Isotherms, Kinetics and Thermodynamic Studies for Removal the Valium from Stomach and Intestine Fluids via Adsorption on Egg Shells Powder

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Abstract

Drug abuse or overdose in accidents is a serious social issue. This study concerned the adsorption behaviour of the Valium drug in both simulated gastric and intestinal pH onto the untreated eggshell powder by using UV spectroscopy. The effects of various experimental parameters such as contact time, pH-solution, an adsorbent dosage of Valium and temperature range (300-320k) on the adsorption capacities have been investigated. The suitability of Langmuir and Freundlich adsorption models to the experimental equilibrium data at different solution temperatures were calculated. The adsorption was well described by the Freundlich isotherm model and Langmuir, S_3 for the stomach and S_2 for the intestine according to the Giles classification. Thermodynamic parameters such as $\Delta H°$, $\Delta G°$, and $\Delta S°$ results showed that the adsorption of the drug increases by increasing the temperature in the stomach solution, i.e., the endothermic reaction decreases by increasing the temperature at the intestinal solution, i.e., the reaction is exothermic. Experimental data were also tested in terms of adsorption kinetics, the results illustrated that the adsorption process was following pseudo-second-order kinetics in the stomach solution and first order in the intestinal solution.

Key words: *Adsorption, Langmuir, Freundlich, Kinetics, Thermodynamics*

Introduction

Sorption and adsorption process have been extensively studied as a low cost, effective method for removing a wide variety of hazardous materials from aqueous solutions. Principle considerations in the manufacturing of a drug product include the therapeutic goal, the position of application, and systemic drug sorption from that position. The drug should preferably be entirely and steadily absorbed from the Stomach and intestine sites. Valium is a trading name for Diazepam drug which widely used to treat various types of epilepsy, insomnia, and anxiety, and muscular spasms [(1)]. Overdose Valium can have serious consequences that can cause a number of side effects and hence death in some cases.

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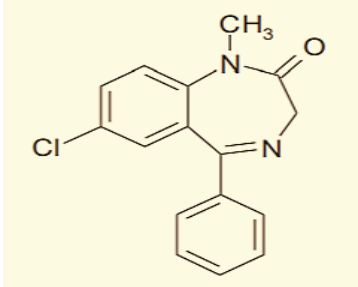


Figure(1):Structure of Valium

Diazepam is one of the most widely prescribed 1,4-benzodiazepine[(2)]. The consumption of Valium along with other substances such as alcohol is known to increase its sedative effects and its increased absorption rate[(1)]. To alleviate these effects a range of analytical approaches has been investigated to determine the adsorption of diazepam on the surface of safe substances like an eggshell powder. Adsorption is a highly effective, economical, promising method that applied for purification wastewaters. Different conventional and non-conventional adsorbents have been used such as Hen egg-shell[(3)]. Hen egg-shell typically consists of ceramic

materials constituted by a three-layered structure, namely the cuticle on the outer surface. The chemical composition of the eggshell has been reported by weight as follows: calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%), and organic matter (4%)[4]. Sorption–desorption studies were carried out for five cycles by Vijayaraghavan and et al. using domestic eggshell to remove copper from aqueous solution in an up-flow packed column[5]. Another study has been described the adsorption isotherms by Otun et al. using Powdered eggshell (particle size 63 μm) as an adsorbent to remove three metal ions Pb (II), Ni (II), and Cd (II) from aqueous solution and from natural water in a batch process[6]. Based on reported research in the literature, it was found that there was a high sorption capacity as compared to other adsorbents for a low-cost sorbent eggshell to remove Cr (III) ions from aqueous solutions[7]. In this work, the equilibrium adsorption characteristics of Valium on the crushed eggshell's surface have been evaluated in batch experiments. The adsorption isotherms, temperature effect, pH adjustment, Kinetic measurements (determined by the pseudo-first-order, pseudo-second-order) and thermodynamic parameters have been calculated.

Waste eggshells have used as adsorbate due to their recycling; it has the potential to reduce environmental pollution while acting as a low cost, safe effective material to reduce Valium absorption by the Digestive.

Experimental methods of adsorption

Chemical materials

Hydrochloric acid (Sigma Aldrich, 99.0%), Sodium chloride (Sigma Aldrich, 99.0%), Sodium hydroxide (Sigma Aldrich, 97.0%), Potassium phosphate (Alfa Aesar, 97%).

Adsorption characterization

All spectral and absorbance measurements were conducted on Shimadzu Uv-Vis 1700 digital double beam recording spectrophotometer (Italy) using 1cm glass cells. this technique provides information about the adsorption of adsorbate on the adsorbent surface whether it is physical or chemical adsorption. The results of the current study show the susceptibility of the eggshells surface to the adsorption of the Valium by using UV spectroscopy. A digital pH meter 720 WTW 82362 has also been used to adjust the acidity or alkalinity of a solution.

Absorbate solutions preparation

Stock solutions of Valium were prepared by dissolving 50 g in distilled water to give a concentration of 100 mg/L and that diluted with distilled water when necessary to prepare other concentrations. The drug may be precipitated with pH between(7.2 – 7.4). To assess the suitability of the approach, the selected pH is important to consider. In the stomach, the pH is about 1 - 2 and in the duodenum, the pH is between 5 to 7.5. so, the degree of solubility is also likely to be influenced as the drug passes through the intestines[8].

To prepare stomach fluid, 2g of sodium chloride and 7ml of hydrochloric acid have been dissolved in distilled water until the pH solution adjusted to 1.2. To prepare intestinal fluid, o.89 g of sodium hydroxide and 6.8g of anhydrous potassium phosphate (KH_2PO_4) have been dissolved in distilled water until the pH solution adjusted to 6.8.

Preparation of biological sorbent

Eggshells were collected from kitchen waste and washed thoroughly in running water for several times and then rinsed with deionized water until no foreign material remained behind. After washing with distilled water, the sample was dried in an oven at 60 °C for two hours to drive off any moisture. The dried eggshells were crushed and milled in an agate mortar and pestle to form a fine powder with a high specific surface area, then passed through a(200 μm) sieve, the portion which passed through the mesh is retaining in a tight container. The chemical compounds of the eggshell are[9]:{%W:Na_2O=0.489, MgO=0.845, Al_2O_3=0.055, SiO=0.010,P_2O_5=0.181, SO_3=0.747,K_2O=0.50, $CaCO_3$=97.015, Fe_2O_3=0.029, SrO=0.140, Cl=0.138}.

Sorption Experiments

Series of batch adsorption tests were conducted to determine the effects of contact time, initial concentration of the drug dosage, amount of adsorbent, and operating temperature on adsorption performance. Therefore, various amounts of egg-shells(0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 0,5, and 1g) were introduced into a series of conical

flasks each filled with 25 mL of Valium solution with 40 ppm at pH 1.2, and pH 6.8 to determine the amount of adsorbent. The flasks were then placed in a thermostat water bath shaker and agitated up to a total contact time of 30 min at a fixed agitation speed of 90 rpm. drug concentration in the samples was analysed by atomic absorption spectrophotometer. Initial drug concentration was determined by shaking(25mL) of five different initial concentrations(10-50ppm) of Valium solution placed in five conical flasks with 0.1 g of eggshells at (pH=1.2), and pH 6.8. for 30 min at 310 k. Equilibrium data were obtained after the solution was filtered and analyzed. In addition to these experiments, the effect of contact time on the drug adsorption was also investigated. Batch adsorption tests were carried out at different contact time from 10 to 120 minutes, 30 min was found to be the best period of contact at equilibrium.

Another experiment, 25 mL of drug solution with a concentration of 40 ppm was added to a fixed amount of adsorbent 0.1g of eggshells in(50 Ml) conical flask and agitated in thermostat shaker with a speed 90 cycle/minute until reaches equilibrium after(30 min) at 310 k temperature, then the solution was filtered and analysed by measuring absorbance at a maximum wavelength of(358nm) and(413nm) for stomach and intestinal solutions respectively. the residual Valium concentration in the supernatant was determined using a UV/Vis instrument.The amount of(Valium) adsorbed was calculated by measuring the difference in concentration between samples that were obtained at two consecutive time intervals over the period of the adsorption experiment.

Again, the experiment was repeated at different temperatures(300 and 320) k to investigate the operating temperature on adsorption performance and to calculate thermodynamic parameters(ΔHº, ΔGº, ΔSº). The sorption capacity was calculated by the following equation[10,11].

$$Q_e = \frac{(C_0 - C_e)V_{sol}}{M} Q_e = \frac{(C_0 - C_e)V_{sol}}{M} \quad (1)$$

$$\%\, Removal = \frac{(C_0 - C_e)}{C_0} * 100 \quad (2)$$

Where: C°: is the initial concentration (mg/L), C_e: is the equilibrium concentration (mg/L), V_{sol}: is the volume of drug solution(L), and M: is the Wight of egg-shells(g).

The experimental data were calculated to describe adsorption equilibrium isotherms by using Two main theories, Langmuir and Freundlich models. the main assumption of the Langmuir adsorption model is that the surface of the adsorbent is covered with a monolayer of adsorbed molecules. Langmuir isotherms which represented by the linear equation:

$$\frac{C_e}{q_e} = \frac{1}{aK_l} + \frac{1}{a} C_e \quad (3)$$

Where a and K_l represent Langmuir's constants related to limiting adsorption capacity when the surface is fully covered with a monolayer adsorbate and rate of adsorption respectively. C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of Valium adsorbed per unit mass of adsorbent. Langmuir's equation assumes the formation of one layer of adsorbate molecules on the surface while the Freundlich isotherm explains the behaviour of adsorption by the formation of more than one layer and consider the heterogeneity of the surface. The linear form of Freundlich isotherm is:

$$Log\, Q_e = Log\, K_f + \frac{1}{n} Log\, C_e \quad (4)$$

Where K_f and(n) are Freundlich constants that depend on the nature of the adsorbent and the gas at a particular temperature which characteristics of the system, including the adsorption capacity and adsorption intensity, respectively[12]. In other words, K_f *can be* K_f *can be* defined as the distribution coefficient and represents the quantity of drug adsorbed onto eggshells at equilibrium concentration.

The equilibrium constant (K_{eq}) for the adsorption process at each temperature is calculated by using the relationship as follow;

$$K_{eq} = Q_e\, (Wt_s)/Ce\, (V_{so}) \quad (5)$$

Where (Wt_s) is the weight of eggshell, (V_{so}) is the volume of drug solutions.

2.5.1. Thermodynamic calculations

Thermodynamic parameters (ΔHº, ΔGº, ΔSº) were calculated using three different temperatures 300, 310, 320K to evaluate the feasibility of the adsorption process. The change in free energy (ΔGº) could be calculated at absolute temperature.(T) with the gas constant 8.314 $J.mole^{-1}.K^{-1}$ as shown in following equation:

$\Delta G^o = -- RT \text{ Lin } K$ (6)

$\Delta G^o = 2.303\ RT \text{ Log } \frac{Qe}{Ce}$ (7)

Vant Hoff's[13] and Gibbs equations were used to determine the heat of adsorption ΔH^o and change in entropy ΔS^o respectively as shown in the equations below. Where K is the equilibrium constant when(Ce)-approaches zero at a certain temperature,(X_m) is the maximum uptake of adsorption at a certain value of equilibrium concentration(Ce).

$$lnK = \frac{-\Delta H^\circ}{RT} + constant \quad (8)$$

$$\text{Log } X_m = \frac{-\Delta H^\circ}{2.303\,RT} + \text{Con.} \quad (9)$$

$\Delta G^o = \Delta H^o - T\ \Delta S^o$ (10)

Kinetics calculations

The effect of time on Valium adsorption was investigated. Adsorption experiments were carried out at 310 k for a period of time ranged between(5-50 minutes) while other conditions were held constant. At the end of each adsorption period, the suspension was centrifuged and filtered. The residual amount of drug in the solutions after adsorption was determined spectrophotometrically, at the maximum wavelength of 314 and 358 nm for the stock solutions of intestinal and gastric fluids respectively. In order to determine the kinetics of Valium adsorption on eggshells, pseudo-first-order (PFO), pseudo-second-order (PSO) were applied. Lagergren[14] suggested a pseudo-first-order equation for the sorption processes of a liquid-solid system based on the solid surface capacity. The pseudo-first-order model equation is:

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \quad (11)$$

the other hand pseudo-second-order model is expressed as [15]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} * t \quad (12)$$

where k_1 (min^{-1}), k_2 (mg. g^{-1} min^{-1}) is the rate constant of the model (PFO), and (PSO) respectively, qt is the amount of solute adsorbed (mg/g) on the adsorbent at time t, and qe is the amount of adsorption (mg/g) at equilibrium. In recent years, the linear forms of the pseudo-first order PFO, and pseudo-second order PSO are the most widely used in liquid-phase sorption processes on solid surface to determine the most fitted kinetic model for the adsorption process.

Results and Discussion

Valium absorption Spectra and Calibration curve

Firstly, The UV detection wavelength at λ_{max}=314 for the stock solutions of intestinal fluid and λ_{max}=358 for the stock solutions of gastric fluid were defined. the calibration curve of the drug solutions has prepared to calculate the concentrations of the samples from each experiment, five different concentrations were prepared, and the absorbance was measured via UV/Vis spectrophotometer from(400 to 700nm). The maximum absorbance and calibration curves were plotted against the concentrations of Valium for the simulated gastric fluid and the simulated intestinal fluid.

Valium Adsorption isotherms

Equilibrium studies determine the capacity of the adsorbent and describe the adsorption isotherm by constants which values express the surface properties and affinity of the adsorbents. Equilibrium adsorption isotherms of Valium have been studied as a function of concentration. The results in figure 3 showed that the adsorption uptake increase with increasing drug initial concentration. This was because when the initial concentration increased, the mass transfer driving force would become larger, and that resulting in higher molecules adsorption. whereas, at lower initial concentration, a high number of active vacant sites available on the eggshell's surface were sufficient to absorb most of the Valium molecules. As observed from the results in figure(2), the shape of the isotherms was S_3 in simulated gastric fluid and S_2 in a simulated intestinal fluid according to Gilles classification[16].

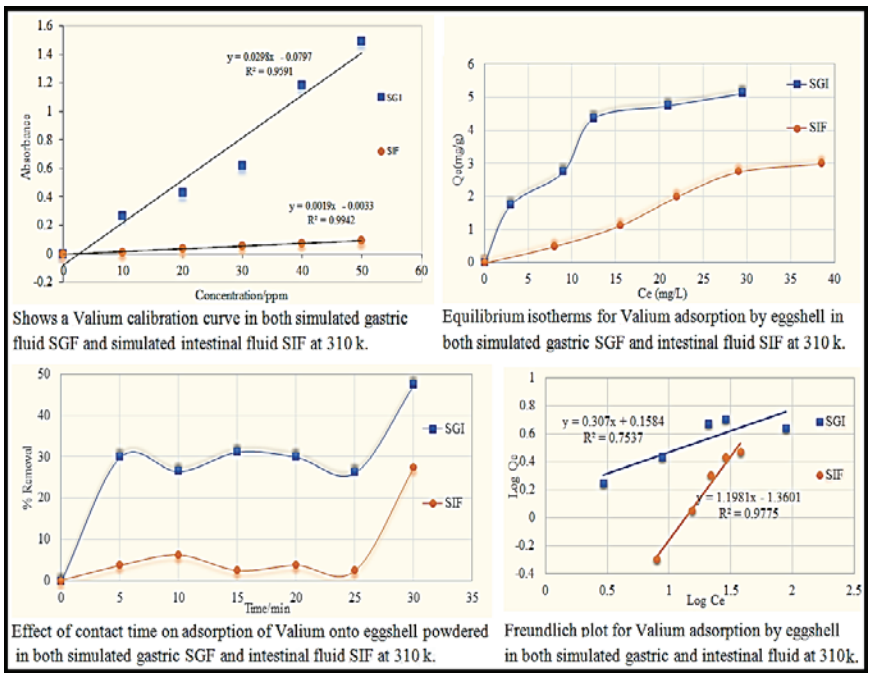
Results in figure(2)demonstrate that the adsorption of Valium continue over the initial stage of the contact time period until reaching the equilibrium. This occurrence was due to the presence of a large number of vacant surface sites was available for adsorption during the initial stage, and near the equilibrium time, the same trends of molecules adsorption were observed in the stock solutions of intestinal and gastric fluids.

Change of pH solution affects the surface charge of the adsorbents as well as the degree of ionization

of adsorbate material. The adsorption of ions such as hydrogen, hydroxyl, and other ions are affected by the pH of the solution. As the pH increases, it is usually expected that the cationic ion adsorption also increases due to increasing of the negative surface charge of adsorbents[17]. Benzodiazepine is a weakly basic or neutral drug[18]. With increasing pH values the adsorption of Valium on eggshell tends to decrease, which can be explained by the electrostatic interaction of anionic species with the negatively charged hydrolysed eggshell composite surface. Experimental data absorption was better fitted to the Freundlich isotherm more than Langmuir in a simulated intestinal fluid SIF and fitted to the Langmuir more than Freundlich in simulated gastric fluid SGF. It can be concluded that the drug was effectively adsorbed onto eggshell at both solutions with significantly higher adsorption in simulated gastric fluid.

Freundlich and Langmuir adsorption isotherm

Analysis of adsorption isotherm is essential importance to describe how adsorbate molecules interact with the adsorbent surface. Adsorption studies were performed at two pH values 1.2 and 6.8 to simulate the environments in the gastrointestinal tract (**stomach and intestine**). Monolayer adsorption uptake onto a surface containing a limited number of adsorption sites has been assumed by Langmuir. When C_e/q_e is plotted against Ce, a straight line with a slope of 1/a and intercept of $\frac{1}{aK_l}\frac{1}{aK_l}$ is obtained as shown in figure(2) Langmuir plots exhibited excellent R^2 value compared to Freundlich plots at pH =1.2 of SGF, indicating excellent fitting of the model to the experimental data. The Freundlich isotherm is a mathematical expression for the adsorption equilibrium between liquid and solid heterogeneous surfaces. It is supposed that the powerful binding sites are occupied first and consequently, the binding strength decreases with the increasing degree of site occupation[19]. Figure(2) shows that the drug concentrations on the eggshell adsorbent will increase and be more than one layer as long as there is an increase in the drug concentration in the liquid. The value of (n) represents the favourability of the adsorption process and K_f is giving an indication about the quantity of drug adsorbed onto eggshell at equilibrium concentration. The slope of 1/n is a measure of the adsorption intensity[20], Table(1) demonstrates the values of R^2 for each isotherm in different pH and gives an indicator about the best adsorption isotherms. By comparing the results presented in this table, greater correlation R^2 value for Langmuir isotherm has registered than those of Freundlich isotherm in the SGF solution. While in SIF solution, the greater correlation R^2 value was for the Freundlich isotherm.

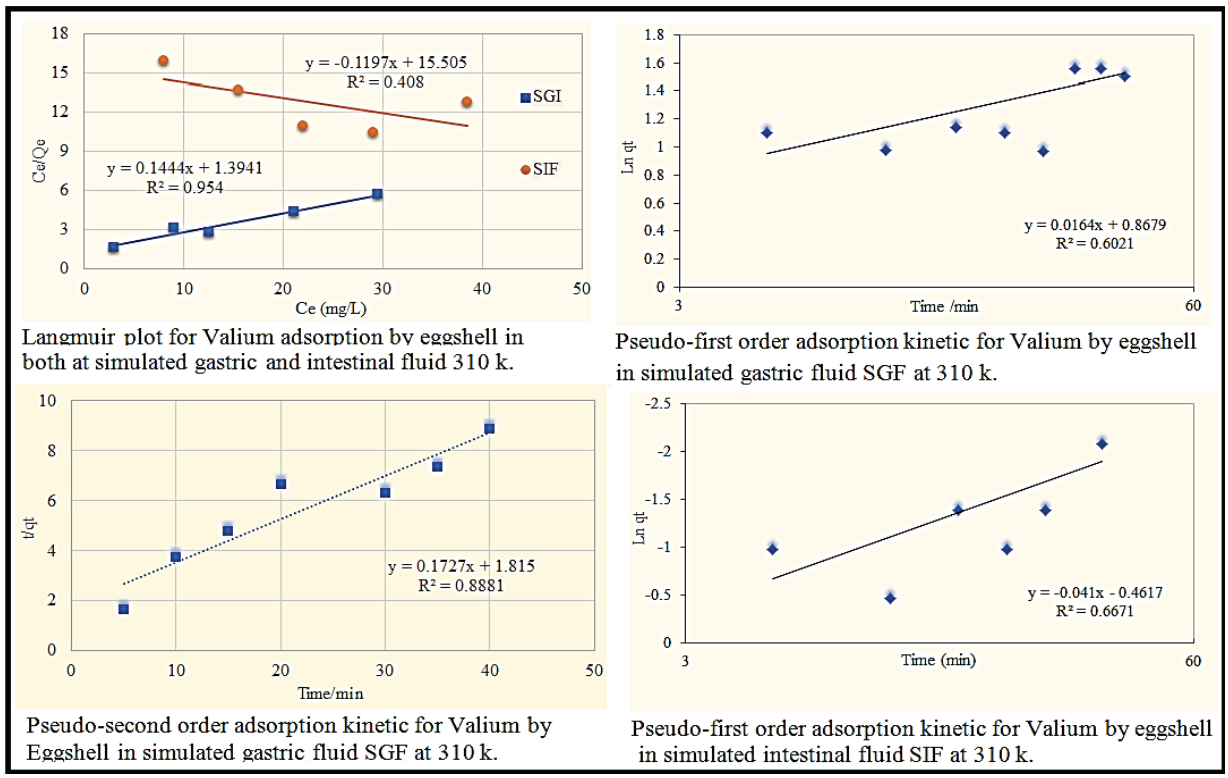


Fig(2): Effect of (contact time, Calibration curve,Isotherm,Freundlich) on adsorption of Valium onto eggshell powdered in both simulated gastric SGF and intestinal fluid SIF at 310 k.

Kinetic models for the adsorption process

Equilibrium of sorption rate is an important factor for the selection of adsorption kinetics that must be taken into account to determine the sorption kinetic constants. The experimental data of the drug adsorption process kinetics Pseudo-first-order PFO and the pseudo-second-order PSO kinetic equations have been investigated in this study. After the data were fitted to kinetic equations, the highest average regression coefficients (R^2=0.881) were obtained for the pseudo-second-order kinetic equation in SGF solution. The lowest R^2 value was for the pseudo-second-order kinetic equation in SIF solution (figure.3).

Equilibrium analysis of adsorption is required for evaluating the possibility or capacity of a sorbent. However, an ideal sorbent for drug control must have not only a large sorption capacity but also a fast sorption rate. (Table.1)shows, in acidic solution (pH=1.2) are likely to be second-order because of the experimental value of q_e approximately equal to the theoretical value, higher value of correlation coefficient. In contrast, very low correlation coefficient was observed for the simulated intestinal fluid. Therefore, the adsorption processes followed well pseudo second-order kinetics for the simulated gastric fluid as shown in figure(3).



Fig(3):Kinetic of Pseudo first and second Order

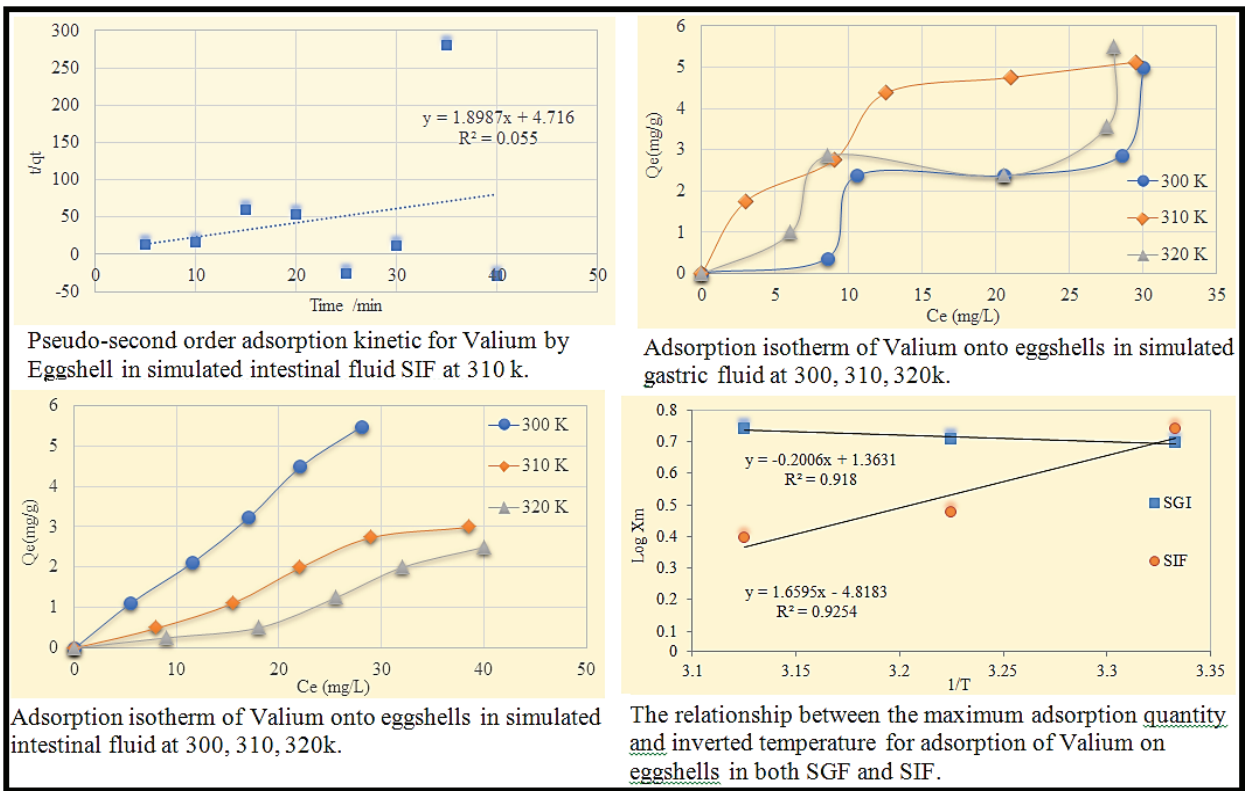
Table(1):Parameters of the Freundlich and Langmuir models extracted from experimental adsorption isotherms data at 310 k in SGF and SIF solutions.,with Constants of pseudo-first and second order

Solution	Freundlich			Langmuir		
	n	K_f	R^2	a	K_l	R^2
SGF	2.032	0.015	0.753	0.717	0.708	0.954
SIF	0.834	-1.360	0.977	0.136	41.666	0.408

Fluids	Pseudo-first-order			Pseudo-second-order		
	q◦ mg/g	k1min-1	R2	q◦ mg/g	k2 mg.g-1 min-1	R2
SGF	7.362	0.172	0.602	5.555	0.094	0.881
SIF	2.890	0.041	0.667	0.526	0.403	0.055

Effect of temperature on drug adsorption and Thermodynamic data

Effect of temperature on adsorption studies were carried out at(300, 310, and 320k) for Valium. The sensitivity of the adsorption process towards temperature is presented in figure(4). It was found that q_e decline with increasing temperature in simulated SIF fluids, which was probably related to desorption of Valium occurred at high temperatures. These results indicate that the exothermic nature of the process (negative ΔH), that occurs may be due to the tendency of drug molecules to escape from the solid phase to bulk phase with an increase in temperature of the solution[21]. The thermodynamic parameters for the drug adsorption on eggshells powder at various at three different temperatures were calculated and listed in table(2). The values of free energy change ΔG°,enthalpy change ΔH° and entropy change ΔS° were calculated Based on the available equations to assess the thermodynamic feasibility of the process and to confirm the nature of the adsorption process, Based on the following literature available equations[22].



Pseudo-second order adsorption kinetic for Valium by Eggshell in simulated intestinal fluid SIF at 310 k.

Adsorption isotherm of Valium onto eggshells in simulated gastric fluid at 300, 310, 320k.

Adsorption isotherm of Valium onto eggshells in simulated intestinal fluid at 300, 310, 320k.

The relationship between the maximum adsorption quantity and inverted temperature for adsorption of Valium on eggshells in both SGF and SIF.

Fig(4): The relationship between the maximum adsorption quantity and inverted temperature for adsorption of Valium on Eggshells in both SGF and SIF.

Table(2):The relationship between the maximum adsorption quantity, inverted temperature and Thermodynamic values for adsorption of Valium on eggshells.

In SGF				
T(K)	**1000/T (K-1)**		**Xm**	**Log Xm**
300	3.333		5	0.698
310	3.225		5.125	0.709
320	3.125		5.5	0.740
In SIF				
T(K)	1000/T (K-1)		Xm	Log Xm
300	3.333		5.5	0.7403
310	3.225		3	0.477
320	3.125		2.5	0.397
In SGF				
T(K)	1000/T (K-1)	ΔG° kJ.mol-1	ΔH° kJ.mol-1	ΔS° kJ.mol-1.k-1
300	3.333	4.467	0.038	- 0.0148
310	3.225	4.509	-	- 0.0145
320	3.125	4.324	-	- 0.0135
In SIF				
T(K)	1000/T (K-1)	ΔG° kJ.mol-1	ΔH° kJ.mol-1	ΔS° kJ.mol-1.k-1
300	3.333	4.054	- 0.031	- 0.013
310	3.225	6.595	-	- 0.021
320	3.125	7.382	-	- 0.023

Fig(4)-displays the Van't Hoff plot for the adsorption of drug from aqueous solutions at different pH. Table 5 shows negative ΔH° values in SIF which indicates the exothermic nature of drug adsorption, in contrast with the value in SGF which is endothermic process. This finding was consistent with the results obtained earlier where the drug uptake increased and or decreased with increasing solution temperature depending on pH solutions. Senthilkumaar, et. al[23] have reported that the increase in adsorption uptake with increase in temperature was due to the possibility of an increase in the kinetic energy of the adsorbate molecules.

The positive value of free energy change shows a non-spontaneous adsorption process at the range of temperatures[24]. On the other hand, the negative ΔG° values give indication about the spontaneous nature of adsorption process which indicates that better adsorption is obtained at low temperature. The negative ΔS° values suggest the decrease in adsorbate concentration in solid–solution interface.

Conclusion

Currently, adsorption has been regarded as an effective technology method for the removal of soluble heavy molecules from aqueous solution. The present results in this study showed that eggshells powder was a promising safe low-cost adsorbent to be used in reducing the effect of drug abused from aqueous solutions. equilibrium data has revealed that the drug adsorption depends on the pH solution as well as the ambient temperature. Drug adsorption was highly temperature dependent. Equilibrium data fitted well to Freundlich

isotherm in SIF solution, which suggests heterogeneity in the sorption sites. kinetics model of the adsorption process was found to follow the PSO in simulated gastric fluid at pH =1.2, while in simulated intestinal fluid at pH =6.8 was fitted to PFO kinetic equations.

Conflict of Interest:There is no any Conflict of Interest

Ethical Clearance:Ethics committee refer that there is no plagiarism and there is no mistakes or wrong results in this work.

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