Original Research Paper

Kinetics and Adsorption Isotherm of Ibuprofen onto Grafted β-CD/Chitosan Polymer

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Abstract: The adsorption of the Ibuprofen (Ibu) drug on β-cyclodextrin (β-CD) grafted chitosan polymer was studied under different experimental conditions. The effect of Ibu concentration, mass of β-CD grafted chitosan polymer as adsorbent, contact time, temperature and pH were investigated. Three equilibrium models, Langmuier, Freundlich and Temkin isotherm models were analyzed to evaluate the adsorption isotherms. The adsorption isotherms were best fitted by Freundlich isotherm model, with correlation coefficient 0.9882, the intensity of adsorption parameters was lower than one and Freundlich adsorption isotherm constant value was more than one. High adsorption was found in acidic media pH 2, 27°C and 1 h adsorption time. In order to investigate the kinetic of the adsorption process four kinetic models were analyzed, pseudo first order kinetic model, pseudo second order kinetic model, the Elovich kinetic model and intraparticle diffusion kinetic model. Kinetic parameters include; binding strength constant, first order adsorption rate constant, intraparticle diffusion rate constant, adsorption half time, rate constant, equilibrium constant and adsorption capacities. Correlation coefficient for each kinetic equation was reported. The adsorption kinetics was best fitted by pseudo-first order kinetic equation, with correlation coefficient 0.9922. The rate determining step is well described by intraparticle diffusion process. The Intraparticle diffusion rate constant values ranging from 0.163 to 1.1441 mgg$^{-1}$min$^{-1/2}$.

Keywords: Grafted Chitosan Polymer, β-Cyclodextrin, Ibuprofen, Adsorption Isotherms

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides of Glucopyranose. CDs may consist of 6 to 12 glucopyranose units connected to each other to form the ring. There are three main types of CD: α, β and γ consist of six, seven and eight of glucopyranose, respectively (Saenger et al., 1998). CDs are obtained from the enzymatic digestion of starch by CD Glycosyl transferase (Biwer et al., 2002; Larsen et al., 1998; De Freitas et al., 2004; Blanco et al., 2009).

The CDs have a hydrophilic outer surface and a lipophilic central cavity that can accommodate a variety of lipophilic drugs due to hydrophobic interactions (Loftsson and Duchene, 2007; Loftsson et al., 2005). One of the most important properties of CDs is their ability to form inclusion compounds with various guest molecules, where the guest is embedded within the host non-polar cavity (Del Valle, 2003). The requirement for the inclusion is that the guest molecule must fit entirely, or at least partially, into the CD cavity to make the complex. Size, shape and polarity of the guest molecule relative to the CDs low polar inner cavity are critical parameters for the host-guest complexation (Singh et al., 2010; Al-Sou’od, 2006; Kawasaki et al., 2001).

Chitosan is a kind of polysaccharide; it is N-deacetylated form of chitin that is obtained by alkaline treatment of chitin at high temperature (Shahidi and Synowiecki, 1991). Chitosan and its derivatives have become useful polysaccharides in the biomedical area because of its biocompatible, biodegradable and non-toxic properties (Ko et al., 2002; Reis et al., 2008). Chitosan has two types of reactive functional groups, amino groups and hydroxyl groups. Due to its intrinsic characteristics, the natural polymer is often chosen as an effective biosorbent for the removal or the recovery of hazardous dyes, proteins and heavy metals (Fan et al., 2013; Wang et al., 2013). The degree of deacetylation controls the amount of free amino groups in the polymer
chain. The free amino groups give chitosan its positive charge. The amino groups along with the hydroxyl group give chitosan its functionality which allows it to be a highly reactive polysaccharide. Chitosan’s positive charge allows it to have many electrostatic interactions with negatively charged molecules. Chitosan has many physicochemical (reactive OH and NH$_2$ groups) and biological (biocompatible, biodegradable) properties that make it an attractive material for use in various applications (Khor and Lim, 2003; Foda et al., 2007). These properties include: Biodegradability, lack of toxicity, anti-fungal effects, wound healing acceleration and immune system stimulation (Prabaharan and Mano, 2005). Because of chitosan's biological and chemical properties it has the ability to bind to particular materials including cholesterols, fats, proteins, metal ions and even tumor cells. This allows chitosan to be used as a chelating agent in various applications (Senel et al., 2000). Chitosan is often used as a pharmaceutical excipient because of its very safe toxicity profile (Kean and Thanou, 2012).

In order to combine the advantages of both CD and chitosan, the CD grafted chitosan has recently gained interest because it can be widely used in various fields such as drug delivery system and drug release (Jayakumar et al., 2011). Therefore, introduction of CD moieties into the chitosan backbones may lead to a molecular carrier that possess the cumulative effects of inclusion, size specificity and transport properties of CDs as well as the controlled release ability of the polymeric matrix (Yuan et al., 2013). Moreover, the β-CD grafted chitosan have attracted attentions due to its easy separation and high adsorption capacity (Fan et al., 2012). However, major applications of the CD grafted chitosan remain limited due to their low water solubility (Sajomsang et al., 2011).

Ibuprofen is the common name of (RS)-2-[4-(2-methyl[propyl]) phenyl] propionic acid and is a pharmaceutical active compound used in drugs. It is a Non-Steroidal Anti-Inflammatory (NSAIF) from the subgroup of propionic acid chemical derivatives (TMC Library, 2014).

Over recent decades, the poor aqueous solubility of many Active Pharmaceutical Ingredients (APIs) has been one of the most challenging issues for the pharmaceutical industry. These drugs with poor aqueous solubility subsequently have low bioavailability, which can limit their therapeutic efficacy (Zhang et al., 2014). In this study, we shed more light on the interactions between poorly soluble drug and the carrier metrics, the equilibrium and the kinetic adsorption models of (Ibu) on CD-grafted chitosan polymer were investigated.

Experimental

Materials: Ibu was obtained from Dr. Reddy’s Company (Hyderabad, India). β-CD (101.0%) was produced by Wacker Chemie (Germany). High molecular weight chitosan with a viscosity average molecular weight of 250 kDa and degree of deacetylation of 93% was obtained from Hongjio Chemical Company Ltd. (China). All of the above materials were kindly provided by The Jordanian Pharmaceutical Manufacturing Company (JPM). Other chemicals were of analytical grade obtained from Merck (Germany) and Across Organic (Belgium).

Instruments: A Spectrodynamic S600 UV/visible single beam spectrophotometer and 1 cm UV matched quartz cells were used. Impact 4100 FTIR spectrophotometer; Quanta 600 for Scanning Electron Microscope, Lab X; XRD 6000 X-ray diffraction spectrometer.

Methods

Preparation of β-CD citrate: β-CD citrate was prepared using a semidry reaction method by mixing of 2 g of β-CD with definite amount of water containing different citric acid concentrations (1-4 mole/1 g CD) in presence and absence of SHP (sodium hypophosphite as a catalyst). The reaction mixture was allowed to react in a circulating air oven at different reaction temperatures for specific times. The cured samples were purified by washing with isopropanol using a soxhlet apparatus for 6 h in order to remove unreacted components as well as any soluble fragments or by products, followed by drying at 60°C for 24 h (El-Tahlawy et al., 2006).

Preparation of Grafted β-CD/Chitosan Polymer

Linking of β-CD citrate onto chitosan was taken place by reaction of the pendant free carboxyl groups of β-CD citrate with the amino groups of chitosan. A definite volume of water containing different β-CD citrate concentrations was introduced into a solution containing chitosan dissolved in different formic acid concentrations (0-0.4 mL$^{-1}$ g chitosan). The reaction mixture was then magnetically stirred and heated at different reaction temperatures for 3 h. At the end of the reaction, products were precipitated by adding 100 mL of (0.2 N) NaOH solution. To ensure the removal of unreacted β-CD citrate, samples were thoroughly washed with distilled water until neutral pH 7 is reached. Finally, samples were washed with acetone and oven dried at 60°C for 24 h.

Preparation of Ibu Solution in Phosphate Buffer (pH 2)

A stock solution of Ibu 100 ppm, was prepared by dissolving 0.1 g of Ibu in 1 L of phosphate buffer at pH 2. After which dilution was used to prepare different concentrations (1, 5, 10, 20, 30, 40 and 50 ppm) of Ibu solution. A spectrophotometer was used to estimate the maximum wavelength of Ibu solution. It was found that Ibu has a maximum wavelength at 223 nm.
Equilibrium trials were conducted for 2 h contact time to ensure the maximum adsorption of Ibu from solution. In these equilibrium trials, mass of adsorbent, pH and temperature were varied. Trials were conducted at pH 2, 4.9 and 7. The initial concentration of Ibu was 20 ppm for each sample. Different adsorbent masses were added to vials of 20 ppm Ibu solution for all proposed pHs. After mixing for 2 h, samples were then analyzed spectrophotometrically at $\lambda_{\text{max}} = 223$ nm to determine Ibu content. The amount (mg g$^{-1}$) of Ibu removal from aqueous solution was calculated according to Equation 1:

$$q_e = \frac{C_i - C_e}{m} V$$  \hspace{1cm} (1)

Where:

- $C_i$ and $C_e$ = The initial and equilibrium concentrations (mg/L)
- $m$ = The mass of grafted polymer (g)
- $V$ = The volume of the solution (L)

The percent adsorption or removal (%RE) is calculated using Equation 2:

$$\% \text{ adsorption} = \frac{C_i - C_e}{C_i} \times 100\%$$  \hspace{1cm} (2)

**Effect of Ibu Concentration**

Samples of 0.2 g grafted polymer were added to different concentrations (1, 5, 10, 20, 30, 40, 50 ppm) of 50 mL Ibu solution. Grafted polymer and Ibu solution were mixed and shaken at 120 rpm and 27°C. Aliquot samples were taken from each solution every 5 min by decantation. Finally absorbance was measured for each individual sample.

**Effect of Grafted Polymer Mass**

About 20 ppm Ibu solution was added to three different masses (0.2, 1 and 2 g) of grafted polymer. Mixtures were shaken at 120 rpm for 80 min. Aliquot sample was taken from each mixture every 5 min by decantation. Finally absorbance was measured for each individual sample.

**Effect of Adsorption Time**

About 50 mL of 20 ppm Ibu solution was added to 0.2 g grafted polymer. Aliquot sample was taken from solution every 5 min by decantation and absorbance of each sample was measured accordingly. The adsorption activation energy was calculated according to Arrhenius Equation 3:

$$k_{\text{ads}} = A e^{-E_a/R T}$$  \hspace{1cm} (3)

Where:

- $k_{\text{ads}}$ = The rate constant in first-order kinetics, A Arrhenius constant
- $E_a$ = The activation energy
- $R$ = The universal gas constant

**Effect of pH**

The effect of solution’s pH level on the adsorption process was evaluated. The adsorption of Ibu solution at three different pH (2, 4.9 and 7) was measured and reported accordingly.

**Adsorption Kinetics**

To understand the effect of contact time and initial concentration of Ibu on the adsorption process, 50 mL of Ibu solution (pH 4.9) with different initial concentrations (10-50 ppm) was added to screw-cap conical flask containing 0.2 g of β-CD grafted chitosan polymer. Mixtures were mechanically shaken at 120 rpm with a temperature-controlled water bath for 60 min. After which samples were filtered using a filter paper to separate adsorbent and the filtrate was analysed. Sample’s concentration was determined accordingly using a UV-visible spectrophotometric ($\lambda_{\text{max}} = 223$ nm).

**Results and Discussion**

β-CD grafted chitosan polymer was characterized by solubility measurements, FTIR, XRD and SEM. It was found that the solubility of β-CD grafted chitosan polymer is significantly different from the solubility of both native β-CD and chitosan. The solubility measurements were carried out in aqueous and organic solvents as shown in Table 1.

Four samples of native β-CD, chitosan, physical mixture between β-CD and chitosan (1:1 molar ratio) and β-CD grafted chitosan polymer were prepared for FTIR XRD and SEM measurements.

Fourier transform infrared FTIR spectroscopy of chitosan, β-CD, 1:1 physical mixture of chitosan and β-CD and β-CD grafted chitosan polymer were studied. Figure 1a displays the basic characteristics peaks of chitosan at: 3364 cm$^{-1}$ (O–H stretch), 2876 cm$^{-1}$ (C–H stretch), 1581 cm$^{-1}$ (N–H bend), 1153 cm$^{-1}$ (bridge-O-stretch) and 1083 cm$^{-1}$ (C–O stretch). The strong peak around 3429 cm$^{-1}$ could be assigned to the axial stretching vibration of O–H superimposed to the N–H stretching band and inter hydrogen bonds of the polysaccharide. Figure 1b represents the spectrum of β-CD which shows a broad band at 3234 cm$^{-1}$ due to the symmetric and antisymmetric O–H stretching mode. Carbonyl stretching intense band located at 1590 cm$^{-1}$ indicating the presence of β-CD. Some bands in the range 1030-1160 cm$^{-1}$ can be associated with the stretching frequency of primary and secondary C–OH...
groups. Figure 1c showed the spectrum pattern of the physical mixture which is apparently different from that of the grafted polymer. As for β-CD grafted chitosan polymer in Fig. 1d, a new shifted band appears at 982 cm⁻¹, proving the formation of a new hydrogen bridge between a C–OH group (900 cm⁻¹) of the β-CD and the chitosan molecule. With respect to β-CD grafted chitosan polymer, the peak at 3353 cm⁻¹ was further broadened due to the presence of a large quantity of hydroxyl groups introduced through of β-CD.

Further evidence for the formation of β-CD grafted chitosan polymer was obtained by X-ray Powder Diffraction (XRD) Fig. 2. β-CD in its crystalline form exhibits many sharp diffraction peaks between 2θ = 6-45°. While no such peaks are visible in the XRD of β-CD grafted chitosan polymer due to the change in crystalloids after β-CD grafted onto chitosan. The diffraction pattern of pure chitosan (a) showed characteristic peaks at 2θ = 10 and 20°. It can be found that the peak at 2θ = 10° disappeared and the characteristic peak at 2θ = 20° decreased and broadened obviously in β-CD grafted chitosan polymer (d). The lack of crystallinity in β-CD grafted chitosan polymer may be attributed to the loss of regularity throughout the polymeric chains due to the introduction of bulky β-CD molecules onto chitosan backbone.

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Fig. 1. IR spectra of (a) chitosan, (b) β-CD, (c) Physical mixture(1:1) and (d) grafted β-CD/chitosan polymer

Fig. 2. XRD spectra of (a) chitosan, (b) β-CD, (c) physical mixture and (d) grafted β-CD/chitosan polymer
Table 1. The solubility of β-CD, chitosan and grafted β-CD/chitosan polymer at 25°C

| Sample       | Water | Benzene | Cyclohexane | Chloroform | DMF |
|--------------|-------|---------|-------------|------------|-----|
| β-CD         | +     | +       | +           | +          | +   |
| Chitosan     | +     | -       | +           | -          | +   |
| Grafted- polymer | -   | +       | -           | +          | +   |

*: Soluble; -: Insoluble

The morphology of the samples was determined with a Scanning Electron Microscope (SEM). Sample of (0.5 mg) was mounted onto a (5×5 mm) silicon wafer affixed via graphite tape to an aluminum stub. The powder was then sputter-coated for 40 s at a beam current of 38–42 mM L⁻¹ with a 100 nm layer of...
gold/palladium alloy. SEM images of (a) chitosan, (b) β-CD, (c) a physical mixture of 1:1 β-CD chitosan and (d) grafted β-CD-chitosan are shown in Fig. 3. The surface texture of β-CD and chitosan changes drastically after the formation of the grafted polymer. Moreover the original morphology of the parent compounds disappeared and it was impossible to differentiate between the two components.

Effect of Contact Time

The effect of contact time on the adsorption of Ibu was studied in order to determine the time required to reach equilibrium. About 50 mL of 20 ppm Ibu solution was shaken with 0.2 g grafted β-CD/chitosan. Equilibrium studies were performed at the selected time intervals ranging from 5 to 60 min. After 60 min of stirring the solution, the removal efficiency did not increase Fig. 4. Therefore, the optimum value of stirring time was found to be 60 min.

Adsorption Isotherm

The equilibrium sorption was carried out by using 0.2 g of β-CD grafted chitosan polymer in 50 mL of different initial Ibu concentrations (10-50 ppm). In 250 mL Pyrex conical flasks samples with pH 2 were shaken at 27°C for 60 min on the orbital shaker. The mixture was then filtered and the filtrate analyzed for Ibu concentration using UV spectrophotometer. The obtained data were fitted into Langmuir, Freundlich and Temkin adsorption isotherms. The Langmuir Equation 4 is the most widely used two-parameter equation, commonly expressed as:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o}$$  \hspace{1cm} (4)

Where:

- $C_e$ = The equilibrium concentration of Ibu remaining in the solution (mg dm$^{-3}$)
- $q_e$ = The amount of adsorbate adsorbed per mass unit of adsorbent at equilibrium (mg g$^{-1}$)
- $Q_o$ and $b$ = Langmuir constants indicating adsorption capacity and energy, respectively

The plot of $C_e/q_e$ versus $C_e$ (Fig. 5) was found to be linear with negative slope, indicating that the adsorption behavior of the tested system do not follow the assumption on which the Langmuir approach is based.

The Freundlich isotherm is an empirical equation 5 and shown to be satisfactory for low concentrations. Freundlich isotherm model has the following linear form:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$  \hspace{1cm} (5)

Where:

- $K_F$ = The Freundlich constant related to sorption capacity
- $1/n$ = The Freundlich constant related to intensity of adsorption
- $K_F$ and $n$ = Both Freundlich related to the strength of the adsorbent-sorbent interaction and to distribution of bond strength among of the surface sites of heterogeneous sorbents

![Fig. 4. Effect of contact time on the adsorption of grafted β-CD/chitosan polymer, $C_i = 20$ ppm, pH = 2, 27°C](image-url)
A linear plot (Fig. 6) was obtained in the case of Freundlich isotherm. Based on $R^2$ value (0.9552), the linear form of the Freundlich isotherm appears to produce a reasonable and applicable model on the ongoing adsorption process. Different constants derived from this plot are presented in Table 2.

The Freundlich isotherm constants determined by non-linear regression are shown in Table 3. The results demonstrate that the $b$ and $Q_o$ values obtained by non-linear regression are remarkably consistent and quite similar to the linear transform values from Table 2. The $n$ value indicates the degree of nonlinearity between solution concentration and adsorption as follows: If $n = 1$, then adsorption is linear; if $n<1$, then adsorption is a chemical process; if $n>1$, then adsorption is a physical process. In this study the $n$ value was found to be 0.642, Table 2.
Temkin Isotherm contains a factor that explicitly takes into account adsorbing species adsorbate interactions. This isotherm assumes that (i) the heat of adsorption of all molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate interactions and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy (Temkin and Pyzhev, 1940). Temkin isotherm Equation 6 has generally been applied in the following from:

\[ q_e = \frac{RT}{b} \ln(K_f C) \]

The linear form of Equation 6 is:

\[ q_e = B_1 + B_2 \ln C_e \]

where, \( B_1 = \frac{RT}{b} \ln(K_f) \) and \( B_2 = \frac{RT}{b} \ln(C_e) \).

For the non-linear method, a trial and error procedure, which is applicable to computer operation was used to determine the isotherm parameters by minimizing the respective coefficients of determination between experimental data and isotherms using the solver add-in with Microsoft Excel. Figure 8 shows the experimental equilibrium data and the predicted theoretical isotherms for the adsorption of Ibu onto β-CD grafted chitosan polymer.

The calculated isotherm parameters by non-linear method were shown in Table 3. The Freundlich model appears to fit the experimental data better than the Langmuir model as shown by the Sum of Squared Errors (SSE) values.

Freundlich adsorption equation is perhaps the most widely used mathematical description of adsorption in aqueous system, while the Langmuir adsorption isotherm is commonly applied to mono layer chemisorption of gases. To apply the Freundlich equation on our work, various concentrations of Ibu 5-50 ppm were adsorbed on fixed pre-weighted 0.2 g β-CD grafted chitosan polymer for 1 h contact time, 37°C and pH 4.9. For the Freundlich adsorption isotherms, \( R^2 \) is closer to 1 more than that of Langmuir and Temkin adsorption isotherm and the n value was 0.642. The resulted nonlinear relationship implies a weaker interaction between Ibu drug and β-CD grafted chitosan polymer. The K values of Ibu drug were more than 1 which indicates that the adsorption capacities were high and the stay time of Ibu on the surface of β-CD-grafted chitosan polymer was slow due to the large surface area of polymer.

### Adsorption Kinetic Models

In order to investigate the mechanism of Ibu drug adsorption process on β-CD grafted chitosan polymer, the pseudo first order kinetic model, Elovich kinetic model and Intraparticle diffusion model were used to test the experimental data, the results are shown in Fig. 9-11 respectively. The correlation coefficients and the other calculated parameters for the pseudo first order, Elovich kinetic and Intraparticle diffusion models are listed in Table 4.

#### The Pseudo First-Order Equation (Lagergren Equation)

The linear plots of \( \log(q_e - q_t) \) versus time at pH 2 with four different initial concentrations (10, 20, 30 and 50 ppm) show the applicability of the lagregren equation (Fig. 9).

The values of Lagergren constants, \( q_e \) and \( k_{ads} \) and the correlation coefficient are calculated and presented in Table 4. The correlation coefficient for the pseudo first-order kinetic model obtained for all studied concentrations have high values. The \( R^2 \) values for the plots were in the range of 0.8475 to 0.9922. The first order adsorption constant (\( k_{ads} \)) values were decreased from 0.0635 to 0.0171 with the decrease in the initial concentration from 50 to 10 ppm except for the 20 ppm concentration which showed the highest value of \( k_{ads} \) 0.06896. Moreover \( k_{ads} \) values increased from 0.0316 to 0.06896 with decreasing pH from 7 to 2.

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| Table 2. Isotherm constants and correlation coefficients by linear regression |
|-----------------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Adsorbent   | Langmuir Isotherm | Freundlich Isotherm | Temkin Isotherm |
| Grafted polymer | Q^1mgg^{-1} | B Lmol^{-1} | R^2 | K_F | 1/n | R_S | B1 | K_T | R^2 |
|----------------|--------------|---------------|-----|------|-----|------|------|------|-----|
| 240.7 | 0.0216 | 13.71 | 0.0683 | 0.886 | 2.88 | 2.84 | 1.417 | 0.9796 |

| Table 3. Isotherm parameters obtained by the non-linear method |
|-----------------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Adsorbent   | Langmuir   | Freundlich | Temkin |
| Grafted polymer | Q^1mgg^{-1} | B Lmol^{-1} | SSE | K_F | 1/n | SSE | K_T | SSE |
|----------------|--------------|---------------|-----|------|-----|------|------|-----|
| 240.7 | 0.0216 | 13.71 | 0.0683 | 0.886 | 2.88 | 2.84 | 1.417 | 0.9796 |
Fig. 7. Linearized form of Temkin isotherm for the adsorption of Ibuprofen onto grafted β-CD/chitosan polymer at 37°C

Fig. 8. Adsorption isotherms of Ibuprofen onto grafted β-CD/chitosan polymer at 37°C

Fig. 9. Lagergren plot for adsorption of Ibuprofen on β-CD-grafted chitosan polymer at initial concentrations (10-50 ppm), pH 2 and 27°C
The Pseudo Second-Order Equation

A plot $1/(q_t - q)$ vs $t$ (not shown) show that the adsorption of Ibu on β-CD-grafted chitosan polymer doesn’t follow pseudo-second-order equation (negative intercept).

Elovich Kinetic Adsorption Model

The Elovich parameters ($\alpha$), the adsorption initial rate of Ibu, was in the range of (0.456 to 3.346). Figure 10 showed an increase in the initial rate with increasing pH from (2 to 7) and the decrease in the initial rate $\alpha$ from (2.903 to 0.373) with increasing the initial concentration ($C_i$) from (20 to 50). $1/\beta$ indicate the number of sites available for adsorption, was increasing from (0.197 to 0.511) by decreasing pH from (7 to 2) and decreasing of $1/\beta$ from (0.360 to 0.045) by increasing temperature from (27 to 47), the highest adjusted correlation coefficient $R^2 = 0.993$ was obtained at pH 2, $C_i = 20$ ppm and at 27°C.

Ritchie’s Equation

Ritchie’s equation can be written using the following Equation 8 (Ritchie, 1977):

$$\frac{q_t}{q_e - q_t} = \alpha t + 1 \quad (8)$$

Where:

$q_t$ = The amount of adsorption after an infinite time
$\alpha$ = The rate constant. The value for $q_e$ = Obtained from the intercept at $(1/t) = 0$ on a plot of $(1/q)$ against $(1/t)$

Ritchie equation is simply a linear equation and plot of $q_t/(q_e - q_t)$ against $t$ would produce a straight line. In recent years, the Ritchie equation has also been applied to solution/solid adsorption (Cheung et al., 2007). In our system, a plot $q_t/(q_e - q_t)$ against $t$ at different concentrations (10-50 ppm), give a straight line (Fig. 11). The parameters of these plots were listed in Table 4.

Intraparticle Diffusion Kinetic Adsorption Model

The intraparticle diffusion plots for the adsorption of Ibu onto β-CD grafted chitosan polymer are shown in Fig. 12. For the Intraparticle-diffusion the straight lines did pass through the origin with no intercept, which indicates that the rate is limited by the mass transfer across the boundary layer and the mechanism of adsorption of Ibu is complex by different $C_i$ and different pH. Moreover surface adsorption intra-particle diffusion may contribute to the rate-determining step (Gregg et al., 1967). As shown in Fig. 8 and Table 4 values of $k_{id}$ were
found to be between 0.18 and 1.31 mg/g min\(^{1/2}\) with \(R^2\) of 0.9960 to 0.9832 and according to values of \(C_i\) which are in the range of 0.4339 and 3.1484, the linear plot in our study did not pass through the origin which indicates some degree of boundary layer control and the intraparticle diffusion was not the only rate controlling step (Ho and McKay, 2004).

In the course of studying the effect of the mass of \(\beta\)-CD grafted chitosan polymer on the adsorption process of Ibu, results showed no potential effect of such factor on adsorption of ibuprofen.

### Adsorption Activation Energy

Ibu adsorption rate constants (\(k_{ads}\)) were determined at different temperatures from experimental data assuming first-order kinetics. Arrhenius equation parameters were fitted using these rate constants to determine temperature independent rate parameters and adsorption type. A plot of \(\ln k_{ads}\) versus 1000/T yields a straight line, with a slope-E\(a\)/R (Fig. 13). The magnitude of the activation energy is commonly used as the basis for differentiating between physical and chemical adsorption. Nollet et al. (2003) suggested that the physical adsorption process normally had an activation energy ranging from 5 to 40 kJmol\(^{-1}\), while chemical adsorption had a higher value (40-800 kJmol\(^{-1}\)).

The activation energy for Ibu adsorption on ton grafted polymer was 13.6 kJmol\(^{-1}\) suggesting that the Ibu was physically adsorbed onto the surface of the polymer.

![Graph of Ibu adsorption onto \(\beta\)-CD-grafted chitosan polymer at different initial concentrations and 27°C](image1)

![Graph of intraparticle diffusion adsorption kinetics for Ibu on \(\beta\)-CD-grafted chitosan polymer at \(C_i\) (10-50 ppm), pH 2 and 27°C](image2)
Conclusion

In this study β-CD grafted chitosan polymer was successfully synthesized as confirmed by solubility, FTIR, XRD and SEM techniques. The adsorption studies showed that adsorption capacity for Ibu depends on pH and initial concentration can be well represented by both Freundlich and temkin adsorption isothermal model. It was found that, the adsorption process doesn’t follow the Langmuir isotherm model. The adsorption followed pseudo-first-order kinetics which suggested that the limit factor of adsorption was adsorption mechanism and physisorption process was rate-controlling step for adsorption. Adsorption was optimized according to the following conditions: 20 ppm of Ibu, PH 4.9, 37°C, 0.2 g of β-CD grafted chitosan polymer, 50 mL of solution and 60 min contact time. Results were studied by adsorption isotherm models. Experimental work showed that the adsorption process is identical to the Freundlich isotherm models as indicated by the values of $R^2$. The intraparticle diffusion is the only controlling step of the process because the plot does not pass through the origin.

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Author’s Contributions

Hashem Bany-Aiesh: Participated in all experiments and collect data.
Raid Banat: Designed the research plan and contributed to the writing of the manuscript.
Khaledoun Al-Sou’od: Coordinated the data analysis and contributed to the writing of the manuscript.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of other authors have read and approved the manuscript.

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