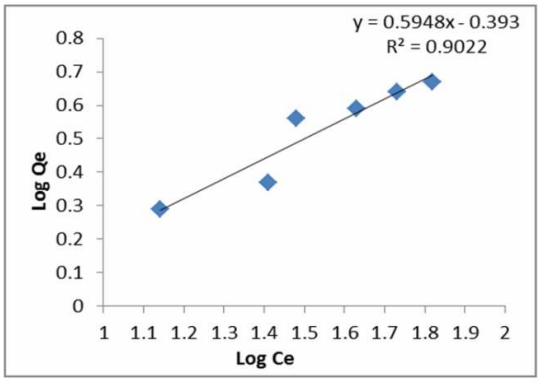


Fig. 3. Freundlich lines of the adsorption of propranolol hydrochloride on cellulose acetate

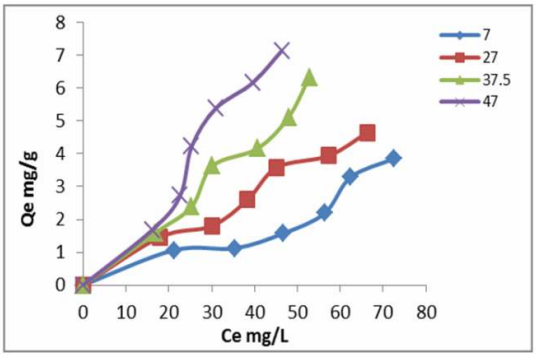


Fig. 4. Adsorption isotherms of the drug on chitosan at different temperatures

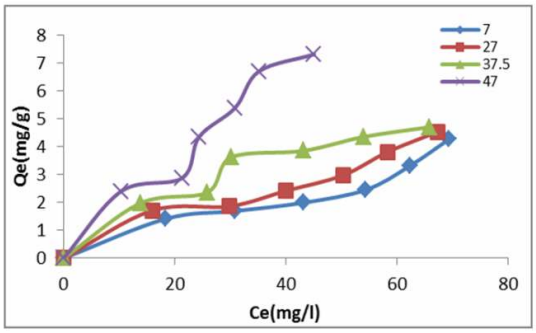


Fig. 5. Adsorption isotherms of the drug on cellulose acetate at different temperatures

3.3 Influence of Ionic Strength

The influence of two NaCl concentration from electrolyte solution has been investigated. The ionic strength effectiveness on adsorption of propranolol hydrochloride on the two surfaces has been studied using (0.15 and .30) M concentration of NaCl solution. The adsorption extend of the drug decreased with increasing the ionic strength in solution. On the fact that, can be interpreted this results to the competition of (Na+) and (Cl-) ions toward the active site on the surfaces are more than that of the drug molecules which lessen their interaction with surfaces as a result of reducing the electrostatic attraction between the adsorbent surface and the drug (Figs. 6 and 7) show the influenced of ionic strength on the amount of drug by two surface from electrolyte solution at normal pH and 37.5℃. These results correspond with the other studies [11] which concerning the influence of brine solution on drug adsorption.

Table 2. Calculated thermodynamic parameters of propranolol hydrochloride adsorption on the adsorbent surfaces at 37.5℃

Adsorbents	ΔH KJ.mol^{-1}	ΔG KJ.mol^{-1}	ΔS J.mol^{-1} . k^{-1}
Chitosan	+22.96	+0.43	+72.55
Cellulose acetate	+16.98	+0.77	+52.2

3.4 Influence of pH

Propranolol hydrochloride drug adsorption on chitosan and cellulose acetate surface at different pH (1.2, 3, 5, 7 and 8) using constant concentration of drug solution using shaker at 37.5℃ to mimic the gastrointestinal motility and body temperature [12] as shown in (Figs. 8 and 9). The adsorption of the drug upon chitosan surface has studied only in neutral medium and (pH > 3). As pH was increased, the amount of adsorption of the drug on all adsorbents also increased. This trend is consistent between (3-7). Further increase of pH beyond 7 generally results in decrease in the adsorption of drug [13,14].

While in pH1.2 the adsorption of propranolol hydrochloride on cellulose acetate an contest made by the hydronium ions is expected upon to bring about a significant decreasing in adsorption of the drug. Besides that, the degree of solubility of the adsorbate might be influenced by the alteration of the pH from acidic to normal affecting on growing in adsorption rapprochement to the surface.

Likewise, could be ascribed the rising in adsorption of the drug with increasing pH of solution to the potential changes in properties of the surface. This direction is fixed between (1.2-7). Previous studies has been proved match the with these results [13] that Related the influence of pH on drugs adsorption utilizing cellulose acetate as an adsorbent surface.

3.5 Desorption of the Drug from the Adsorbents Surfaces

The influence of desorption on the amount of propranolol hydrochloride has been studied using distilled water as an eluent. The result show the release extend of propranolol hydrochloride from two surface an increase with increasing the concentration of this drug which can be interpreted that this drug molecules are strongly bound to the surfaces.

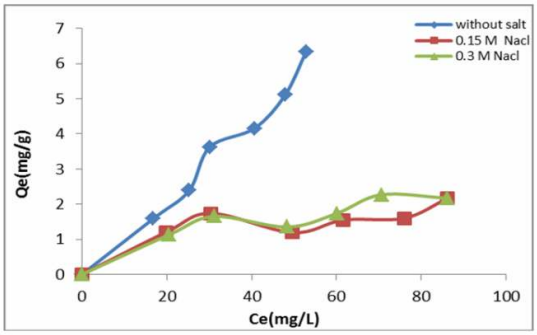


Fig. 6. The effect of ionic strength on the adsorption of propranolol hydrochloride on chitosan surface

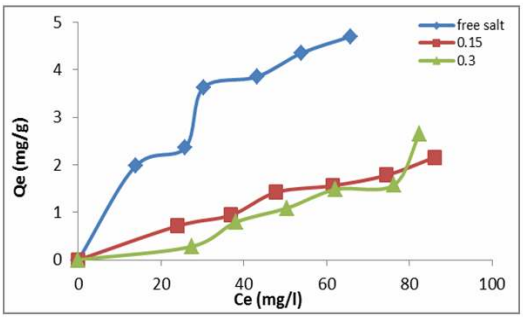


Fig. 7. The effect of ionic strength on the adsorption of propranolol hydrochloride on cellulose acetate surface

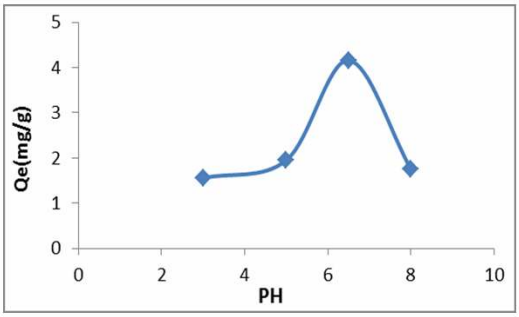


Fig. 8. The effect of pH on the adsorption of propranolol hydrochloride on chitosan surface

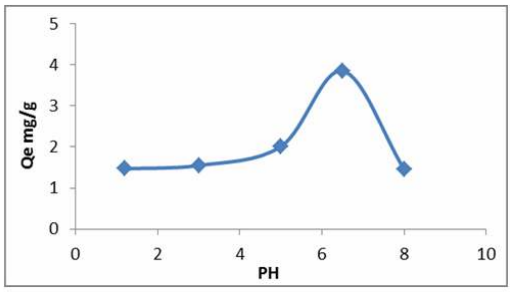


Fig. 9. The effect of pH on the adsorption of propranolol hydrochloride on cellulose acetate polymeric surface

The percent release of the drug and quantity desorption from chitosan and cellulose acetate surfaces after one washing at normal pH and 37.5℃ show in Table 3 and (Figs. 10 and 11) explain the effect of this eluent on the amount of the drug release from two surface.

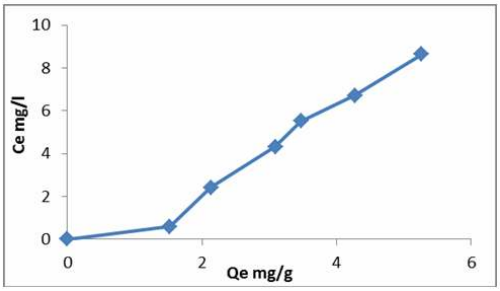


Fig. 10. Desorption of Propranolol hydrochloride from chitosan at (37.5℃) using distilled water

The percent quantity of drug desorbed from chitosan and cellulose acetate were (17.03) and (9.00) respectively. The kind of forces that effect between the surface and the drug molecules can be interpreted the low percentage desorption from cellulose acetate. Also, another kinds of interaction.

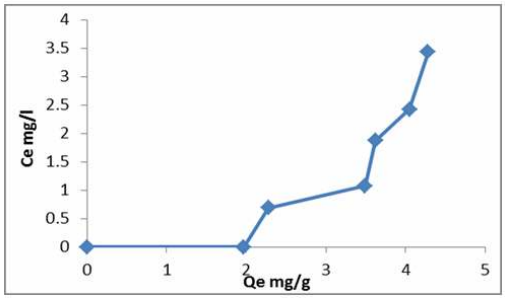


Fig. 11. Desorption of Propranolol hydrochloride from cellulose acetate at (37.5℃) using distilled water

3.6 Theoretical Study

By studying the electron density sites for both surfaces theoretically by using (hyperchem 8.08) to determine probability association with drug through electrostatic forces. The cellulose acetate surface showed a higher active site than chitosan due to the electronic density of sites Fig. 12 and furthermore the polarity of cellulose acetate is higher than that of chitosan surface, as dipole moment values showed. The results of the adsorption experiments when compared with theoretical properties of the drug and the surfaces, it was concluded that the higher the dipole moment, the higher adsorption efficiency.

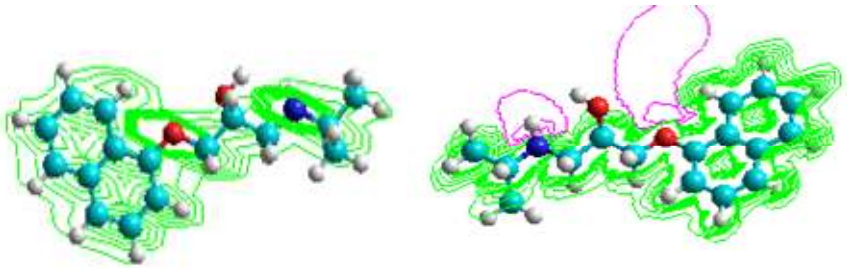
On other hand the number of the active site was an important factor for the adsorption efficiency of the surface. The theoretical study showed that a higher electron density and more HOMO and LUMO sites, which the cellulose acetate surface had made it a better surface toward the drug adsorption Table 4 show dipole moment values for both the drug and surfaces.

Table 3. Quantity desorption and percent desorption of propranolol hydrochloride on chitosan and cellulose acetate surfaces at (37.5℃) using di stilled water as an eluent

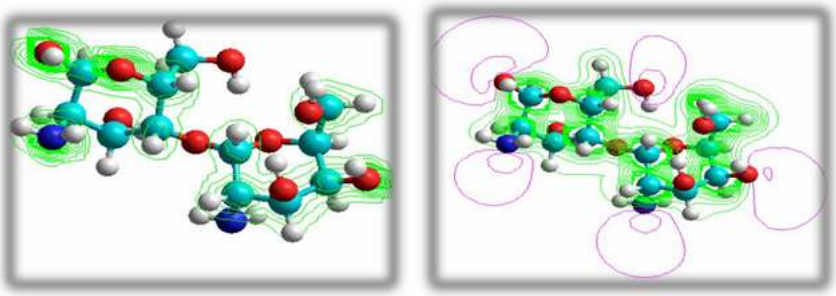
Adsorbents	Elution No.	Quantity Desorbed mg/g	Percent Desorption
Chitosan	1	1.08	17
Cellulose acetate	1	0.429	9.00

Table 4. Show dipole moment values both drug and surfaces by using semiempirical (PM3, AM3)

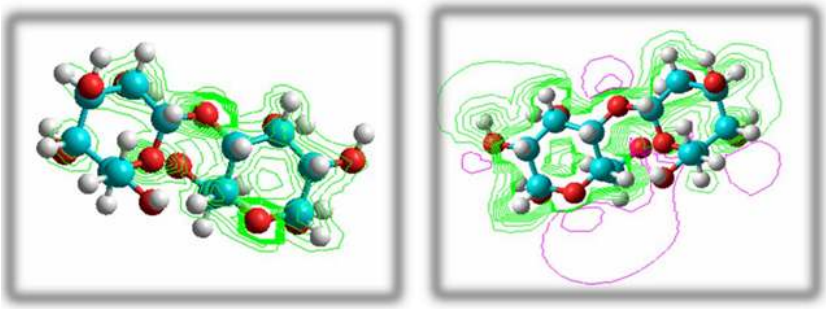
Dipole moment (Dybes)	drug	Chitosan	Cellulose acetate
PM3 AM3	2.585	1.765	5.716
	2.294	1.682	5.98



(Propranolol hydrochloride)



(Chitosan)



(cellulose acetate)

(a) **(b)**

Fig. 12. HOMO electrostatic potential as contours for drug and surface;
a) TCD -2D; b) Ep -2D
Ep= Electrostatic potential TCD=Total charge density 2D= two dimension
White: hydrogen atoms; cyan: carbon atoms; blue: nitrogen atoms; red: oxygen atoms

4. CONCLUSION

The adsorption of propranolol hydrochloride drug from aqueous solutions on both chitosan and cellulose acetate surfaces is a function of temperature, ionic strength and pH. Although the two surfaces used in this study can adsorb propranolol hydrochloride drug, but the most selective surface observed was cellulose acetate which appeared to posses' highly active adsorption capacity. This conclusion could be applied in medicine for the treatment of poisoning by the above drug.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Panthe S, Lohani SP. In Vitro adsorption studies of paracetamol to activated

charcoal capsule, powder and suspension. The Open Toxicology Journal. 2008;2:22-25.
2. Hayes AW. Principle and methods of toxicology, 4th ed, Taylar and Francis, Philadelphia. 2001;1215.
3. Akintonwa A, Orisakwe OE. Arch. Int. Pharmcodyn. Ther. 1990;304:290-295.
4. AL-Bayati Reem A. Adsorption – Sorption systems of some drugs on naturally occurring polymers and bentonite cay PhD Thesis, AL-Mustansirya University; 2007.
5. Annual book of ASIM Standards. 1988;15(04):D871-72.
6. Baldrick P. The safety of chitosan as pharmaceutical excipient. Regul Toxicol Pharmacol. 2010;56:290-299.
7. Bean DC, Livermore DM, Papa I, Hail LM. Resistance among *Escherichia coli* to sulphonamides and other antimicrobials now little use in man. J. Anti Microb Chemother. 2005;56(5):962-4.
8. Hallander S, Ekwall B. MEIC Monograph: Propranolol; 1997. Available:http://www.cctoxconsulting.a.se/23_propranolol.pdf
9. Sorby DL. Effect of adsorbents on drug absorption. J. Pharm. Soci. 1965;54(5): 677-683.
10. Kobya M. Adsorption, kinetic and equilibrium studies of Cr(VI) by hazelnut shell activated carbon. Adsorption Science & Technology. 2004;22(1):51-64.
11. Marc Linden Berg, Cornelia Wiegand, Dressman Jennifer B. Comparison of adsorption of several drugs to typical filter materials. Dissolution Technologies. 2005; 22-25.
12. Onyekweli Anthony, Usifoh Cyril O, Zuofa Jessica D, et al. Adsorptive property of kaolin in some drug formulations. Tropical Journal of Pharmaceutical Research. 2003;2(1):155–159.
13. Al-Bayati RA, Ahmed AS. Adsorption – Desorption of trimethoprim antibiotic drug from aqueous solution by two different natural occurring adsorbents. International Journal of Chemistry. 2011;3(3):20-30,.
14. Karthikeyan G, Anbalagan K, Andal NM. Adsorption dynamics and equilibrium studies of Zn (II) onto chitosan. J. Chem. Sci. 2004;116(2)119–127.

Peer-review history:
The peer review history for this paper can be accessed here:
http://sciencedomain.org/review-history/13469