

CHAPTER-4

THEORY AND CORRELATION OF DATA

The adsorption-desorption have been used in our work to accomplish our main aim; the extraction of naringin. The theories which describe the observations of adsorption and desorption are well developed. It has been mentioned earlier in the experimental chapter that adsorbent is a macroporous (biporous solid). The theory of adsorption on biporous solid and desorption from it has been taken from literature and discussed in the context of present work.

4.1. Physical situation of adsorption process

A macroreticular/macroporous resin bead (particle) is almost spherical in shape about 0.40 to 0.50 mm consists of a large number of microspheres of 1-10 μm diameter each. The schematic cross section is shown in Figure 4.1. When the beads are in contact with a liquid, the voidage in between the microspheres, i.e., macropores will be filled with the liquid. The diameter of macropores is 1-2 μm . The adsorbate molecules diffuse through macropores (which act as diffusion paths) from outside the resin particle to microspheres. The microspheres consist micropores in them. The diameter of micropore is of the order of a few Angstroms. Adsorbents containing macropores and micropores are said to have a 'bi-dispersed' pore structure. In macroporous resin there are two diffusion resistances, one is macropore, and the other is micropore.

The macropores, i.e., voidage are initially filled with adsorbate-free liquid, when such a biporous adsorbent is contacted with a large volume of bulk liquid with concentration of adsorbate C_o , the adsorbate solution diffuses inwards.

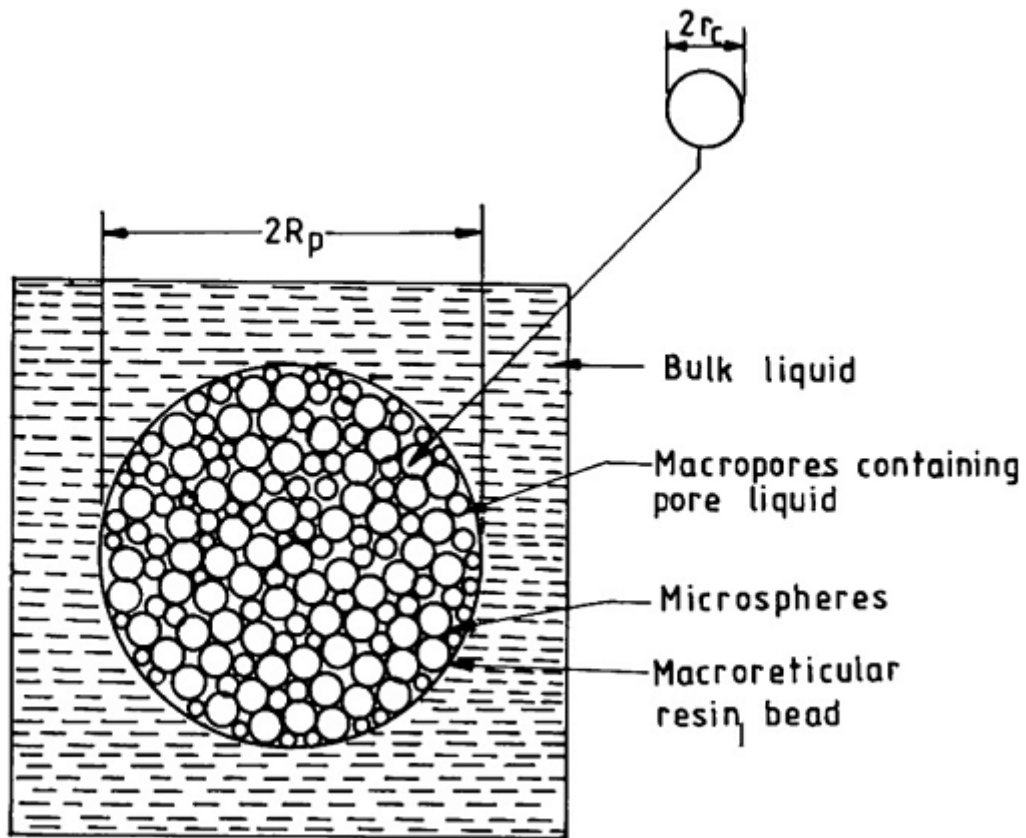


Figure 4.1: Macroporous/macoreticular resin particle (schematic)

As the adsorbate diffuses inwards, a rapid equilibrium is established between the liquid phase in macropores and surface of microspheres in the vicinity, and the surface of microspheres is saturated to an equilibrium concentration q_e , corresponding concentration of adsorbate in contacting adsorbate solution.

4.2. Adsorption equilibrium

An adsorption isotherm describes the relationship between the amount of adsorbate that is adsorbed on the adsorbent (q_e) and the concentration of dissolved adsorbate in the liquid (C_e) at equilibrium at constant temperature, i.e., relationship between q_e and C_e at constant T.

4.2.1. The correlation of adsorption equilibrium data:

As mentioned earlier in section 3.5.1, the values of concentration were measured at equilibrium, and the values of mass of adsorbate (naringin) were calculated by mass balance using the following relation.

$$q_e = \frac{V(C_o - C_e)}{w} \quad (3.1)$$

where q_e (kg/kg) is the amount of naringin adsorbed at equilibrium, V (m^3) is the volume of solution (KPBW), C_o (kg/m^3) is the initial concentration of naringin in solution, C_e (kg/m^3) is the final concentration (at equilibrium) of naringin in solution and w (kg) is a weight of the resin

The equilibrium data obtained were correlated using the following isotherm model equations.

Freundlich isotherm:

The basic isotherm model was developed by Freundlich (1907). It is an empirical expression and valid below the saturation concentration where condensation or crystallization occurs and adsorption is not significant. This isotherm attempts to incorporate the role of substrate, interaction on the surface and derived by assuming heterogeneous surface with non uniform distribution of heat of adsorption over the surface.

$$q_e = K_f C_e^{1/n} \quad (4.1)$$

where K_f and n are the Freundlich isotherm constants, at $n = 1$ reduces Henry's law equation

Langmuir isotherm:

The Langmuir isotherm model (Langmuir, 1916) is based on assumptions that monolayer adsorption on the adsorbent surface, all adsorption sites equivalent in terms of adsorption energy and no interactions between adjacent adsorbed molecules. The following equation represents it.

$$q_e = \frac{aC_e}{1+bC_e} \quad (4.2)$$

where a (m^3kg^{-1}) and b (m^3kg^{-1}) are the Langmuir adsorption isotherm constants, the term a/b gives maximum adsorption capacity and a represents multiplication of maximum adsorption capacity and energy parameter.

Redlich–Peterson isotherm:

The Redlich–Peterson isotherm (Redlich and Peterson, 1959) is a three parameter adsorption isotherm equation (4.3). At low concentrations, the Redlich-Peterson isotherm limits to Langmuir equation, and at high concentrations, it's behaviour approaches that of the Freundlich isotherm. The Redlich–Peterson equation is represented as

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta_R}} \quad (4.3)$$

where a_R (m^3kg^{-1})^{-1/β_R} and K_R (m^3kg^{-1}) are Redlich-Peterson isotherm constants, and exponent β_R lies between 0 and 1, at $\beta_R = 1$ equation reduces to Langmuir equation and at $\beta_R = 0$ reduces to Henry's law equation

Dubinin–Radushkevich isotherm:

The Dubinin–Radushkevich isotherm (Dubinin and Radushkevich, 1947) is based on Polanyi potential theory of adsorption and is given by equation 4.4.

$$q_e = q_D \exp(-B_D \varepsilon_d^2) \quad (4.4)$$

where q_D (kg/kg) is the Dubinin–Radushkevich isotherm constant, ε_d ($kJmol^{-1}$) is the Polanyi potential and correlated to equilibrium concentration (C_e) as

$$\varepsilon_d = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (4.5)$$

where R is the gas constant ($8.314 \times 10^{-3} \text{ J mol}^{-1} \text{ K}^{-1}$) and T is temperature (K). The term B_D ($\text{mol}^2 \text{ kJ}^{-2}$) is correlated to mean free energy of sorption E (kJ mol^{-1}) by the following

$$\text{equation. } E = \frac{1}{\sqrt{2B_D}} \quad (4.6)$$

If the value of E lies between 8 and 16 kJ mol^{-1} the sorption process is a chemisorption one, while values of below 8 kJ mol^{-1} indicate a physical adsorption process.

Toth isotherm:

Toth (1971) proposed a three parameter model by modifying the Langmuir equation to reduce the error between experimental data and predicted values of equilibrium adsorption data. The application of this equation is best suited to multilayer adsorption on heterogeneous adsorbents. This reduces Henry's law equation at small concentrations of solute.

$$q_e = \frac{AC_e}{(B + C_e^D)^{1/D}} \quad (4.7)$$

where A, B, and D are Toth isotherm constants, the term A represents the maximum adsorption capacity, B and D are empirical constants.

Several two or three parameter models have been used to describe experimental adsorption equilibrium data, and the model constants for various isotherms are determined from equilibrium data. Linear regression was used to determine the two parameters in the Langmuir and Freundlich equations. The model constants for three parameters models namely Redlich–Peterson, Dubinin–Radushkevich, and Toth equations were determined by using non-linear regression using “SOLVER” add-in for “EXCEL”.

4.2.2. Thermodynamic studies

Since solute (naringin) concentration is low, by Henry's law activity coefficient can be taken unity. The thermodynamic parameters (ΔH , ΔG , ΔS , and $K_{a/d}$) for the adsorption process were determined using the relations.

$$\Delta H = T\Delta S + \Delta G \quad (4.8)$$

$$\Delta G = -RT \ln(K_{a/d}) \quad (4.9)$$

Above equations can be combined and written as follows

$$\ln(K_{a/d}) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4.10)$$

where $K_{a/d}$ is the equilibrium constant between adsorption-desorption at temperature T (K).

It is equal to the adsorption affinity C_{ad}/C_e , where $C_{ad}(kg/m^3)$ is the reduction of adsorbate concentration of solution at equilibrium and $C_e(kg/m^3)$ is the equilibrium concentration of the adsorbate in the liquid phase.

$$\ln\left(\frac{C_{ad}}{C_e}\right) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4.11)$$

where $\Delta H (kJmol^{-1})$, $\Delta G (kJmol^{-1})$, and $\Delta S (kJmol^{-1}K^{-1})$ are the change in enthalpy, free energy and entropy respectively, R ($8.314 \times 10^{-3} Jmol^{-1}K^{-1}$) is the gas constant.

4.3. Adsorption kinetic data

When the solution (in present case KPBW) and adsorbent particles (the adsorbent resin) are brought into contact with each other, adsorbate (naringin) is adsorbed on adsorbent particles. The rate of adsorption is defined as the mass of adsorbate picked up per unit mass of adsorbent in a unit time.

It is well known that kinetic studies pertain to the rate of adsorption. In a batch kinetic study, the adsorption rate is high initially which is gradually reduces with increase of time.

Fractional attainment of equilibrium is defined as

$$u_t = \frac{\text{Amount of adsorbate picked up in time } t}{\text{Amount of adsorbate picked up at time } t \rightarrow \infty} \Rightarrow \frac{V(C_o - C_t)/w}{V(C_o - C_e)/w} = \frac{(C_o - C_t)}{(C_o - C_e)} \quad (4.12)$$

where $C_o(kg/m^3)$ is the initial concentration of adsorbate and $C_t(kg/m^3)$ is concentration of adsorbate at time t.

In a batch system rate of adsorption is dependent on following

- (i) The volume of the solution, concentration of adsorbate and amount of adsorbent.
However, for a fixed volume of solution the ratio of the quantity of adsorbate and adsorbent.
- (ii) Adsorption equilibrium behaviour (affinity of adsorbate towards adsorbent particles)
- (iii) Size and structure of adsorbent particle
- (iv) Relative motion of particles in the adsorbate solution, i.e., agitation or stirring speed

As mentioned in chapter 3, in these studies, a known amount of adsorbent is brought into contact with a solution of known volume and a known concentration of adsorbate and the adsorbate concentration change is recorded with time. The studies are the batch. Therefore, material balance gives

$$V(C_o - C_t) = \bar{V} \bar{C}_t$$

$$-V \frac{dC_t}{dt} = \bar{V} \frac{d\bar{C}_t}{dt} \quad (4.13)$$

$$V(C_o - C_t) = wq_t$$

$$-V \frac{dC_t}{dt} = w \frac{dq_t}{dt} \quad (4.14)$$

where $V (m^3)$ is the volume of the solution, $\bar{V} (m^3)$ is the volume of the adsorbent (resin), $C_o (kg/m^3)$ is the initial concentration of adsorbate in the solution, $C_t (kg/m^3)$ is the concentration of adsorbate at any time t , $\bar{C}_t (kg/m^3)$ is the average concentration of adsorbate in the adsorbent at any time t , w is the mass of the dry adsorbent and $q_t (kg/kg)$ is the mass of adsorbate/mass of dry adsorbent at time t .

4.3.1. The correlation of adsorption kinetic data

To correlate the adsorption kinetic data the following are the existing approaches.

Pseudo-first-order model:

The Pseudo-first-order rate equation also known as the Lagergren rate equation (Lagergren, 1898) has been used widely for describing the rate of adsorption from the liquid phase.

$$\frac{dq}{dt} = k_f (q_e - q_t) \quad (4.15)$$

The above equation can be integrated with B.C.; $q = 0$ at $t = 0$ to get

$$\ln (q_e - q_t) = \ln (q_e) - k_f t \quad (4.16)$$

where q_e (kg/kg) and q_t (kg/kg) are the adsorption capacity at equilibrium and at time t respectively and k_f (s^{-1}) is the rate constant of the pseudo-first-order adsorption.

Pseudo-second-order model:

It was developed by Ho and McKay to describe the adsorption of metal ions onto adsorbents (Ho and McKay, 1998). The rate expression is represented as

$$\frac{dq}{dt} = k_s (q_e - q_t)^2 \quad (4.17)$$

where k_s ($kg\ kg^{-1}\ s^{-1}$) is the rate constant for the pseudo-second-order adsorption

The above expression can be integrated with B.C.; $q = 0$ at $t = 0$ to get

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{t}{q_e} \quad (4.18)$$

Banghams equation:

If the pore diffusion is the only rate controlling step, then the Bangham model (Aharoni *et al.* 1979) can use to test the adsorption data. The following equation can represent the model

$$\log\left\{\log\left(\frac{C_o}{C_o - q_t w}\right)\right\} = \log\left(\frac{k_o w}{2.303V}\right) + \sigma \log(t) \quad (4.19)$$

where $k_o (m^3 kg^{-1})$ and $\sigma (<1)$ are the Bangham's equation parameters, $C_e (kg/m^3)$ is the final concentration of naringin in solution and $w(kg)$ is weight of resin

Elovich kinetic model:

The Elovich's kinetic model (Roginsky and Zeldovich, 1934) is also a type of chemisorption model but does not predict any definite mechanism. It is expressed as

$$\frac{dq}{dt} = \alpha \exp(-\omega q) \quad (4.20)$$

where α is the initial adsorption rate, ω is the adsorption rate at time t

The above equation can be integrated with B.C.; $q = 0$ at $t = 0$ for the condition $\omega t \gg 1$ to get

$$q_t = \frac{1}{\omega} \ln(\alpha\omega) + \frac{1}{\omega} \ln(t) \quad (4.21)$$

Intra-particle diffusion model:

The intra-particle diffusion model (IPD) proposed by Weber and Morris (Weber and Morris, 1963) has been widely applied for the analysis of adsorption kinetics. This is expressed as

$$q_t = k_d t^{1/2} + I \quad (4.22)$$

where $k_d (kg kg^{-1} s^{-1/2})$ is the intra-particle diffusion rate constant and I is the adsorption boundary layer thickness

During the process of adsorption, the transportation of the adsorbate particles to the surface of the adsorbent surface takes place in several steps. The adsorption process may be controlled by (i) film or external surface diffusion, (ii) pore diffusion, (iii) surface diffusion

and adsorption on the pore surface or (iv) combination of one or more steps. For a stirred batch process, an apparent diffusion coefficient can be used to relate diffusive mass transfer from solution to the adsorbent. This apparent diffusivity can be used to get experimental adsorption kinetic rate data. Usually, the adsorption process is diffusion controlled if its rate is dependent on the rate at which the adsorbate diffuses towards the surface.

Boyd's diffusivity model:

Boyd *et al.* (1947) developed a theoretical model for ion-exchange kinetics and mostly to determine the rate-controlling step. This model is based on diffusion through the boundary liquid film, considering adsorption kinetics as a chemical phenomenon. The simplified form of the rate equation can be expressed as

$$\ln\left(\frac{1}{1-u_t^2}\right) = \frac{\pi^2 D_e t}{R_p^2} \tag{4.23}$$

where $u_t = \frac{q_t}{q_e}$ is the fractional attainment of equilibrium at time t, $D_e (m^2 s^{-1})$ is the effective diffusivity, and $R_p (m)$ is the radius of the spherical adsorbent particle

In bi-porous solids, the two resistances are as mentioned in earlier. The Boyds diffusion model is likely to hold good at negligible macropore diffusion resistance. Furthermore, our case adsorption is physisorption. Therefore this model has not been adopted.

Modified adsorption shell Model:

The adsorption of naringin on macroporous resin from its aqueous solution (Singh *et al.* 2008) and stored as well as fresh kinnow juice (Singh *et al.* 2015) have been correlated by modified adsorption shell model. The same model has been used in the present work. Adsorption shell model was developed by Anand (1990), Manoja (1994) and Anand *et al.* (1994); by solving rate equations numerically. They found that for adsorption in macroporous

resin occurs in the distinct zones: (i) outer zone in which microspheres are almost completely saturated (ii) middle zone where adsorption is taking place at a given moment and (iii) the inner zone where adsorption is yet to take place.

It may be noted that, there is a time delay in development of the three zones. Once the three zones are developed, the outer saturated zone increases, and inner zone (fresh core) shrinks, and an adsorption zone (middle zone) moves inward. The thickness of adsorption zone is finite. Figure 4.2 represents physical picture envisaged, during adsorption in macroporous resin bead.

There will be two diffusion resistances viz. in macropores and micropores. The term defined

as $\beta = \frac{3(1-\varepsilon)q_o D_c / r_c^2}{\varepsilon C_o D_p / R_p^2}$ combines the diffusion and concentration characteristics in

macropores and microspheres. Where $D_p(m^2 s^{-1})$ and $D_c(m^2 s^{-1})$ are macropore and micropore diffusivities respectively, C_o is initial concentration of adsorbate in the solution (KPBW), q_o is sorption capacity of adsorbent microspheres at equilibrium, R_p is the average radius of the adsorbent particles, r_c is the radius of micro spheres, ε is a void fraction in the adsorbent particle.

For very thin adsorption shell $\beta \rightarrow \infty$, the above group of research workers derived following relationship between fractional saturation u_t and time of adsorption t for the condition: amount of adsorbate initially present in the solution \gg adsorption capacity of adsorbent

$$\left[\frac{1}{(1-u_t)^{2/3}} - 1 \right] = \frac{2KD_p \varepsilon C_o}{5(1-\varepsilon)q_o R_p^2} t \quad (4.24)$$

where K is a parameter related to accumulation of adsorbate in adsorption zone. The physical meaning of parameter K is as follows: For $\beta \rightarrow \infty$, and quasi-steady state conditions the flux

of the adsorbate through the macropores get utilized in reducing the radius of the unexposed core.

The above equation was used to analyse the numerical results obtained for finite values of β , as well.

An empirical relation between K and β was expressed as:

$$\log_{10} K = 1.357 \exp(0.207 \log_{10} \beta)$$

$$\text{for } 6 \leq \beta \leq 1,000,000 \quad 40 \leq K \leq 50,000 \quad (4.25)$$

In other words the kinetic data over a wide range of experimental conditions (indicated by the wide range of β be correlated by this approach.

However, for batch kinetic experiments the above equation (4.24) was modified by Singh *et al.* (2008) by replacing q_o with q_e of the corresponding run as follows:

$$\left[\frac{1}{(1-u_t)^{2/3}} - 1 \right] = \frac{2KD_p \varepsilon C_o}{5(1-\varepsilon)q_e R_p^2} t \quad (4.26)$$

The above equation (4.26) was used to correlate their data for naringin adsorption on polymeric resin Indion NPA-1 from aqueous solution (Singh *et al.* 2008) and kinnow juice (Singh *et al.* 2015).

When function $F_n(t) = \left[\frac{1}{(1-u_t)^{2/3}} - 1 \right]$ is plotted against time t a straight line passing

through origin should be obtained with the slope equal to $\frac{2KD_p \varepsilon C_o}{5(1-\varepsilon)q_e R_p^2}$. Thus for a kinetic run

K could be determined from the slope; β could be determined from the equation (4.25). It may be noted in present case, q_o is replaced by q_e of corresponding run therefore β becomes

$$\beta = \frac{3(1-\varepsilon)q_e D_c / r_c^2}{\varepsilon C_o D_p / R_p^2} \quad (4.27)$$

$$\beta = \psi \frac{q_e}{C_o} \quad (4.28)$$

$$\text{where } \psi = \frac{3(1-\varepsilon) D_c / r_c^2}{\varepsilon D_p / R_p^2} \quad (4.29)$$

Experimental data were analysed by following approach .

- a) In a given experiment, change in solution concentration as a function of time was measured, and fractional attainment of equilibrium u_t was calculated.
- b) $F_n(t) = \left[\frac{1}{(1-u_t)^{2/3}} - 1 \right]$ was calculated using above values of u_t .
- c) $F_n(t)$ was plotted against time (t).
- d) K was determined by the relation (4.26). (using slope of $F_n(t)$ vs. t)
- e) β was calculated using the equation (4.25).
- f) The parameter ψ , for bidispersed solids in adsorption, is a characteristic of any adsorbent– adsorbate system. ψ was calculated from β by the substituting value of C_o and q_e .

Generation of kinetic data

The experimental change in concentration for any run may be generated with following steps:

1. From the value of ψ , the value of β is calculated, $\beta = \psi \frac{q_e}{C_o}$, the experimental values of C_o and q_e of that run need to be used.
2. From value of β , the value of K is calculated by using the relation

$$\log_{10} K = 1.357 \exp(0.207 \log_{10} \beta) \quad (4.25)$$

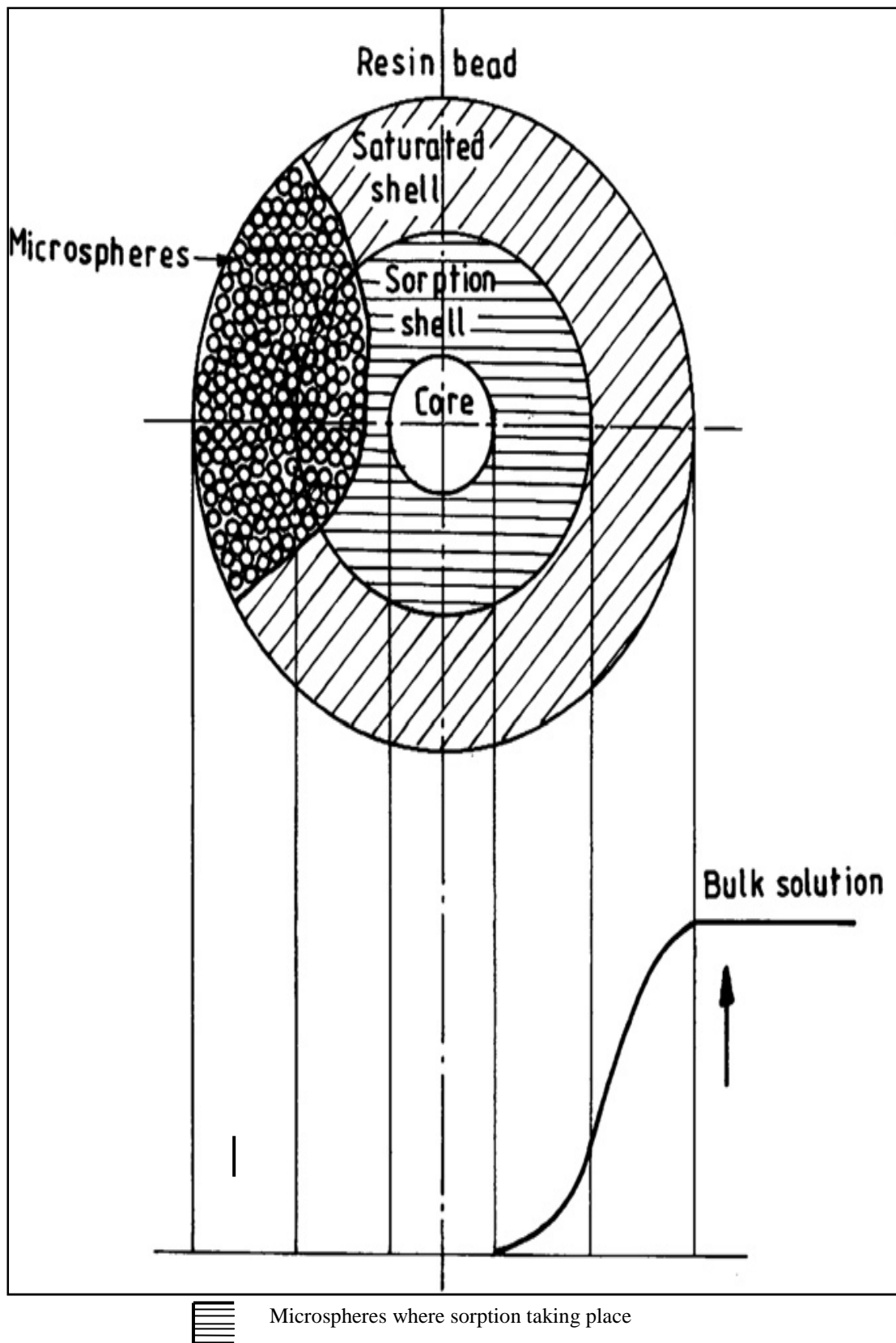


Figure 4.2: Concentration profile through a macroreticular resin bead
 (physical picture envisaged)

3. The value of K obtained in step (ii) is used to calculate the value of u_t by using the relation (4.26) rewritten as (4.27)

$$u_t = 1 - \frac{1}{\left(1 + \frac{2}{5} \frac{KD_p \varepsilon C_o}{(1-\varepsilon)q_e R_p^2} t\right)^{3/2}} \quad (4.30)$$

4. From u_t , C_t can be calculated

$$\text{as } u_t = \frac{C_o - C_t}{C_o - C_e} \quad \Rightarrow \quad C_t = C_o - u_t(C_o - C_e) \quad (4.31)$$

However, by the slight modifications it becomes

$$C_t = C_o^I - u_t(C_o^I - C_e) \quad (4.32)$$

where C_o^I is a concentration of naringin at the start of three distinct zones. When the resin is brought into contact with solution, microspheres of outer layers of the bead are exposed to naringin solution of the initial composition. The outer layers of the bead are saturated with an adsorbent to form a saturated shell initially within few seconds, therefore in early period there is a sharp drop of the concentration of naringin in solution. The adsorbate adsorbed by the resin in early period q_{ess} is given by

$$q_{ess} = kq_e w \quad (4.33)$$

where k is mass or volume fraction of adsorbent bead saturated with adsorbate to form the saturated shell before the start of three distinct zones. q_e is equilibrium resin phase concentration corresponding to the initial concentration of the solution, w is a mass of adsorbent.

The concentration of naringin at the start of three distinct zones C_o^I (i.e. Modified adsorption shell model) is given by

$$C_o^I = C_o - \frac{kq_e w}{V} \quad (4.34)$$

where V is the volume of solution.

Microspheres in a bead are 1–10 μm diameter taking the thickness of initially developed saturated shell (ΔR) equal to 8 μm (equal to the diameter of 2–3 microspheres). The volume fraction of the shell will be $k = 3\Delta R/R_p$ where R_p is the radius of the bead. Putting the values the estimated value of k was found to be $k = 0.064$ for resin PA-500 and 0.050 for resin PA-800.

4.4. Fixed bed adsorption column studies

The design of a fixed-bed column involves estimation of the shape of the breakthrough curves and the appearance of the breakpoint, which is an important factor in accessing the feasibility of using the adsorbent in real applications. For a given column bed height, the plot of exit concentration versus time or volume throughput collected are known as breakthrough curves. The performance of a packed bed is obtained through the concept of breakthrough curves. The characteristic shape of the breakthrough curves along with the time axis depends on the inlet flow rates and other properties such as column diameter and bed height. Hence, successful design of an adsorption column requires prediction of the concentration–time profile from breakthrough curves.

When adsorption reaches the breakthrough point (the point of maximum saturation, when the resin cannot hold the adsorbate molecules), the adsorption effect decreases and solute starts to leak from the resin. Thus, it is important to define the breakthrough point to calculate the resin quantity, processing volume of sample, and proper sample flow rate.

The breakthrough time (t_b) in this study is defined as the time at which adsorbate (in our case naringin) concentration in the outgoing KP BW from column (C_t) reaches 5% of the

inlet concentration (C_o), and bed exhaustion time (t_e) is the time at which naringin concentration in the outgoing KPBW exceeds 95% of C_o (Dutta, 2009).

Time equivalent to total or stoichiometric capacity is

$$t_t = \int_0^{\infty} \left(1 - \frac{C_t}{C_o}\right) dt \quad (4.35)$$

Time equivalent to usable capacity is

$$t_u = \int_0^{t_b} \left(1 - \frac{C_t}{C_o}\right) dt \quad (4.36)$$

Usable capacity of bed up to the breakthrough time point t_b

where the area under the curve $\int_0^{\infty} \left(1 - \frac{C_t}{C_o}\right) dt$, gives t_t value (total time), whereas area under

the curve $\int_0^{t_b} \left(1 - \frac{C_t}{C_o}\right) dt$ gives the t_u value.

The total KPBW volume (V_{eff}) can be estimated as follows

$$V_{eff} = Q t_{total} \quad (4.37)$$

where Q ($m^3 s^{-1}$) and t_{total} (s) are the volumetric flow rate and the total flow time

The total adsorbed naringin quantity q_{total} (g) in the column is calculated as follows

$$q_{total} = Q \times C_o \times \int_0^{\infty} \left(1 - \frac{C_t}{C_o}\right) dt \quad (4.38)$$

where C_o is initial concentration of kinnow peel boiled water

Saturation loading capacity of the adsorbent bed or equilibrium naringin uptake q_s (kg/kg) in the column is calculated as the following:

$$\text{Naringin adsorbed / kg dry resin, } q_s = \frac{q_{total}}{w} \quad (4.39)$$

where w is mass of dry resin

When the adsorption occurs in a column three zones are observed. If adsorbate solution is flows downwards, there (i) top most zone of adsorbent will be saturated with adsorbate (ii) The zone where the adsorption will be taking place called mass transfer zone (MTZ) (iii) The lowest zone free of adsorbate. The mass transfer zone moves downwards with progress of time. it has a fixed height for constant flow rate.

Mass transfer zone (*MTZ*) is formed at the front of the column where adsorption takes place. The controlling factors for the depth of *MTZ* are the nature of adsorbate, characteristics of adsorbent, bed height, the particle size of adsorbent, and solution flow rate. The *MTZ* moves toward the outlet from inlet of the fixed bed during operation as adsorption proceeds.

The unused bed length (H_{UNB}) is given by

$$H_{UNB} = \left(1 - \frac{t_u}{t_t}\right) H_T \quad (4.40)$$

where H_T (m) is the total bed height.

MTZ can be calculated as

$$MTZ = \frac{H_T}{\left(\frac{t_t}{t_t - t_b}\right) - \gamma} \quad (4.41)$$

where $\gamma = \frac{t_u}{t_t}$ represents the degree of saturation in the *MTZ* .

4.5. Correlation of desorption equilibrium data

The same isotherms as used in adsorption are applicable for desorption because it is understood that adsorption-desorption are reversible and occurs simultaneously, only equilibrium shift is important. Freundlich isotherm was used to correlate desorption equilibrium data.

$$q_{ed} = K_{fd} C_{ed}^{1/n_d} \quad (4.42)$$

where K_{fd} and n_d are Freundlich isotherm constants for desorption

4.6. Correlation of desorption kinetic data

The Boyds diffusivity model (Boyd *et al.* 1947) equation was used to correlate desorption experimental kinetic data. Although this has been derived and used to relate kinetics of chemical reaction, these can be used to correlate desorption kinetic data. The same have been used to correlate desorption kinetic data in the present work.

The simplified form of the rate equation can be expressed as

$$\ln\left(\frac{1}{1-u_d^2(t)}\right) = \frac{\pi^2 D_{ed} t}{R_p^2} \quad (4.43)$$

$$\text{where } u_d(t) = \frac{C_{td}}{C_{\max}}, \quad C_{\max} = \frac{q_{od} W^I}{V_e} \quad (4.44)$$

$u_d(t)$ is the fractional attainment of equilibrium at time t in desorption, $D_{ed}(m^2 s^{-1})$ is the effective diffusivity for desorption and $R_p(m)$ is the radius of the adsorbent particle.

Generation of desorption kinetic data

- (i) The concentration of naringin desorbed in ethanol at any time C_{td} for any run can be generated by the Boyd's diffusivity model equation using average value of effective diffusivity $D_{ed}(m^2 s^{-1})$.
- (ii) From the value of D_{ed} , the value of $u_d(t)$ is calculated by relation (4.43).
- (iii) From value of $u_d(t)$, the value of C_{td} is calculated by relation (4.44).

4.7. Desorption fixed bed column studies:

The total naringin desorbed from the column can be calculated using the equation (4.45).

$$\text{Amount of naringin desorbed} = Q_e \times \int_0^t (C_{td}) dt \quad (4.45)$$

where Q_e is flow rate of eluent at effluent, C_{td} is concentration of naringin in ethanol at time t

The above mentioned relations and approaches have been used to correlate the observed data in present study. The results are given in the Chapter 5.