"MATHEMATICAL MODELING OF ADSORPTION KINETICS USING FILM-SOLID-DIFFUSION MODEL TOWARDS EVALUATION OF MASS TRANSFER PARAMETERS IN THE CONTEXT OF WASTE WATER TREATMENT AND EFFLUENT TREATMENT AND ADVANCED FBC SYSTEMS FOR BETTER SUPPORTING ECOLOGICAL DYNAMICS"

DR.DAVIDSANTOSH CHRISTOPHER[1]/Associate Professor/Mechanical

Engineering/WolaitasodoUniversity/

Ethiopia.

DR.G.KALIVARATHAN[2]/Associate Professor/Mechanical Engineering/Woliatasodo

University/Ethiopia.

MR.S.V.VIJAYASUNDARAM[3]/Assistant Professor/Electrical &Computer

Engineering/Woliatasodo University/

Ethiopia.

MR.MEBRATU MARKOS[4]/Head of the Depatrment/Mechanical Engineering/Woliatasodo

University/Ethiopia.

ABSTRACT

KEYWORDS:

Adsorption kinetics

Mathematical modeling

Film-solid-diffusion-model

Mass transfer

Waste water-treatment

Ecological dynamics

Chromatographic effects

Psuedo-equibrium effects

Batch modelling

Column studies

FBC/Fludized Bed Combustion

The design of adsorption columns for industrial proposes has been based, over last few decays, upon emperial basis. Information gathering to be by a series of bench scale and pilot plant experiments. The data so obtained was emperial and valid for the particular system condition under experimentation, i.e, any deviation in any system variable would lead to widest prediction of the adsorber performance. This approach of obtaingadsorber performance data is tedious and slow as every change in system condition needs a new set of experiments. However, the massive growth of numbers, sizes and diversity of industrial effluents and waste water necessiates a more modern approach-one that has flexibility, speed and versatality to match the growing demands for high quality design.on the otherhand, a new approach must have a sound theoretical foundations that lays a firm background for their analysis and computer aided design, the latter being the main feature of modern industry adsorbtion modelling in the

deiscription of the process in terms of mathematical equations. Based on the fundementals of mass transfer and conservation of matter, the partial equations developed are combined with initial and boundary system conditions such that they are solved;they yield a solution equations that has a physical significance. This makes mathematical modelling, a most appropriate approach to consider for providing design information. It is noticed that the information provided by mathematical modelling is only preliminary, yet it is vital design information. Modelling is done on batch processes as these yield accurate information that is "isolated" from the chromatographic and pseudo-equlibrium-effects encountered in column studies. Further to batch modelling, column modelling may be carried out to include the above mentioned effects. In this context, a modest attempt has been made to formulate mathematical modelling of adsorption kinetics using Film-Solid-Diffusion model towards evaluation of mass transfer parameters in the case of waste water treatments and effluent treatments for better ecological dynamics as a viable theoretical model.

Author correspondence:

Dr.DavidSantosh Christopher[1],

Associate Professor, Mechanical Engineering,

WolaitaSodo University, Ethiopia.

1.PRELIMINARY REQUIREMENTS OF ADSORBER DESIGN:

i. The rate of adsorption, i.e, the time lapsed before a given amount of solute is removed from solution. This is provided by studies of the system kinetics (on process dynamics). It provides information on the adsorption time and hence the size of the adsorber and the solution residence time. The kinetic data is normally given interms of the effluent concentration as a function of time. It yields an exponential decay function termed as the "concentration decay curve".

ii.   The "affinity" of the adsorbent for the solute and hence the dosage of adsorbent required to remove a unit mass of solute from solution. This is provided by equilibrium studies that yield information on the process statics, adsorbent weight, and hence the pressure drop that is likely to develop across the column. Equilibrium data is described as the concentration os solute in the adsorbent surface (solid-phase-concentration) as a function of the concentration of the solute in solution (fluid-phase-concentration). However, inorder to provide the information theoretically by mathematical modeling, complete basics/concepts of adsorption mechanism is required. It is essential to be aware of the physical variable that affects the process rate and the factors that control its approach to equilibrium.

Once the adsorption mechanism is understood, the model is structured by providing:

(i)   Mass transfer equations to describe film mass transfer and intraparticle diffusion. These normally contain mass transfer parameters to measure the process rate.

(ii)   Material balance equation to secure the conservation of matter. Continuity equations are also required to preserve the system continivity.

(iii) Equlibrium description represented by an appropriate adsorption isotherm to describe the sorbate/sorbent system behaviour.

(iv)   Invital / boundary condition.

Therefore, a set of partial-differntial equation that are getting solved numerically or analytically- depending on the model.

1.   PROCEDURE FOR MATHEMATICAL MODELLING:

The inputs are generally the system variables and outputs are the system kinetics data. For faster and efficient, computer programs are used. However, it is important to emphasize that a mathematicalmodel should be mathematically convenient. It should yield accurate results with a reasonable computation time. Mathematical complexity is a disadvantage. It should also have flexibility, so that it can be tailored to handle a wide range of system conditions and still be applicable.

2. Film-solid-diffusion-model:

This model exhibits the most theoretical approach and according to this model, intraparticle diffusion occurs by surface hopping mechanism. Adsorbate molecules diffuse within the sorbent particles by surface migration from one site to another on the outer surface and the porewalls. This model assumes a homogeneous adsorbent with a uniform internal structure and therefore it is designated as "film-homogenous-model". Adsorption occurs in the radial direction, and sites on the same radial position have similar energies of adsorption. However, this model has been successfully applied to hetrogenous adsorption systems, by taking heterogeneity effects into account upon equilibrium description.

2.1 Mathematical description:

Sorbent particles are assumed to be spherical with identical radius, and mathematically the following equations are used;
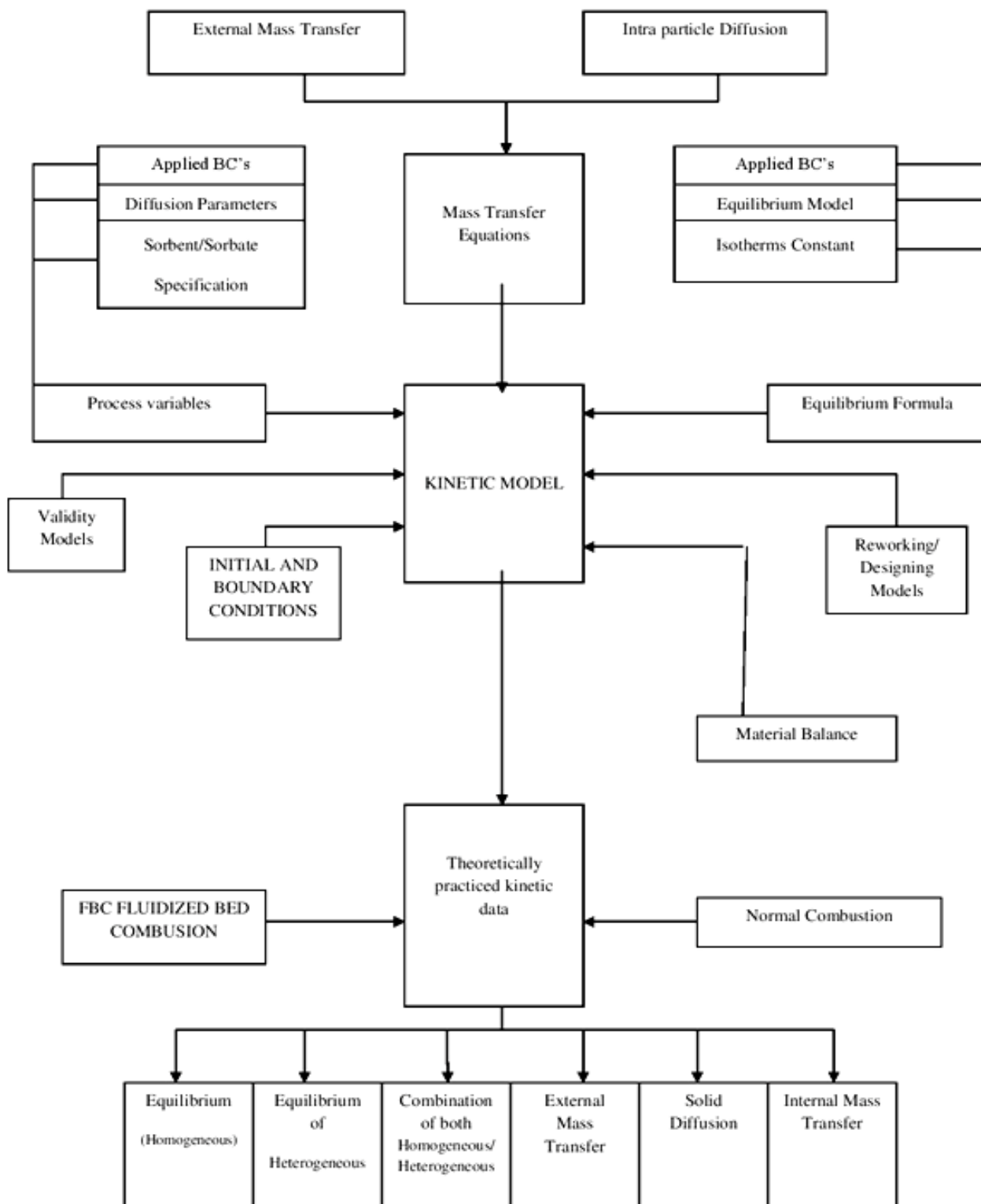
Fig-1. Steps involved in mathematically modelling

TABLE-1

Values of effective defectives:

Sorbate	sorbent [a]	$D_{eff}*10^6$ (cm²/s)	concentration range [b]
Basic blue69	GAC[C]	1.00 – 3.00	40.00 - 600
Basic red22	GAC[C]	2.20 – 0.8	30.00 - 300
Basic yellow21	GAC[C]	10.00- 0.720	50.0 - 300
Dichlorophenol	GAC[C]	3.59	20.0
Phenol	GAC[C]	2.50 – 2.00	200 – 600
(Dodecylbenzene Sulfonate)	GAC[C]	0.15	200
H_g^{2+}	GAC[C]	2.50	-
Acid blue25	Lignite	0.06	100 – 300
Basic red22	Peat	0.70 – 0.340	300 – 500
Basic yellow21	Peat	0.19 – 0.130	100 - 500
Basic blue69	Bagasse pith	6.70	50.0 - 300
Basic red22	Bagasse pith	2.70	50.0 – 300

a→ for all systems, particle size 355 – 500μm, mass varies from 0.10 – 2.00g, v=1.7*10³m³

b →units are mgdm⁻³

c →GAC – Granular activated carbon

A) External mass transfer:

$$N_t = \frac{dc_r}{dt} = k_f . A.(c_r - c_s) \text{----------------------------------}(1)$$

B) Solid diffusion:

$$\frac{dq}{dt} = \frac{D_s}{r^2} \frac{\partial}{\partial r}\left[r^2 \frac{\partial q_i}{\partial r}\right] \text{------------------------}(2)$$

$$= D_s \left[\frac{\partial^2 q_i}{\partial r^2} + \frac{2}{r} \frac{\partial q_i}{\partial r} \right] -$$
$$- - - - - (3)$$

Where "q" (mg g^{-1}) is the average solid phase concentration;

$q_i \rightarrow$ (mg g^{-1}) is the point solid phase concentration and it is the function of the radial position "r" and time "t".

$D_s \rightarrow$ (cm^{2}s^{-1}) is the solid diffusivity (and it is assumed to be constant for mathematical convenience) over the process.

The average solid concentration "q" is related to the point solid concentration q_i by,

q_t

$$= \frac{3}{R^3} \int_0^R q_i(r,t) r^2 dr - - - - - - - - - - - - - - -$$
$$- - - - - - - - - - (4)$$

C) **Keeping the system continuity, external mass transfer and internal mass transfer rates are equal;**

$\frac{dq}{dt}$

$$= \frac{3k_f}{R(1 - \varepsilon_p)\rho_s} [c_t - c_s] - - - - - - - - - - - - - -$$
$$- - - - - - - - - - (5)$$

Where ρ_s (kgm^{-3}) is the sorbent solid density

$\varepsilon_p \rightarrow$ is the particle voidage

By material balance, the inputs and outputs of the system are equal.

$$c_t = \left[c_0 - \frac{m}{v} q_t \right] -$$
$$- - - - - - (6)$$

From the material balance equation,

$$N_t = -v \frac{dc_t}{dt}$$

$$= m \frac{dq_t}{dr} -$$
$$- - - - - (7)$$

D) Initial/Boundary condition are expressed as;

$$c_t(0) = c_0 ; \qquad q_i(r, 0)$$
$$= 0 \quad (@ \ r = R, \qquad all \ t) - - - - - - - - - - -(8)$$

$$c_t$$

$$= c_s -------------------- (9)$$

$$q_i(R,t)$$

$$= q_s -------------------- ----(10)$$

These equations contain a large number of variables that can be reduced by introducing dimensionless groups;

$$u = [q_i X]$$

$$\tau = \left[\frac{D_s.t}{R^2}\right], X = \frac{r}{R} \quad \text{(are the dimensionless concentration, time and position)}$$

Therefore the equations becomes,

$$\frac{\partial u}{\partial x}$$

$$= D_s \frac{\partial^2 u}{\partial x^2} ------------------- (11)$$

$$q(\tau)$$

$$= 3 \int_0^1 u(x,\tau)x dx --------------- ----(12)$$

$$\frac{dq}{d\tau}$$

$$= \frac{3k_f^R}{D_s \rho_s (1-\varepsilon_p)}(c_r - c_s) -------------- ----(13)$$

$$u(0,\tau) = 0 = u(x,0) ----------------------(14) \, u(1,\tau) =$$

$$q_s(\tau) ------------------------(15)$$

One of the major criteria remains to be emphasized, that is equilibrium description. In this model the redich-peterson-isotherm has been selected with minimum deviation/modification.

$$\text{i.e} q_s = \left[\frac{k_J c_s}{1+b_J c_s^\beta} + \frac{kc_s}{A+Bc_s^D} + \frac{k_L c_s}{1+a_L c_s}\right] ----------------$$

$$(16)$$

$$q_s = (90\% + 5\% + 5\%)$$

Where

q_L , k_L = (dm^{3}g^{-1}), Langmuir constants

k_L= solute adsorptivity

a_L= energy of adsorption

$\frac{k_L}{a_L}$→Monolayer adsorbent capacity

K, A, B, D→ isotherm constants.

2.2 SOLUTION METHODS:

Due to the practical importance of the kinetic models in general and Film-Solid-Diffusiuon model in specific the solution methods followed must be mathematically convinent with a reasonable computation time, applicable to a wide range of system conditions, and veralite.

The equation, $q_s = \frac{k_J c_s}{1+b_J c_s^\beta}$ and the initial / boundary condition oriented governing equation can be solved by using Crank-Nicolson's numerical finite difference method.

The input variables include the following:

a) Adsorbent specification, i.e, mass/density/voidage/particle size.
b) Solution specifications, i.e, volume, initial sorbate concentration.
c) Equilibrium data, i.e, isotherm constants.
d) Mass transfer dta, including the external mass transfer co-efficient k_L and the solid diffusivity D_s
e) Mathematical data suh as the number and size of integration steps.
   The output data is the form of concentration decay or the solute fluid phase concentration as a function of time.

2.3) EVALUATION OF THE MASS TRANSFER PARAMETERS:

A non linear combination of K_f and D_s values determines the overall shape of the "concentration decay curve'' reflecting physical system, the value of K_f expresses, the rate of external mass transfer, which takes the first few minutes of the process, after which the D_s value becomes dominant as it measures the solid diffusion rate throughout the process till the equilibrium.

In order to evaluate the mass transfer co-efficient K_f, a starting value is obtained by the initial-slope method.

At t = 0, C_t=C_0

Therefore $k_f = \dfrac{d\left(\frac{c_t}{c_0}\right)}{dt} \cdot \dfrac{1}{A}$ $- -(17)$

Where "K_f" is evaluated from the slope of the concentration decay curve at t=0. The solid diffusivity "D_s" is a very complicated parameter to evaluate, due to the large number of factors that controls the solid diffusion rate. Some of these factors are the types of adsorbents, its initial structure and particle size, the particle loading, the solid/liquid ratio in the system and the initial concentration in the solution. All these and many other factors interfere with evaluating D_s from the classical diffusivity equation. However litreture has some values that can be used as an original estimation of D_s. Therefore both starting values of K_g and D_s can be input to the model. The corrected values are obtained by super position of experimental and theoretical data in such a way that they yield "congruent curves".

2.4) APPLICATIONS AND CONCLUSION:

This model has a firm and fair-enough theoretical foundation-especially when the solid diffusion mechanism was found to contribute 20 times as much as pore diffusion. It has been already adapted and applied to the adsorption of phenol and its derivatives on activated carbon. Ofcourse these pollutants are abundant in wastewater and effluents from modern industries. For a huge application, this model can be extended to a model that predicts "multicomponent kinetic data", so that the high degree of complexities in the analysis can be accomodated and minimized for applications. However, many practical issues addressing the kinetic models related to advanced Fluidized Bed Combustion systems which are employed with critical adsorption kinetics are captured with better supporting models for efficient combustion processes, especially in sugar industries and its allied industries.
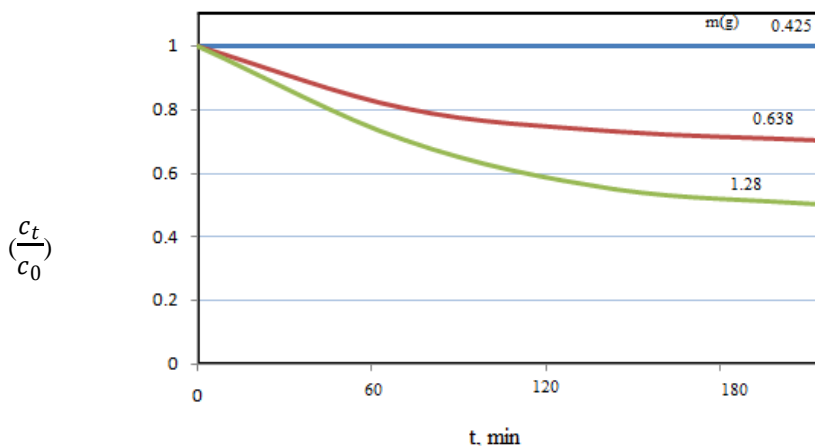

Fig-2, Application of the FSD model to basic red22/carbon system using several carbon masses [C_0=100mg dm^{-3}; d_p = 355 to 500μm].
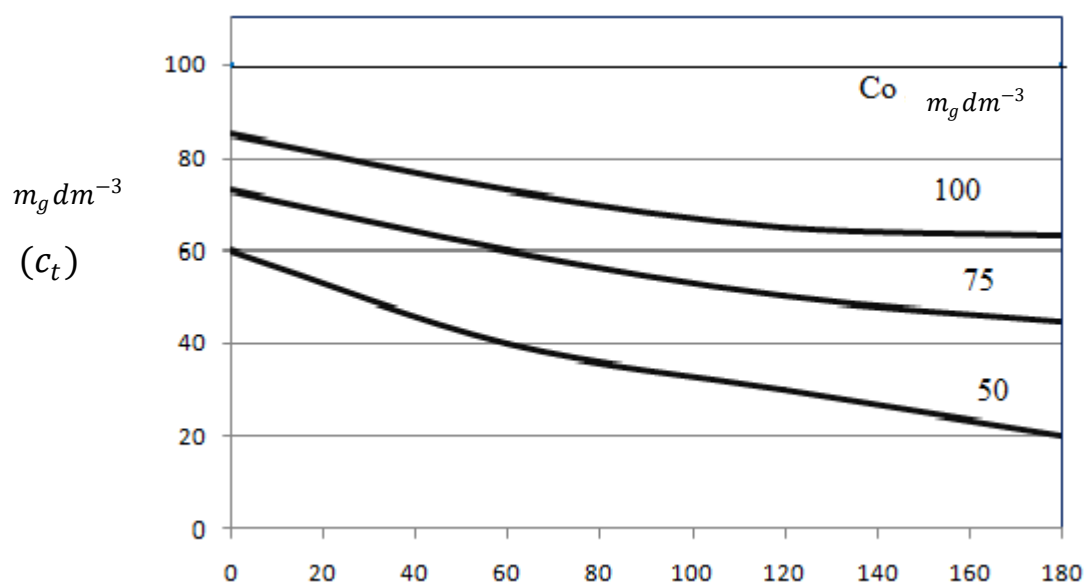
Fig-3, Application to FSD model to basic red22/carbon system using several initial dye concentration (m=0.425g, dp= 355 to 500 μm).

REFERENCE:

1) Gordon Mekay "Removal of Poluutants from Wastewater" CRC press-Newyork, London, Tokyo.

2) Fernand.J, Belltran, "Ozone reaction kinetics for wastewater system", Lewis publications. CRC press LLC. USA.

3) Butterworth-Heinemaan" Reactor design and product yield, BIOTOL, An inspirit of Elsevier, 1992, Jordon Hill, oxford.

4) Enger, eldon.D, and Bradley F.Smith, Mathematical modeling of environmental pollutants-a study of interrelationship; McGraw Hill, Newyork, 2001.

5) Horward A.G, Aquatic Environmental Chemistry, oxford university press, Newyork, 1998.

6) Stumm Werner Ed. Aquatic chemical kinetics-Reaction rates of processes in natural water, johnwiley and sons, Newyork, 1990.

7) Stumm Werner, chemistry of the Solid-water interface, John wiley and sons, Newyork, 1992.

8) Hem.J.D, study and interpretation of the chemical characteristics of natural water, 2nd edition, U.S.Geological survey paper, 1473, Washington DC, 1970.

9) Knapp, Brain, Air and water chemistry, Atlantic Europe, Henley-on-Thames, U.K, 1998.

10) Kumar, Arvind Ed; aquatic ecosystems, A.P.H; publishing corp., New Delhi, 2003.

11) Schmitt, R.J., and Osenberg, C. (1995), Defecting ecological impacts, concepts and applications; Academic press San Diego, CA.