

**MATHEMATICAL MODELING EQUATION OF A SIMULATED
(FIXED) BED FOR DESALTING OPERATION**

RESEARCH WORK UNDERTAKEN

BU

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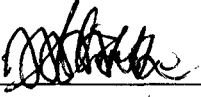
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DECLARATION

I Whole-heartedly declare that this research thesis is solely undertaken by me and has not been presented in this form for the award of degree elsewhere. Works of contributors have been greatly acknowledged.



Signature

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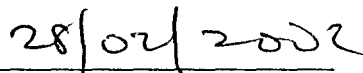
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CERTIFICATION

This research thesis is as original work undertaken by EMMANUEL J. I. SANI (96/5139 EH), under the articulate and dynamic supervisor of Engr. (Mr.) Olutoye M. A to met the quality (standard) and scope in compliance with the requirements of the Department of Chemical Engineering, Federal University of Technology, Minna, for the award of the degree of Bachelor of Engineering (B. Eng. Hons.) in Chemical Engineering.



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DR. J. D ODIGWE
HEAD OF DEPARTMENT

DATE

EXTERNAL EXAMINER

DATE

DEDICATION

This project is dedicated to my parents Mr. & Mrs Emmanuel Sani and Elder Brother Physicist Friday, and to all those who know that nothing is impossible, difficult certainly, improbable most likely, but never impossible.

ACKNOWLEDGEMENT

All praises due to Allah (S.W.T), the God of the entire world, for seeing me through all the hurdles and hard terrain in search for Academic waters!

Every success that I have recorded in life, the glory goes to him, only the mistakes are mine.

To you my parents Mr. & Mrs Emmanuel Sani, for esteeming my education above their comfort to them I say bravo! my jewels of inestimable worth, the life breath of my existence, the passion of soul. I owe you greatness, absolute indeptness and unquantifiable gratitude for the remaining days, I will spend on earth. You are the best parents on earth. You stood by me, when I was nothing and insignificant, you raised me from grass to grace, you transformed my life and made me exulted. In my voyage for the best of parent around the world, I found none but you two! What a wonderful and unique companion.

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To Mr. Adeniyi, late Mr. (Engr.) Akinbode A., Mr. (Engr.) Femi Olugbooji, Engr. (Mr.) Akpan, Engr. (Mr.) David A, Engr. (Mr.) Edoga, Engr. (Mr.) Saka, Engr. (Mr.) Abdulwasiu, Engr. (Mr.) Dr. Onifade, Engr. (Mr.) Dr. Aberengba, Engr. (Mrs.) Elizabeth, Engr. (Mr.) Attah (ELECT.) my contributing supervisors, I say Kudos for all your individual contributions in seeing me starts this career, even though you all did not see me through to the successful end.

Compliments for all your contributions. As you all have contributed to our success today, God in his greatness and uniqueness will make you all among the foremost. (Amen.)

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Oneness should be our watchword; our faith through oneness is greater than our losses, comforting than our grieves, stronger than our struggles and more powerful than our worries
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ABSTRACT

The work aimed at modeling a fixed simulated bed that can be used to predict the performance of adsorption process in terms of concentration of adsorbate and the amount of the adsorbate. From the experimental results obtained, the experimental results permitted the development of a mathematical model consistent with the experimental observation. The model can be used to predict the changes in concentration of the adsorbate and amount down the depth of the column.

This was achieved by using a prototype simulated fixed bed. The adsorbent used for the experiment was Silical – Alumina. A model equation was developed from the prototype (model). It was found from the graph of concentration against bed height (depth) for the adsorbate that the concentration of the effluent stream decreases as the height increases down the column, this means effective adsorbate adsorption until the concentration reaches 2.483104Kmol/m^3 , while the amount of the adsorbate increases down the depth of the column to an amount 28.288783Kmol , The experimental results viz – a – viz the simulated results showed a close agreement with the graphical comparison method and a ranking of 0.8. The optimum height for the adsorbent bed design obtained was approximately 5.67m

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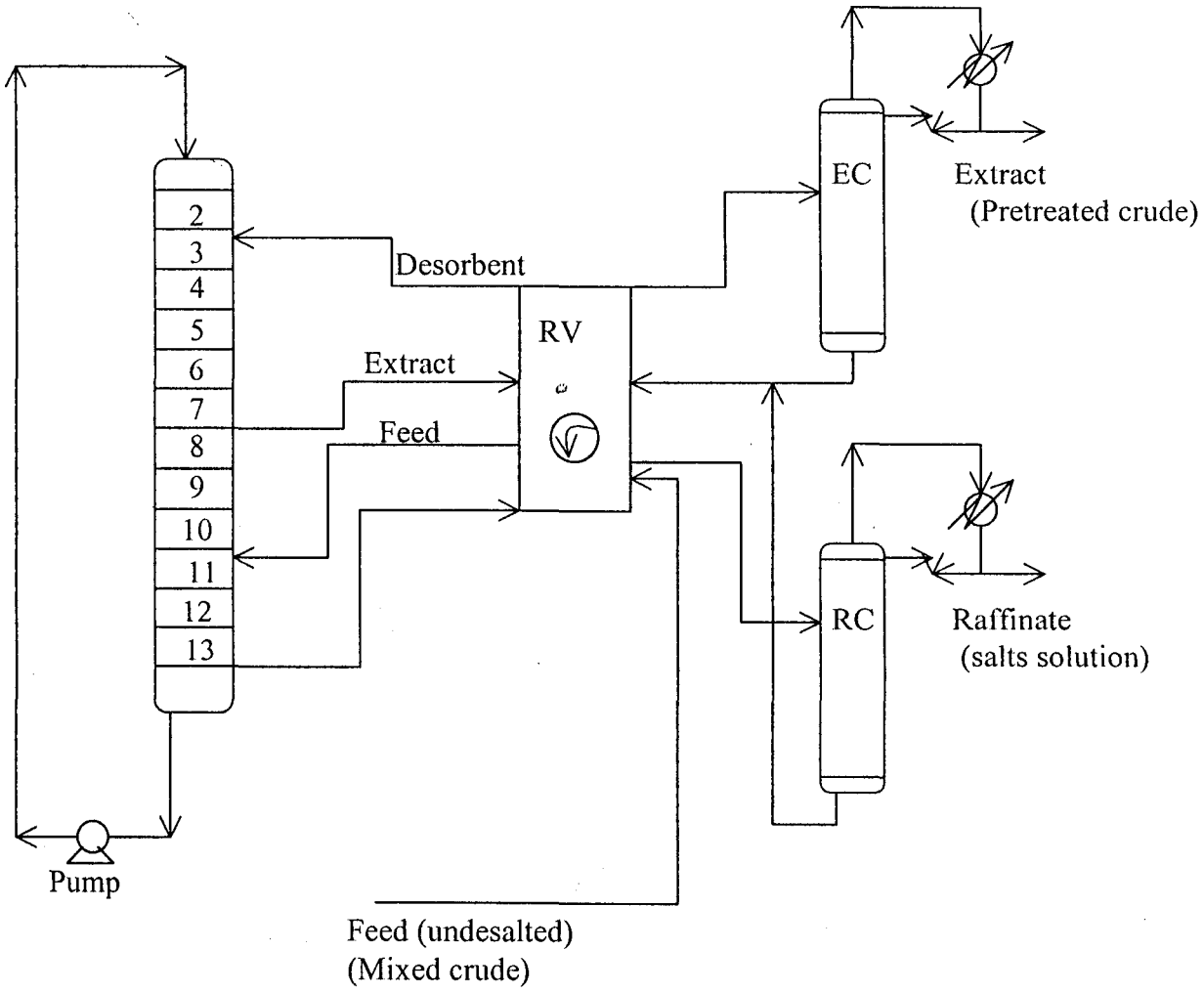
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PROTOTYPE SIMULATED BED FOR DESALTING OPERATIONS USING SILICA – ALUMINA AS ADSORBENT.



key :

EC = Extraction column

RC = Raffinate column

RV = Rotary valve

CHAPTER ONE

1.0 INTRODUCTION

1.1 BACKGROUND OF STUDY

Development enhanced by innovation in technology to man have been rather period. From the Stone Age; to the Iron Age; to the Bronze Age and now the computer age and the age of artificial intelligence.

Man had had to be swept by changes in technology. Today's man is engulfed with the considerable excitement from the dividend he derives from oil refinery industries, the fuel and lubricating industries. Advances in technology of crude oil processing have prompted new products that are fast replacing the traditional materials for better performance and are creating a host of new application. Advancement in processing technology worldwide has increased; demanding new not only improved new tools and process equipment. There have not only improved the standard of living of today's man and his life expectancy, but have contributed significantly to the success achieved in the various sectors of our national life. With the fuel, oil, lubricating industries comes their attendant benefits, which include a wide production range of the Petrochemicals. This include the Polyethylene, used for making our disposable hand bags, Vinyl resins, solvents, leadtetraethyl used for improving petrol (pms) octane rating and burning characteristic, Refrigerants, syndetics, detergents, just to mention but a few.

For the continue survival of the petrochemical industry, in the face of advancement in processing technology, our technology must also change for better performance variant. In doing these, the pre – treatment stage of crude, which include desalting will go a long way at improving the overall quality of the product obtained.

It is in the light of this trend, that a mathematical modeling of adsorption of a fixed simulated bed for desalting operation was carried out. The results obtain is suitable for desalting operation and for research and development, can be built from the pilot scale

to the plant stage ⁽²⁾. A combine effort of both the industry and academic for strategic research and development will help to become fully aware of the problem, prospects and get challenged for sustainable development.

Adsorptions from the liquid phase have long been used for removal of contaminants present at low concentrations in process streams. ⁽³⁾ In some instances, the objective is removal of specific compounds ⁽³⁾. In the case of this work, the main objective in the removal of basic salts, which include NaCl, KCl, CaCl₂ and organometallic impurities from crude oil. In others, the contaminants are not well defined, and the objective is the improvement of general properties such as colour, taste, odour and storage stability ^(4 - 7).

The first know commercial acceptance of adsorption over other separation technique ^(3, 8) .Is the Sorbex technology. These technology have not, however met the demand for it usage in the case of crude oil pretreatment before distillation. With continuous research and development the fixed adsorbent bed and simulated for other beds can be fully exploited in usage for crude pretreatment. The designed simulated adsorbent bed uses Zeolite – alumina adsorbent for the removal of the salts defined. Its advantage includes the fact that adsorption offers a more efficient route to this method of separation of commercial interest than do the desalting method using electrodialysis. This stems in part from the fact that adsorbents are know i.e. silica – alumina that are much more selective in their affinity for the materials to be removed, basic salts than are any known solvents ⁽⁸⁾ i. e the emulsifier used in the desalting equipment.

Another item of comparable importance in the used of the fixed adsorbent bed and simulated for other beds is the fact that much higher efficiency ^(3,8) of these beds than in the conventional desalting equipment, using the method of electro dialysis. This high efficiency of the use of an adsorbent bed result from the use of small particles adsorbent "silica - alumina" to give high interfacial area and from the absence of

significant axial mixing of either phase (3,8). This is in contrast to the desalting equipment designed to obtain practically complete axial mixing in each physical element.

1.2 AIM OF THE RESEARCH WORK.

1. Mathematical modeling of a fixed simulated bed for desalting operation.
2. To determine the optimum depth of an adsorption column needed for a satisfactory adsorption of the adsorbate from the effluent stream.
3. Determine the best adsorbent for the operation of fixed simulated bed.
4. Derive an alternative and cheap processing method of desalting.
5. Encourage the use of mathematical modeling in areas in which design data are not sufficient or limited. Encourage the design and construction of adsorption equipment and laboratory prototypes.

1.2 LIMITATION OF EXISTING TECHNOLOGY

- 01 The quality of crude charged to the desalting will affect the desalting efficiency⁽⁹⁾
- 02 Normally light density (low) crude is relatively easy to desalt than the heavy (high) density crude oils.⁽⁹⁾

Reason

- 021 The differential density between the crude and H₂O is small⁽⁹⁾
- 022 Heavier tend to contain more naturally occurring emulsifier than do lighter ones.
- 023 Heavier crude's often contain more sulphur and hence more iron sulphide. Where iron sulphide is present, it is insoluble in both oil and water and tend to accumulate at the oil / H₂O interface.⁽⁹⁾
- 03 The presence of slope oil will typically contain high levels of metal additives from tube oils, sand, silt and a variety of other contaminants. As a result emulsion breaking is

often difficult to accomplish. The inclusion of slop naphtha in crude feeds containing asphaltic crude or heavy fuel oil can also give rise to desalting problems, notably dissolved effluent H₂O.

04 Raw crude quantity.

Since the desalting process is largely a physical and dynamic function, their velocity and residence time will affect performance. Though put changes will affect flow character. ⁽⁹⁾

05 The wash water obtained from the desalter is often of pH 5.7 range. The injection of caustic soda to raise the pH may results to severe desalter problem due to emulsion stabilization

CHAPTER TWO

2.0 LITERATURE SURVEY

2.1 HISTORICAL DEVELOPMENT OF ADSORBENTS (CARBON)

In the thirteenth century Macopolo found that the ashes of a certain wood UN – GUESS were used to refine sugar ⁽⁵⁴⁾ priestly ⁽⁵¹⁾ unknowingly produced a particularly activated carbon in his effort to increase the conducting power of carbon. ⁽¹¹⁾

According to vinlippman ⁽⁵⁴⁾ ill smelling wires were purified with wood charcoal by Transport in 1788.

In (1971) Fuller, Schats being and Nagy ^(55, 56) developed adsorbents from wood – dust and straw, used as floating adsorbents for oil removal in U.S.A Olaoye had in Netherlands, investigated as part of his M. Sc thesis, the production of adsorbents from maize cob rice husk, coconut husk and wood in 1977 ⁽¹⁰⁾ (these are all amorphous activated carbon adsorbent). In 1980 Bugaje. ⁽⁵¹⁾ Produced activated carbon from bagasse with a yield of 24% as a means of convertinsg industrial waste into usable raw material. In 1986 Odozi et al. ⁽¹²⁾ worked on corncob to be converted into adsorbent for the removal of hydrocarbon contaminant from rivers and stream during oil spillage.

In 1988 the production of activated carbon from coconut shells and activated clay from Benin was conducted by Hymore and Iyayi ⁽⁵⁸⁾.

In Nigeria, 1990 Mark Muse. A. did as extensive study on the development of locally available potential adsorbents. ⁽¹¹⁾

In November 1997, Obiora Okeke and A. A Osakwe Akofe presented paper during the proceedings of the 27th Annual conference of the Nigeria society of chemical Engineers in application and prospects for local sourcing of some available adsorbent ⁽¹³⁾. On the availability of sourcing locally made adsorbents, the stages of development and the sources needed were fully discoursed. The resources could be classified as ⁽¹³⁾.

- A Relevant manpower (expertise)
- B Equipment and related infrastructure
- C Raw materials
- D Fund

2.2 ADSORBENT OPTIMIZATION. ⁽¹³⁾

Laboratory development adsorbent need to be optimized to establish fully, the correlation defines during its developmental stages. This optimization encompasses. In physisorption. The process is reversible; a low concentration in the fluid will cover the surface of the adsorbent only up to the point when the pressure exerted by the adsorbed phase is equal to that in the fluid.

Given a sufficient concentration in the fluid, forces of physical adsorption may continue to have influence until several layers of molecules, perhaps five or six, have accumulated on the surface. If the surface exists in narrow pores. Then the maximum number of layers may be restricted by the dimensions of the pore itself. The forces in chemisorptions are more specific, the chemical attraction between the solid and molecules in the fluid occupied. Chemisorptions does not extend beyond the first layer, but it is then possible that additional physical adsorption will occur ⁽¹⁶⁾.

From available literature and materials the following can be deduced;

Adsorption is the mechanism, which the molecules of a fluid (gas, vapour or liquid) spontaneously concentrate at contacting surface without undergoing chemical reaction ⁽¹¹⁾.

The unit operation of adsorption is concerned with the separation of components from mixed system by utilizing this unique phenomenon ⁽¹⁹⁾. In this operation the contacting surface is called the " ADSORBENT" and the concentrated specie is called the "ADSORBATE"⁽¹⁹⁾.

Adsorption appears to take place as a result of unbalanced forces in a surface creating a force field in the immediate environment. Which attract and hold for a finite time the molecule of the contacting species. The residence time of the molecule on the surface is a direct function of the energy with which the molecule is held.

In practical terms, the adsorption energy determines the strength with which the molecule is adsorbed relative to the other molecule in the force field and therefore the efficiency by which the molecules can be separated. ⁽¹¹⁾

Adsorption is a unique unit operation in a number of respects. In some cases, the separation performed involves the accomplishment of literally hundreds of theoretical transfer units. In others, the nature of the adsorbent allows the highly specific and selective removal of one species from a mixture, based on difference in molecular size that would be practically impossible by other means.

Furthermore, purification involving the removal of contaminants from liquids can achieve essentially undetectable level of the contaminants in the product.

Adsorption as a unit operation has been developed relatively recently and the published literature offer little help to the engineer faced with a practical problem of designing a commercial unit.

2.3 MOVING BED PROCESS ⁽³⁾

Continuity of operation and the process advantages of counter current could theoretically be obtained in an adsorptive process by actually conveying the adsorbent through the system counter to the fluid stream. However, the physical movement of solids introduces problems, which tend to nullify the potential advantages of adsorption.

One obvious hazard is that of attrition of the adsorbent. Another basic difficulty is that of maintaining uniform plug flow of both phases over the entire cross – section of columns of large diameter. It would be most difficult to move a bed of solids uniformly down a

column of large diameter and to do this without creating packing, non uniformity down a column of large diameter and to do this without creating packing, non uniformity which would allow extensive channeling of the fluid phase.

The significance of the axial mixing that would be induced by non-uniform flow is shown by the following approximate equation

$$\frac{1}{n_a} = \frac{1}{n_p} + \frac{1}{n_m}$$

Where n_a = theoretical equivalent of actual bed

n_p = theoretical tray equivalent of bed in the absence of axial mixing

n_m = number of perfect mixers in series which would give axial dispersion equal to that existing.

The term n_p is governed by the mass – transfer coefficient and n_m by the flow pattern.

Since many adsorptive systems exhibit high mass – transfer rates and correspondingly high values of n_s , potential performance can be seriously degraded by modest degrees of axial mixing. Schemes have been proposed in which adsorbent is conveyed counter currently to process fluid in a series of fluidized beds. These suffer from the same limitation as trayed fractionators, namely. That n_m is substantially equal to the number of physical mixing elements in series and that n_a therefore cannot exceed the number regardless of the value of n_p .

Studies shows that, for flow of homogeneous fluids through stationary beds of densely packed, uniform impermeable spheres, the value of n_m is the order of the bed height divides by the particle diameter. This presumably sets an upper limit on the efficiency of an ideal packed bed. In practice, however, this limit cannot be approached because additional axial mixing is induced by such items as porosity of the particles, density and viscosity gradients in the fluid distribution, and the effect of obstructions such as bed – supporting structural elements.

Great care with respect to all these items is required to obtain high efficiency in beds of large diameter. ⁽³⁾

2.4 ROTARY FOR SIMULATED BEDS (MOVING)⁽³⁾

The rotary valve is a directing device for the liquid. It serves the same principle as multiport stop clock. At the right – side face of the valve, the four net streams to and from the process are continuously fed and withdrawn. From the left side of the valve, a number of lines are connected; these terminate in distributors within the adsorbent bed (29, 30, 31, 32, 33, 34)

2.5 DIFFICULTIES OF MOVING BED OPERATION ⁽³⁾

Continuity of operation and the process advantages of counter current could theoretically be obtained in an adsorptive process by actually moving or conveying the adsorbent through the system counter to the fluid stream.

However, the physical movement of solids introduces problems which tend to nullify the potential advantages of adsorption.

- (a) Available adsorbent were not strong enough to resist the abraission that would be encountered in a moving bed.
- (b) Another obvious problem was that of obtaining uniform flow of both liquid and solid phases in a moving – bed operation.
- (c) In addition, it was anticipated that an attempt to move the bed would lead to non- uniformity in packing, which would lead to channeling of the liquid.

2.6 SIMULATED MOVING BED⁽³⁾

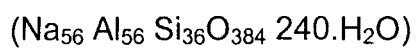
In view of these difficulties, a flow scheme has been devised which maintains the process features of continuous counter current flow of liquid and solid without actual

movement of the solid. Although commercial separation do not use an actual moving bed, the action taking place is most easily visualized in terms of a hypothetical moving – bed operation.

In the moving bed system, solid in moving continuously in a closed circuit part fixed positions of introduction and withdrawal of liquid. The same process results can be obtained by holding the bed stationary and periodically moving the positions at which the various streams enter and leave. A shift in the positions of liquid feed and withdrawal, in the direction of fluid flow through the bed, stimulates the movement of solid in the opposite direction. It is, of course, impossible to move the liquid feed and withdrawal points continuously. However, approximately the same effect can be produced by providing multiple liquid access lines to the bed and periodically switching each net streams to the next adjacent line. In this concept, the adsorbent is maintained as a stationary bed. A liquid circulating pump is provided to pump liquid from the bottom outlet to the top inlet of the adsorbent chamber. Functionally, the adsorbent bed has no top or bottom; it is equivalent to an annular bed. Therefore, the four liquid access positions can be moved around the bed continuously, always the same distance between the various net streams. To complete the simulation the liquid velocity relative to the vessel wall must be higher

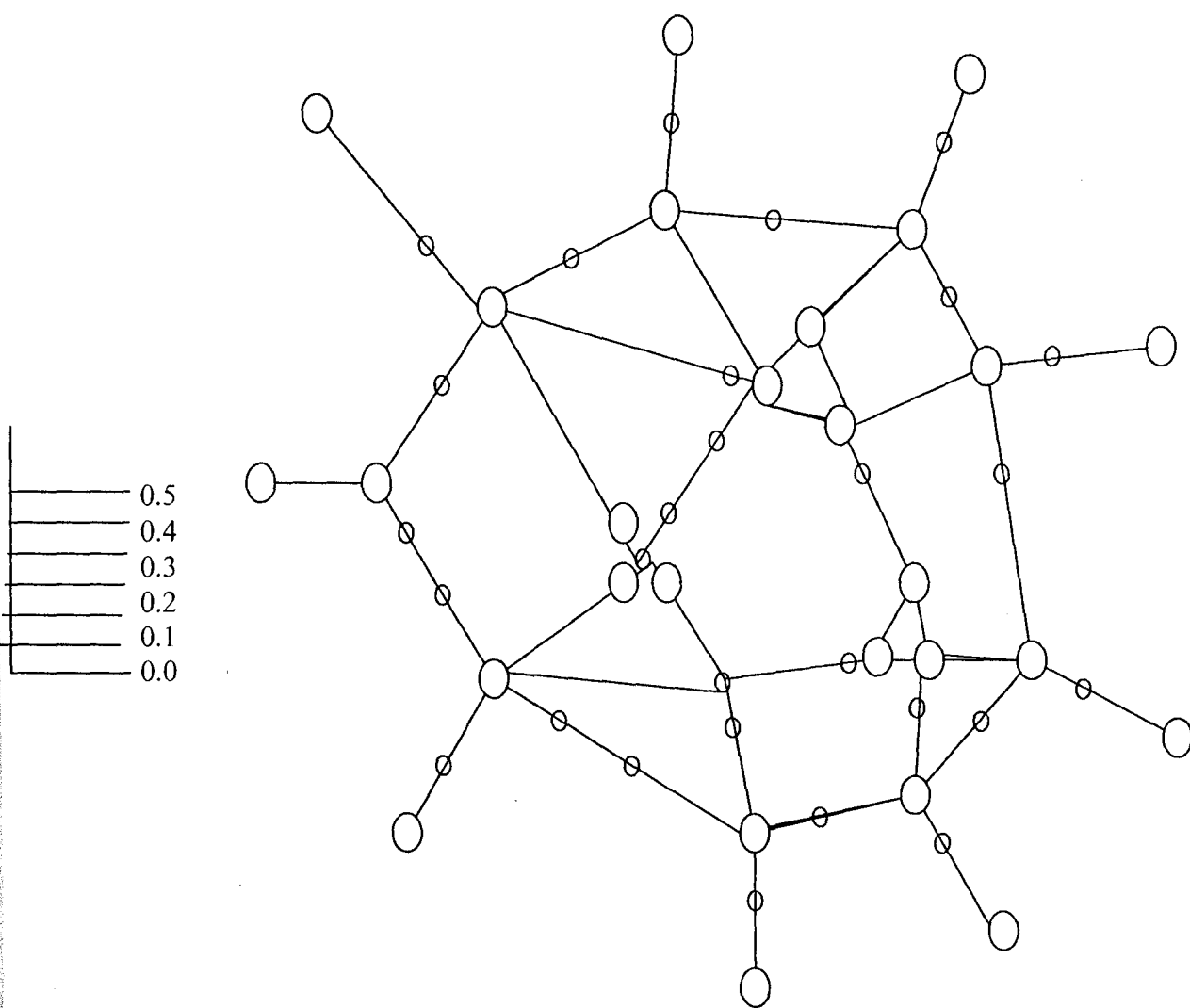
2.7 DESCRIPTION OF HYDROPHILIC ADSORBENTS (16)s

A CUBO - OCTAHEDRAL UNIT COMPOSED OF SiO_4 AND AlO_4 TETRAHEDRA (24)



○ = Si or Al

○ = oxygen



CHAPTER THREE

3.0 THE RATIONAL FOR MATHEMATICAL MODELLING

1. A model is nothing more than mathematical abstraction of a real process. The equation or sets of equations that comprise the model are best an approximation to the true process. Hence, the model cannot incorporate all of the features, both macroscopic and microscopic of the real process. The engineer normally must seek a compromise involving the cost of obtaining the model, that is, the time and effort required to obtain and verify it. These considerations are related to the level of physical and chemical details in the model and the expected benefits to be derived from its use. The model accuracy necessary is intertwined in this compromise and the ultimate use of model influences how accurate it needs to be. The importance of mathematical modelling of a process are explain as follows:

2. To improve understanding of the process: - process model can be analysed or used in a computer simulation of the process to investigate process behaviour without the expense and perhaps, without the unexpected hazard of operating the real process

This approach is necessary when it is not feasible to perform dynamic experiments in the plant or before the plant is actually constructed.

3. To train plant-operating personnel: - plant operator can be trained to operate a complex process and to deal with emergency situation by use of process simulator. By interfacing a process simulate to standard process control equipment, a realistic environment can be created for operator training without the cost or exposure to dangerous conditions that might exist in a real plant situation.

4. To design the control strategy for a new process: - A process model allow alternative control strategies to be evaluated such as, for example, the selection of the variables that are to be measured (controlled) and those that are to be manipulated. With more complicated processes or with new processes for which we have little operating experience, the design of an appropriate control strategy seldom is straightforward.
5. To select controller settings. A dynamic model of the process may be used to develop appropriate controller settings, either via computer simulation or by direct analysis of the dynamic model. Prior to start-up of a new process, it is desirable to have reasonable estimates of the controller settings.

For some operating processes, it may not be feasible to perform experiments that would lead to better controller settings.
6. To design the control law: a Modern control technique often incorporates a process model into the control law. Such techniques are called model – predictive or model-based control.
7. To optimise process-operating conditions: In most processing plants there is an incentive to adjust operating conditions periodically so that the plant maximizes profits and minimizes costs. A steady state model of the process and appropriate economic information can be used to determine the most profitable process conditions as in supervisory control. (Serborg et al. 1989)

3.1 DEVELOPMENT OF A PROCESS MATHEMATICAL MODEL

Because models account more completely for what is happening in a process, fundamental model based on mass and energy balance offers better accuracy and greater insight than do regression models. Thus they are of greater

value in improving process yield or through put or in debottled necking and optimising. Fundamentals models may be in existence for a long time without being used because they involved a lot of calculations and are considered difficult to develop. However, today a calculation can be done quickly and conveniently, at low cost, using an advanced computer having an arithmetic coprocessor and some graphics capability. As for building the model, there is a systematic hand-on approach that will ease the perceived development difficulties.

A model, can be developed by fitting a set of equations to actual plant or pilot plant data, and the range of these data is the range over which the model can be used.

For this reason, it is important to have data that covers a fairly wide range of steady state process conditions.

In a pilot plant, such data can be collected by systematic experimentation. The experiment designed should explored high, average and low values for each of the principal process variables. Such a range of data can also be found in plant operating history. Overall, ten to twenty steady state data sets may be required.

The kind of data needed to develop a mathematical model are those that define the material and energy balances around the equipment i.e., the pressure, temperature and composition of feed and product streams etc. The three major steps for building models are as follows: the first step is to develop a process flow diagram for the process. Next, is to develop a set of material and energy balance equations for the systems or around the equipment being considered and the third step is to fit the model to the data by adjusting the parameters. For large number of parameters, this step involves a number of iterations and must be done with the help of a computer. If the Mathematical model is accurate and more useful than any single material balance being written, it can be used to predict the behaviour

of the process under different conditions. Then it can be used for process optimisation, supervisory control, debottlenecking and dynamic analysis.

Obviously, success in any of these areas can pay for the mathematical model development in a very short time. (Wansbrough. 1985)

3.2 PRIMARY MATHEMATICAL MODELING OF A FIXED SIMULATED BED FOR THE REMOVAL OF SALTS (DESALTING) FROM CRUDE OIL INTRODUCTION; (SEMI – IMPERICAL MODEL)

The mathematics of adsorption in beds i.e. the adsorption of solute from liquids on the surface of solids is either diffusion control or kinetic control. There is a fundamental difference in the mathematical analysis, depending upon whether one assumes that equilibrium obtains or whether one assumes a kinetic approach of some sort. In the first case the basic problem of a first order partial differential equation. Since the definition of linearity for first order equations is somewhat more fearer, that, it is for second order equation from available theorem, the solution to first order term is obtained for general Isotherms. This problem has been considered for possible alternatives by various researchers. For the second order case the solution is not as simple and the solution only for special cases can be solved analytically.

In finding a solution to the problem of desalting in simulated fixed bed we start thus;

Let us assumed we have an adsorbent bed of depth (or height) are measured as;

- 1 Concentration in moles of a adsorbate (salts) per unit volume of solution in the crude streams be c ;
- 2 Amount of adsorbate in moles (salts) per unit volume of solution in the bed be n ;
- 3 Volume of the adsorbent bed be v ;

4 Where α fractional void volume of bed

5 Where t is the time taken for the adsorbent bed; in the primary mathematical modeling.

Then on, considering an elemental thickness of bed Δz , we obtain the equation (see Klotz (6))

$$v \frac{\partial c}{\partial t} + \frac{\partial c}{\partial t} + \frac{1}{\alpha} \frac{\partial n}{\partial t} = 0 \dots \dots \dots (I)$$

Considering that of the local rate of removal in the bed was governed by

$$\frac{1}{\alpha} \frac{\partial n}{\partial t} = kc(N_0 - n) \dots \dots \dots (II)$$

where N_0 is the saturation capacity of the bed and K is the velocity constant.

Based in the assumption in the model, we require a redistribution of the velocity constant K_1 and K_2

The complete statement of the problem is:

$$v \frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} + \frac{1}{\alpha} \frac{\partial n}{\partial t} = 0 \dots \dots \dots (I)$$

for local rate of removal adsorbate in the bed

$$\frac{1}{\alpha} \frac{\partial n}{\partial t} = kc(N_0 - n) \dots \dots \dots (ii)$$

$$v \frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} + \frac{1}{\alpha} \frac{\partial n}{\partial t} = 0 \dots \dots \dots (I)$$

$$\frac{1}{\alpha} \frac{\partial n}{\partial t} = k_1 c - k_2 n \dots \dots \dots (ii)$$

$$c(z, t) = c_0(t) \text{ where } z = 0 \dots \dots \dots (iv)$$

$$n(z, t) = n_0(z) \text{ where } z \leq \frac{z}{v} \dots \dots \dots (v)$$

changes of variables results

$$x = \frac{z}{v} \text{ and } y = \alpha(t - \frac{z}{v})$$

the equation (i), (ii), (iv) & (v) becomes :

$$\frac{\partial n}{\partial y} + \frac{\partial c}{\partial n} = 0 \text{-----(vi)}$$

$$\frac{\partial n}{2y} = k_1 c - k_2 n \text{-----(vii)}$$

$$c(z, t) = c_0(y, 0) = c_1(y) \text{ when } x = 0 \text{-----(ix)}$$

$$n(z, t) = n_0(v, x) = n_1(x) \text{ when } y = 0 \text{-----(x)}$$

and hence exist a function $f(x, y)$

such that $\partial f(x, y) = n \partial x - c \partial y$

$$n = \frac{\partial f}{\partial x} \text{ and } c = -\frac{\partial f}{\partial y} \text{-----(x)}$$

utilizing this fact it follows from equation (vii), becomes :

$$\frac{\partial^2 f}{\partial x \partial y} + k_1 \frac{\partial f}{\partial y} + k_2 \frac{\partial f}{\partial x} = 0 \text{-----(xi)}$$

by changes of variable (re-arrangement of expression starting with known values

of k_1, k_2, n_0, c_0 to get $n_1(x)$ and $c_1(y)$

It is well known that the change of dependent variable

$$f(x, y) = \ell^{-K_1 z - K_2 y} \phi(x, y) \text{-----(xii)}$$

equation (ii) reduces to;

$$\frac{\partial^2 \phi}{\partial x \partial y} - K_1 K_2 \phi(x, y) = 0 \text{-----(xiii)}$$

If we combine (x) and (xii) with equation (viii) and (ix)

We obtain;

$$n_1(x) = -k_1 \ell^{-K_1 x} \phi(x, 0) + \ell^{-K_1 x} \frac{\partial \psi(x, 0)}{\partial x}$$

$$-c_1(y) = -k_2 \ell^{K_2 y} \phi(0, y) + \ell^{K_2 y} \frac{\partial \phi(0, y)}{\partial y}$$

$$\phi(x, 0) = \ell^{K_1 x} \int_0^x n_1(\xi) d\xi = f(x) \dots \dots \dots (xiv)$$

$$\phi(x, 0) = \ell^{K_1 x} \int_0^x n_0 dx \dots \dots \dots (xv)$$

$$\phi(0, y) = \ell^{-K_2 y} \int_0^y c_1(\Gamma) d\Gamma = g(y) \dots \dots \dots (xvi)$$

$$\phi(0, y) = \ell^{-K_2 y} \int_0^y c_0 dy \dots \dots \dots (xvii)$$

$$n_1(x) = -k_2 \ell^{-K_1 x} \ell^{K_1 x} \int_0^x n_0 dx + \ell^{-K_1 x} \frac{\partial \phi(x, 0)}{\partial x} \dots \dots \dots (xix)$$

$$-c_1(y) = -k_2 \ell^{-K_2 y} \ell^{-K_2 y} \int_0^y c_0 dy + \ell^{-K_2 y} \frac{\partial \phi(0, y)}{\partial y} \dots \dots \dots (xx)$$

starting with known values of K_1, K_2, n_0, c_0 to get $n_1(x)$ and $c_1(y)$

$$n_1(x) = -K_1 \ell^{-K_1 x} \ell^{K_1 x} \int_0^x n_0 \partial n + \ell^{-K_1 x} \partial \left(\frac{\ell^{K_1 x} \int_0^x n_0 \partial n +}{\partial x} \right) \dots \dots \dots (xxi)$$

$$-c_1(y) = -K_2 \ell^{-K_2 y} \ell^{-K_2 y} \int_0^y c_0 dy + \ell^{-K_2 y} \partial \left(\frac{\ell^{-K_2 y} \int_0^y c_0 dy}{dy} \right) \dots \dots \dots (xxii)$$

$$n_1(x) = -K_1 \int n_0 dx + \ell^{-K_1 x} \partial \left(\frac{\ell^{K_1 x} \int_0^x n_0 \partial n +}{\partial x} \right) \dots \dots \dots (xxi)$$

$$-c_1(y) = -K_2 \ell^{-2K_2 y} \int_0^y c_0 dy + \ell^{-K_2 y} \partial \left(\frac{\ell^{-K_2 y} \int_0^y c_0 dy}{dy} \right) \dots \dots \dots (xxii)$$

By rearrangement :

(xxi) becomes;

$$n_1(x) = -K_1 n_0 \int_0^x dx + \ell^{-K_1 x} \partial \left(\frac{\ell^{K_1 x} \int_0^x n_0 \partial n +}{\partial x} \right) \dots \dots \dots (***)$$

(xxii) becomes;

$$-c_1(y) = -K_2 \ell^{-2K_2 y} c_0 \int_0^y dy + \ell^{-K_2 y} \partial \left(\frac{\ell^{-2K_2 y} c_0 \int_0^y dy}{dy} \right) \dots \dots \dots (***)$$

$$-c_1(y) = -k_2 \ell^{K_2 y} \phi(0, y) + \ell^{K_2 y} \frac{\partial \phi(0, y)}{\partial y}$$

$$\phi(x, 0) = \ell^{K_1 x} \int_0^x n_1(\xi) d\xi = f(x) \dots \dots \dots (xiv)$$

$$\phi(x, 0) = \ell^{K_1 x} \int_0^x n_0 dx \dots \dots \dots (xv)$$

$$\phi(0, y) = \ell^{-K_2 y} \int_0^y c_1(\Gamma) d\Gamma = g(y) \dots \dots \dots (xvi)$$

$$\phi(0, y) = \ell^{-K_2 y} \int_0^y c_0 dy \dots \dots \dots (xvii)$$

$$n_1(x) = -k_2 \ell^{-K_1 x} \ell^{K_1 x} \int_0^x n_0 dx + \ell^{-K_1 x} \frac{\partial \phi(x, 0)}{\partial x} \dots \dots \dots (xix)$$

$$-c_1(y) = -k_2 \ell^{-K_2 y} \ell^{-K_2 y} \int_0^y c_0 dy + \ell^{-K_2 y} \frac{\partial \phi(0, y)}{\partial y} \dots \dots \dots (xx)$$

starting with known values of K_1, K_2, n_0, c_0 to get $n_1(x)$ and $c_1(y)$

$$n_1(x) = -K_1 \ell^{-K_1 x} \ell^{K_1 x} \int_0^x n_0 \partial n + \ell^{-K_1 x} \partial \left(\frac{\ell^{K_1 x} \int_0^x n_0 \partial n +}{\partial x} \right) \dots \dots \dots (xxi)$$

$$-c_1(y) = -K_2 \ell^{-K_2 y} \ell^{-K_2 y} \int_0^y c_0 dy + \ell^{-K_2 y} \partial \left(\frac{\ell^{-K_2 y} \int_0^y c_0 dy}{dy} \right) \dots \dots \dots (xxii)$$

$$n_1(x) = -K_1 \int_0^x n_0 dx + \ell^{-K_1 x} \partial \left(\frac{\ell^{K_1 x} \int_0^x n_0 \partial n +}{\partial x} \right) \dots \dots \dots (xxi)$$

$$-c_1(y) = -K_2 \ell^{-2K_2 y} \int_0^y c_0 dy + \ell^{-K_2 y} \partial \left(\frac{\ell^{-K_2 y} \int_0^y c_0 dy}{dy} \right) \dots \dots \dots (xxii)$$

By rearrangement :

(xxi) becomes;

$$n_1(x) = -K_1 n_0 \int_0^x dx + \ell^{-K_1 x} \partial \left(\frac{\ell^{K_1 x} \int_0^x n_0 \partial n +}{\partial x} \right) \dots \dots \dots (***)$$

(xxii) becomes;

$$-c_1(y) = -K_2 \ell^{-2K_2 y} c_0 \int_0^y dy + \ell^{-K_2 y} \partial \left(\frac{\ell^{-2K_2 y} c_0 \int_0^y dy}{dy} \right) \dots \dots \dots (***)$$

CHAPTER FOUR

4.0 EXPERIMENTAL MATERIAL

Prototype of a fixed simulated bed for carrying out the desalting operation, the equipment is made up of an inlet stream, an outlet stream, a rotary device called multi port stopcock.

- 1 Nigerian crude oil is used as the feedstock for the desalting operation. (Napthalene base or intermediate base) (key quality 31.10 and $AP1^0=20.33$)
- 2 Flow rate meter; for measuring the flow rate of the crude oil.
- 3 Electric weighing balance; to measure the weight of the adsorbent used and other materials used
- 4 Measuring cylinder for measuring the volume of the catalyst.
- 5 Beakers and bottles as containers for various crude oil samples.
- 6 Adsorbent made up of Silica – Alumina .

4.1 PROCEDURE OF EXPERIMENT

The simulated bed is set and the crude oil passed through the bed at a controlled temperature and pressure close to atmospheric condition. From the samples obtained a recorded value of concentration changes with the depth of the bed is recorded as follows.

TOPIC: Mathematical modeling of a fixed simulated bed for desalting operation

OBJECTIVE

- 1 To develop a mathematical model that can be used to predict the amount of adsorbate in moles per unit volume of solution in the bed and also the concentration in moles of the adsorbate per unit volume of solution in the crude stream.

- 2 To determine the most suitable adsorbent (hydrophilic) with the best selectivity, activity and stability for used in the simulated fixed bed.
- 3 To determine the optimum depth (height) of the adsorption columns (bed), needed for satisfactory adsorption operation in the simulated system.
- 4 Provision of design materials and condition needed for the smooth operation of a simulated fixed bed and its design.

CHAPTER FIVE

5.0 EXPERIMENTAL RESULTS

5.1 SIMULATED GRAPH FOR AMOUNT ADSORBATE WITH BED DEPTH

5.2 SIMULATED GRAPH FOR CONCENTRATION OF ADSORBATE WITH THE BED DEPTH

5.3 GRAPHICAL RESULT COMPARISON

EXPERIMENTAL RESULT OF A FIXED SIMULATED BED FOR THE REMOVAL OF SALTS FROM NIGERIA CRUDE OIL

Y	CA	K
1	10.685	1.682
2	9.538	1.682
3	8.614	1.682
4	7.853	1.682
5	7.215	1.682
6	6.674	1.682
7	6.208	1.682
8	5.802	1.682
9	5.447	1.682
10	5.132	1.682
11	4.852	1.682
12	4.601	1.682
13	4.374	1.682
14	4.169	1.682

Table 1.0

TABLE OF SIMULATED RESULT OF AMOUNT OF ADSORBATE

x	n1	K1	n0
1	2.08	2.085	2.1
1.000001	2.0800021	2.085	2.1
1.0003475	2.0807298	2.085	2.1
1.1043475	2.2991298	2.085	2.1
1.2083475	2.5175298	2.085	2.1
1.3123475	2.7359298	2.085	2.1
1.4163475	2.9543298	2.085	2.1
1.5203475	3.1727298	2.085	2.1
1.6243475	3.3911298	2.085	2.1
1.7283475	3.6095298	2.085	2.1
1.8323475	3.8279298	2.085	2.1
1.9363475	4.0463298	2.085	2.1
2.0403475	4.2647298	2.085	2.1
2.1443475	4.4831298	2.085	2.1
2.2483475	4.7015298	2.085	2.1
2.3523475	4.9199298	2.085	2.1
2.4563475	5.1383298	2.085	2.1
2.5603475	5.3567298	2.085	2.1
2.6643475	5.5751298	2.085	2.1
2.7683475	5.7935298	2.085	2.1
2.8723475	6.0119298	2.085	2.1
2.9763475	6.2303298	2.085	2.1
3.0803475	6.4487298	2.085	2.1
3.1843475	6.6671298	2.085	2.1
3.2883475	6.8855298	2.085	2.1
3.3923475	7.1039298	2.085	2.1
3.6003475	7.5407298	2.085	2.1

3.7043475	7.7591298	2.085	2.1
3.8083475	7.9775298	2.085	2.1
3.9123475	8.1959298	2.085	2.1
4.1203475	8.6327298	2.085	2.1
4.2243475	8.8511298	2.085	2.1
4.3283475	9.0695298	2.085	2.1
4.4323475	9.2879298	2.085	2.1
4.6403475	9.7247298	2.085	2.1
4.7443475	9.9431298	2.085	2.1
4.8483475	10.16153	2.085	2.1
4.9523475	10.37993	2.085	2.1
5.1603475	10.81673	2.085	2.1
5.2643475	11.03513	2.085	2.1
5.3683475	11.25353	2.085	2.1
5.4723475	11.47193	2.085	2.1
5.6803475	11.90873	2.085	2.1
5.7843475	12.12713	2.085	2.1
5.8883475	12.34553	2.085	2.1
5.9923475	12.56393	2.085	2.1
6.2003475	13.00073	2.085	2.1
6.3043475	13.21913	2.085	2.1
6.4083475	13.43753	2.085	2.1
6.5123475	13.65593	2.085	2.1
6.7203475	14.09273	2.085	2.1
6.8243475	14.31113	2.085	2.1
6.9283475	14.52953	2.085	2.1
7.0323475	14.74793	2.085	2.1
7.2403475	15.18473	2.085	2.1
7.3443475	15.40313	2.085	2.1
7.4483475	15.62153	2.085	2.1
7.5523475	15.83993	2.085	2.1

7.7603475	16.27673	2.085	2.1
7.8643475	16.49513	2.085	2.1
7.9683475	16.71353	2.085	2.1
8.0723475	16.93193	2.085	2.1
8.2803475	17.36873	2.085	2.1
8.3843475	17.58713	2.085	2.1
8.4883475	17.80553	2.085	2.1
8.5923475	18.02393	2.085	2.1
8.8003475	18.46073	2.085	2.1
8.9043475	18.67913	2.085	2.1
9.0083475	18.89753	2.085	2.1
9.1123475	19.11593	2.085	2.1
9.3203475	19.55273	2.085	2.1
9.4243475	19.77113	2.085	2.1
9.5283475	19.98953	2.085	2.1
9.6323475	20.20793	2.085	2.1
9.8403475	20.64473	2.085	2.1
9.9443475	20.86313	2.085	2.1
10.048348	21.08153	2.085	2.1
10.152348	21.29993	2.085	2.1
10.360348	21.73673	2.085	2.1
10.464348	21.95513	2.085	2.1
10.568348	22.17353	2.085	2.1
10.672348	22.39193	2.085	2.1
10.880348	22.82873	2.085	2.1
10.984348	23.04713	2.085	2.1
11.088348	23.26553	2.085	2.1
11.192348	23.48393	2.085	2.1
11.400348	23.92073	2.085	2.1
11.504348	24.13913	2.085	2.1
11.608348	24.35753	2.085	2.1

11.712348	24.57593	2.085	2.1
11.920348	25.01273	2.085	2.1
12.024348	25.23113	2.085	2.1
12.128348	25.44953	2.085	2.1
12.232348	25.66793	2.085	2.1
12.440348	26.10473	2.085	2.1
12.544348	26.32313	2.085	2.1
12.648348	26.54153	2.085	2.1
12.752348	26.75993	2.085	2.1
12.960348	27.19673	2.085	2.1
13.064348	27.41513	2.085	2.1
13.168348	27.63353	2.085	2.1
13.272348	27.85193	2.085	2.1
13.480348	28.28873	2.085	2.1
13.584348	28.50713	2.085	2.1
13.688348	28.72553	2.085	2.1
13.792348	28.94393	2.085	2.1
14	29.38	2.085	2.1

Table 1.1 showing the amount of adsorbate with increase in bed depth at a constant k.

POLYMATH Results

No Title 12-25-2001, Rev5.1.228

Calculated values of the DEQ variables

<u>Variable</u>	<u>initial value</u>	<u>minimal value</u>	<u>maximal value</u>	<u>final value</u>
y	0	0	14	14
C1	10.685	2.483104	10.685	2.483104
K2	1.618	1.618	1.618	1.618
C0	10.685	10.685	10.685	10.685

ODE Report (RKF45)

Differential equations as entered by the user

$$[1] \frac{d(C1)}{d(y)} = -K2 \cdot \exp(-2 \cdot K2 \cdot y) \cdot C0 \cdot y + \exp(-K2 \cdot y) \cdot \exp((-K2 \cdot y) \cdot C0) + C0 \cdot y \cdot (-K2) \cdot \exp(-K2 \cdot y)$$

Explicit equations as entered by the user

$$[1] K2 = 1.618$$

$$[2] C0 = 10.685$$

Comments

$$[1] \frac{d(C1)}{d(y)} = -K2 \cdot \exp(-2 \cdot K2 \cdot y) \cdot C0 \cdot y + \exp(-K2 \cdot y) \cdot \exp((-K2 \cdot y) \cdot C0) + C0 \cdot y \cdot (-K2) \cdot \exp(-K2 \cdot y)$$

Change in concentration of the adsorbate across the depth of the bed

$$[2] K2 = 1.618$$

Velocity constant

$$[3] C0 = 10.685$$

Initial concentration of the adsorbate in the fluid stream

Independent variable

variable name : y

initial value : 0

final value : 14

Precision

Step size guess. h = 0.000001

Truncation error tolerance. eps = 0.000001

General

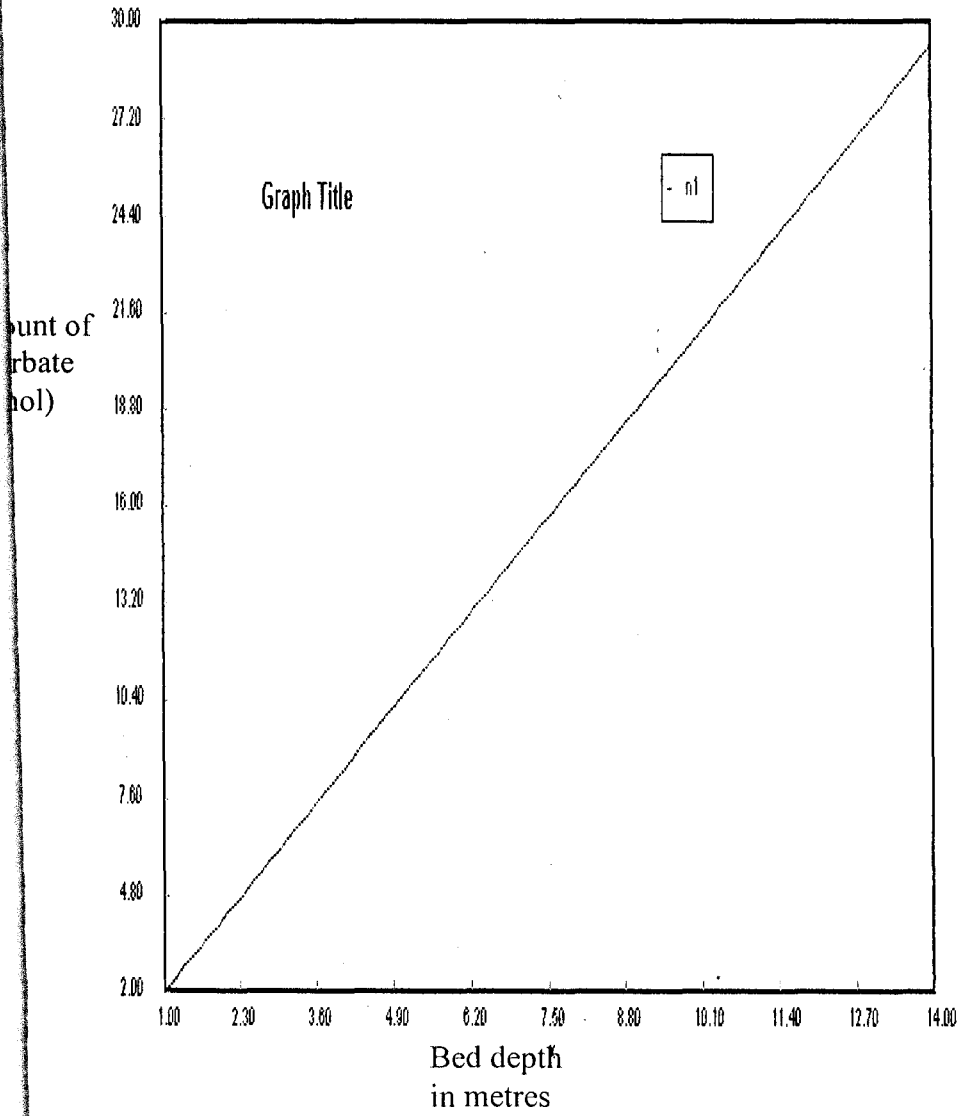
number of differential equations: 1

number of explicit equations: 2

Data file: D:\Documents and Settings\Administrator.LEADTECH\My

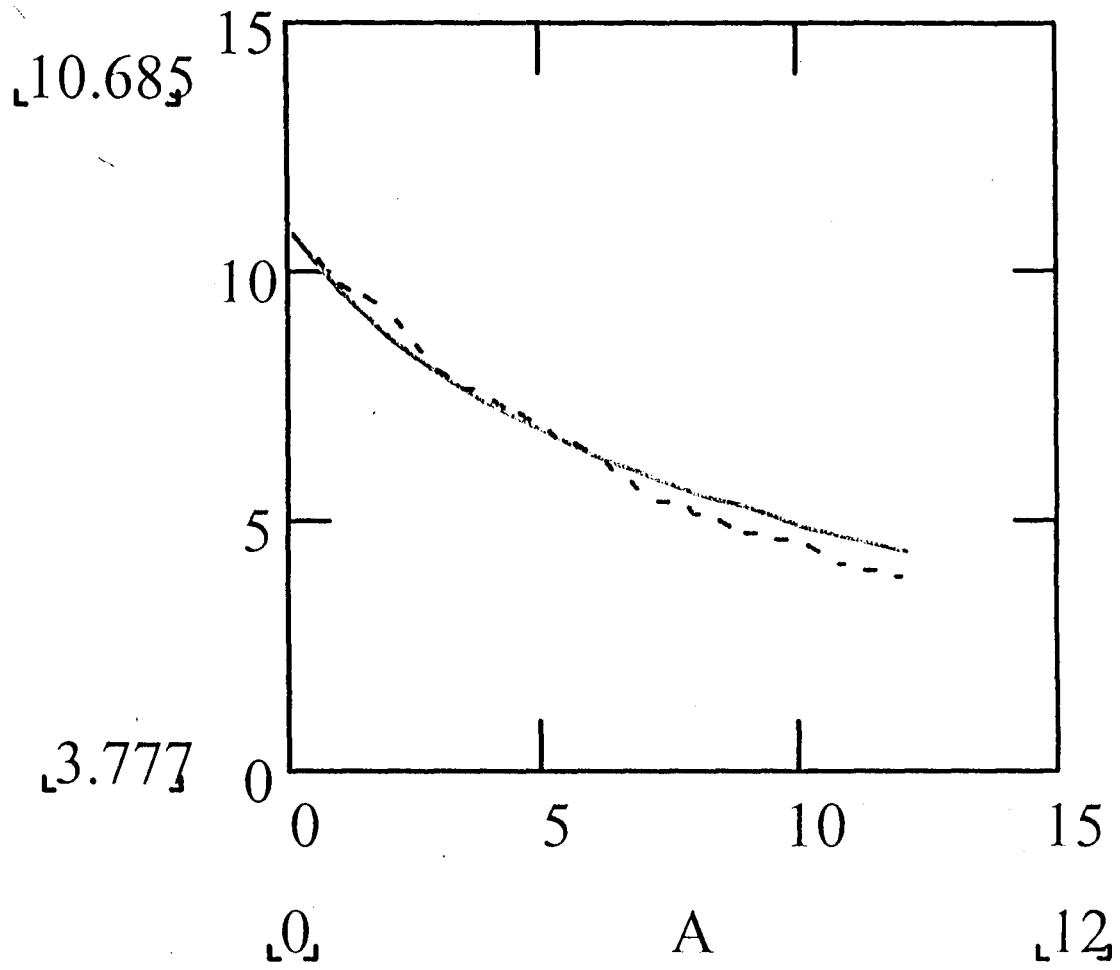
Documents\Ahmad's simulation.pol

A GRAPH OF AMOUNT OF ADSORBATE WITH DEPTH



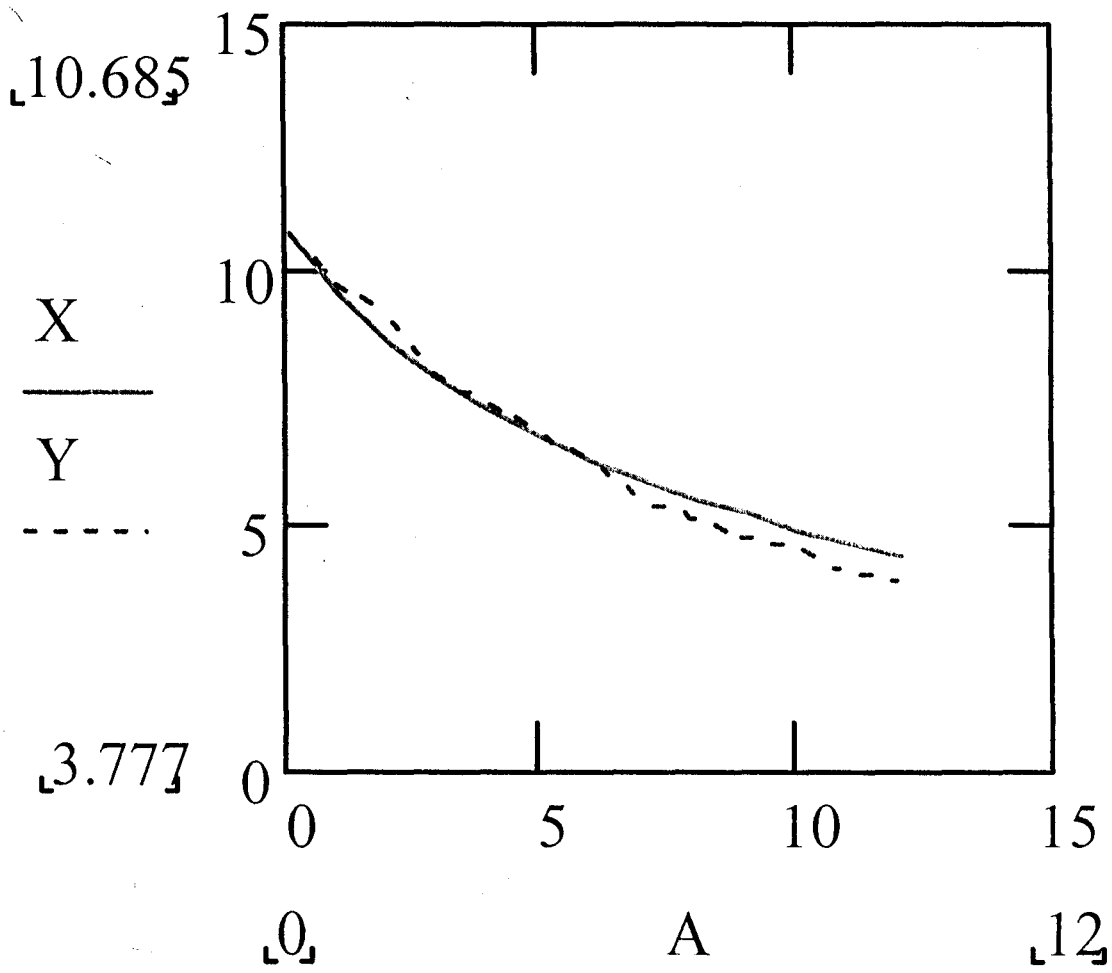
GRAPH 1.10a

GRAPH OF COMPARISON OF SIMULATED AND EXPERIMENTAL RESULT.



KEY
 X = experimental result ———
 Y = simulated result - - -
 A = bed depth

GRAPH OF COMPARISON OF SIMULATED AND EXPERIMENTAL RESULT.



KEY
X = experimental result
Y = simulated result
A = bed depth

CHAPTER SIX

6.0 DISCUSSION OF RESULTS

From the experimental results and the simulated result, the results of both experiments were analyzed:

- (I) From the table (1.10) the amount of adsorbate in the bed in the bed increases as the depths of adsorption increases to a maximum value about 29.38k mol/m^3
- (II) From table (1.20) the concentration of adsorbate in the fluid stream decreases until it reaches a minimum value of 2.483104k mol/m^3 ...
- (III) A comparison of the graph of the experimental and simulated results, show that the model is acceptable within the experimental limitation.
- (IV) The result obtained from the table(1.10) and graph 1.10a. show that the concentration of the adsorbate in the fluid stream remain practically constant at a height of approximately 14m.

From the experimental and simulated result,the following can be deduced;

- (1) The mount of adsorbate in the bed increases with depth
- (2) The concentration of adsorbate in the effluent stream decrease with depth until a minimum value of 2.483104kmol/ m^3 which it remain fairly constant
- (3) The depth of the bed was optimum at 5.60m

6.1 CONCLUSION

Based on the experimental and the results of the simulated bed modeling results, the following conclusion can be drawn from the project.

1. The model is fairly satisfactory since the results obtained agreed with the experiment.
2. The model was able to determine the amount of adsorbate present in the bed and the concentration of adsorbate.
3. The model results recorded [$r = +0.8$] compared with the experimental results.

6.2 RECOMMENDATION

1. The kinetics of the desalting of crude oil by adsorption using a fixed simulated bed should be carried out, in order to know the viability of the process and its economic implication.
2. In view of the colossal importance of the desalting operation in the upstream petroleum industry and to the growth of the Nigerian economy .It is imperative, to recommend that the oil industry and the government, with combined effort of the academia should intensify efforts in the research in this area of crude oil pretreatment to avoid the electro dialysis and its subsequent replacement with the adsorptive technology. These is possible, through joint research effort, adequate financing by the oil industry and the government.
3. Furthermore, development of more active adsorbent should be embarked upon, that can carry out the same operation with less severity of operating condition and accelerate the wide acceptance of the fixed simulated bed, ahead of other desalting method i.e. electro dialysis.

APPENDIX

V = volume of the adsorbate bed (dm^3)

α = fractional adsorbate oil volume of bed

n = adsorbate amount in moles (salts) per unit volume of solution (kgmoles)

C = concentration in moles of adsorbate (salt) per unit volume of solution in the crude stream (kgmol/dm^3)

C_0 = initial value of c .

n_0 = initial value of n

k_1 = velocity constant

t = time taken in (sec)

$n_1(x)$ = changes of n with depth

$-c_1(y)$ = changes of c with depth.

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