

Simulation of Low-Concentration Heavy Metal Removal from Industrial Effluents with a Bulk Liquid Membrane Using MATLAB

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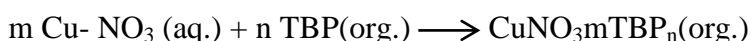
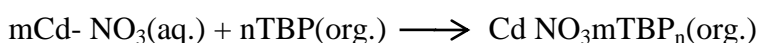
Abstract: Mathematical models have been observed and utilized in many sciences, especially in engineering. They are used to simulate various processes in many chemical engineering sciences. In general, the determination of kinetic parameters for the transports of a bulk liquid membrane process is important because it supplies basic information for the system. Mathematical modeling is simple and easily achievable without the need for a practical experimental system, and therefore, it has attracted growing attention in recent decades. This paper describes the kinetics of transport mechanisms of heavy metals, and a mathematical model explains the behavior of bulk liquid membrane. A simulation has made on the results of practical experiments, but with wider limits, and a control system was built in a fuzzy logic control method, design and programming a software interface (Zainab_gui) that includes the process of separating heavy metals by bulk liquid membrane and includes all the variables that affect the separation by using MATLAB.

Keywords: fuzzy logic, Kinetic Parameters, Mathematical model, Transports, Bulk Liquid Membrane Process.

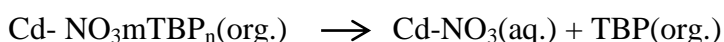
Introduction

The transport mechanisms related to Cd and Cu ions from the feed to the strip phases, TBP's role and stepwise explanation regarding the process has been exhibited in figure (1). The following stages demonstrate the entire procedure:

TBP is coupled to a metal ion at interface I to form a complex of metal.



- In the process starting from (interface I) to (interface II), the diffuses of complex of metal across the membrane.
- TBP is recreated when the Metal-complex breaks off at interface II.



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➤ Through the membrane, TBP returns to interface I.

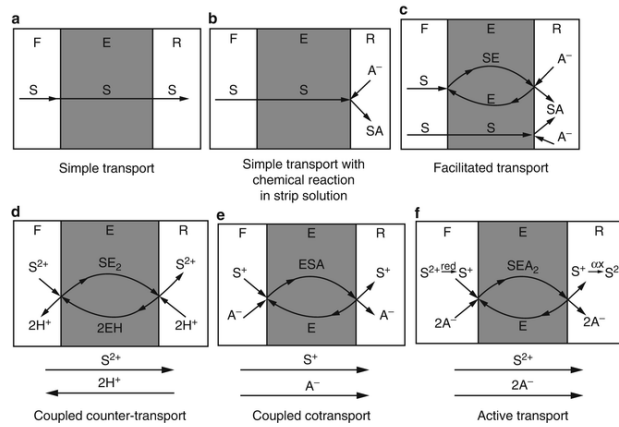
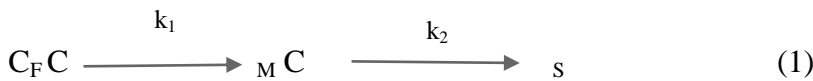


Figure 1: Transport mechanisms.

This mechanism will be adopted to the extraction of copper or cadmium ion compounds from the feed solution by the bulk liquid/ membrane phase and the subsequent stripping by the aqueous solution, and can be approximated by the mechanism of two consecutive unimolecular irreversible reactions type (first order reaction) (Nabieyan et al., 2007), (Muthuraman, et al., 2009), (Leóna & Guzmánb, 2010), (Muthuraman & Ibrahim, 2013) and (Hameed, 2015).



Where C_F : is used to express the concentration of solute in the feed stage.

C_M : is used to express the concentration of solute in the membrane phase.

C_S : During the stripping step, the concentration of the solute is measured.

k_1, k_2 : For solute extraction and stripping extraction operations, is the apparent first-order constant.

The hyperlink between the solute concentrations in quite a several phases is necessary for theoretical concerns:

$$C_F + C_M + C_S = C_0 \quad (2)$$

C_0 is the concentration of solutes at the start of the feeding period.

The rate of change in solute concentration in different phases is calculated using equation (1):

$$\frac{dC_F}{dt} = -k_1 C_F \quad (3)$$

$$\frac{dC_M}{dt} = k_1 C_F - k_2 C_M \quad (4)$$

$$\frac{dC_S}{dt} = k_2 C_M \quad (5)$$

The time development expressions for C_i are given through the integrals of equations (3), (4), and (5):

$$C_F = C_0 e^{-k_1 t} \quad (6)$$

$$C_M = \frac{C_0 k_1}{(k_2 - k_1)} \left[e^{-k_1 t} - e^{-k_2 t} \right] \quad (7)$$

$$C_S = C_0 \left(1 - \frac{k_2 e^{-k_1 t}}{k_2 - k_1} + \frac{k_1 e^{-k_2 t}}{k_2 - k_1} \right) \quad (8)$$

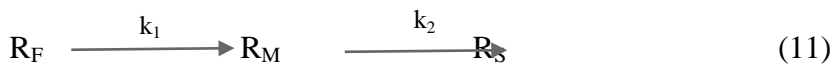
Substituting Equation (6) in (8):

$$C_S = \frac{C_F}{e^{-k_1 t}} \left(1 - \frac{k_2 e^{-k_1 t}}{k_2 - k_1} + \frac{k_1 e^{-k_2 t}}{k_2 - k_1} \right) \quad (9)$$

To consider the actual state, a dimensionless simplification of the solute concentration ($R_i = C_i/C_0$) is introduced below, so that the expression for the concentration becomes:

$$R_F = \frac{C_F}{C_0}, R_M = \frac{C_M}{C_0}, R_S = \frac{C_S}{C_0} \quad (10)$$

Equation (1) then becomes:



Where: The instantaneous lowered concentrations of solute in the feed, membrane, and stripping phases are denoted by the letters R_F , R_M and R_S , respectively.

The decreasing concentrations of solute in the different stages have a link, as:

$$R_F + R_M + R_S = 1 \quad (12)$$

The rate of change of solute concentration for different phase reductions can be derived from equation (11), as shown below:

$$\frac{dR_F}{dt} = -k_1 R_F = J_F \quad (13)$$

$$\frac{dR_M}{dt} = k_1 R_F - k_2 R_M = J_M \quad (14)$$

$$\frac{dR_S}{dt} = k_2 R_M = J_S \quad (15)$$

Where: The feed's immediate solute flux membrane and stripping phases are J_F , J_M and J_S , respectively.

The time progression formulas for R_i are given by the integrals of equations (13), (14), and (15) :

$$R_F = e^{-k_1 t} \quad (16)$$

$$R_M = \frac{k_1}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}] \quad (17)$$

$$R_S = 1 - \frac{1}{(k_2 - k_1)} [k_2 e^{-k_1 t} - k_1 e^{-k_2 t}] \quad (18)$$

As t indicates the amount of time elapsed. Replacing Equations (16)–(18) into Equations (13)–(15), J_i can be written as:

$$J_F = -k_1 e^{-k_1 t} \quad (19)$$

$$J_M = \frac{k_1}{(k_2 - k_1)} [k_2 e^{-k_2 t} - k_1 e^{-k_1 t}] \quad (20)$$

$$J_S = \frac{k_1 k_2}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}] \quad (21)$$

When J_M Equation (20) equals 0, the maximal solute transport go with the flow throughout the physique fluid membrane is reached. That is the case:

$$J_F^{\max} = -k_1 e^{-k_1 t_{\max}} \quad (22)$$

$$J_M^{\max} = \frac{k_1}{(k_2 - k_1)} \left[k_2 e^{-k_2 t_{\max}} - k_1 e^{-k_1 t_{\max}} \right] = 0 \quad (23)$$

$$J_S^{\max} = \frac{k_1 k_2}{(k_2 - k_1)} \left[e^{-k_1 t_{\max}} - e^{-k_2 t_{\max}} \right] \quad (24)$$

Where: In the feed and stripping stages, J_F^{\max} and J_S^{\max} largest solute transport fluxes are represented, respectively, and t_{\max} represents the time taken to attain the maximum flux.

t_{\max} may be calculated using Equation (23):

$$t_{\max} = \frac{\ln\left(\frac{k_2}{k_1}\right)}{(k_2 - k_1)} \quad (25)$$

Equation (25) is substituted into equation (17) to obtain the R_M value at t_{\max} , i.e. R_M^{\max} :

$$R_M^{\max} = \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{(k_2 - k_1)}} \quad (26)$$

From equation (26):

$$\ln R_M^{\max} = \ln \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{(k_2 - k_1)}} = \frac{k_2}{(k_2 - k_1)} * \ln \left(\frac{k_1}{k_2}\right)$$

$$\ln \left(\frac{k_2}{k_1}\right) = \frac{(k_2 - k_1)}{k_2} * \ln \left(\frac{1}{R_M^{\max}}\right) \rightarrow \text{Substituted into Equation (25):}$$

$$t_{\max} = \frac{\ln\left(\frac{1}{R_M^{\max}}\right)}{k_2} \quad (27)$$

At $t = t_{\max}$, the first-order temporal differentiation of equations (13 - 15) yields the following result:

$$\left(\frac{dR_F}{dt}\right)_{\max} = -k_1 \left(\frac{k_1}{k_2}\right)^{\frac{-k_1}{k_1 - k_2}} = J_F^{\max} \quad (28)$$

$$\left(\frac{dR_M}{dt}\right)_{\max} = 0 = J_M^{\max} \quad (29)$$

$$\left(\frac{dR_S}{dt}\right)_{\max} = k_2 \left(\frac{k_1}{k_2}\right)^{\frac{-k_2}{k_1 - k_2}} = J_S^{\max} \quad (30)$$

$$\left(\frac{dR_F}{dt}\right)_{\max} = - \left(\frac{dR_S}{dt}\right)_{\max} \quad (31)$$

Equation (29) and the reality that the solute attention in the membrane is consistent at $t = t_{\max}$, i.e.:

$$\left(\frac{dR_M}{dt}\right)_{\max} = 0$$

Since J_M is 0, steady-state kinetics dictates that the sum permeate as well as exit fluxes ultimately between the two phases (J_F^{\max} (Equation (28)) as well as (J_S^{\max} (Equation (30)) be equivalent yet opposite sign, i.e. $-J_F^{\max} = J_S^{\max}$.

Simulation environment

In this study, simulation by MATLAB, is used to simulate dynamic model of bulk liquid membrane equations (6 - 10) then equations (2 and 3) as shown in figure (2). Through the simulation system of previous equations and the experiments between the practical (7 hours) and theoretical (10 hours), this study has concluded that the simulation system for the theoretical is better than the practical because it gave a higher extraction about (14%) but the stripping increased about (7%) only. In order to prove the validity of the simulation, practical results of previous researchers were applied to the simulation system, and the results appeared close to their practical results. The theoretical results proved identical to the practical, with fewer experiments and a lower cost of examinations than previous researchers. Thus, the study shortened time, effort and helped researchers to predict the ideal conditions of the system in different elements.

```

function [cf, cs, cm, rf, rs, rm, Ef, Es] = css(k1, k2, co)
for t=1:10
    cf(t) = co * exp(-k1*t)
    cs(t) = (cf(t) / exp(-k1*t)) * (1 - (k2 * exp(-k1*t) / (k2 - k1)) + (k1 * exp(-k2*t) / (k2 - k1)))
    cm(t) = co - (cf(t) + cs(t));
    rf(t) = cf(t) / co;
    rs(t) = cs(t) / co;
    rm(t) = cm(t) / co;
end
Ef = ((co - cf) / co) * 100;
Es = (cs ./ (co - cf)) * 100;
result = [cf' cs' cm' rf' rs' rm' Ef' Es'];
save cf cf;
save cs cs;
save cm cm;
save rf rf;
save rs rs;
save rm rm;
save Es Es;
save Ef Ef;
    
```

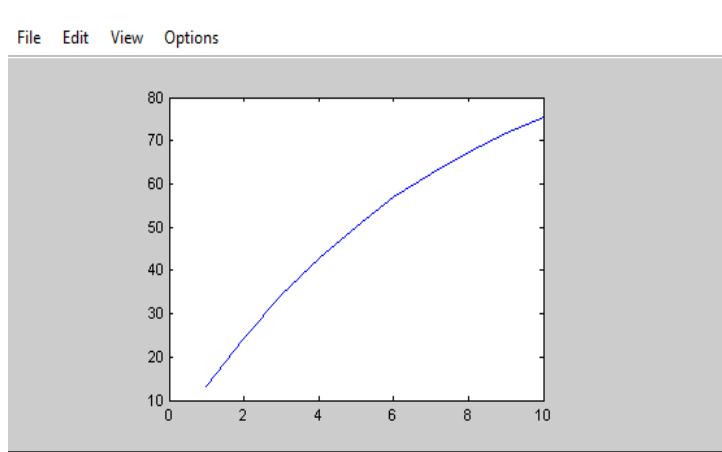
Figure 2: Equations codes and behaviour study of C_f , C_s , C_m , R_f , R_s , R_m , Extraction and stripping for 10 hr.

As an applied example of simulation for one of the experiments as shown in figure (3), the equations are fixed for all experiments, only the variables are changed. After entering the required variables such as C_0 and k_i , running the simulation. Simulation in MATLAB gave the results for each hour in the form of an excel table that is stored in the program to be compared it with the practical results. Here, the percentage of extraction efficiency in practical in 7 hours (62.5 %), knowing that the results are the same theoretically at the same time, while in 10 hours it has given (75.36%). On the other hand, the stripping efficiency in practical in 7 hours (88 %) while in 10 hours it has given (95%). In addition to that the results can be drawn and it made a curve fitting for the results, found the equation and R^2 .

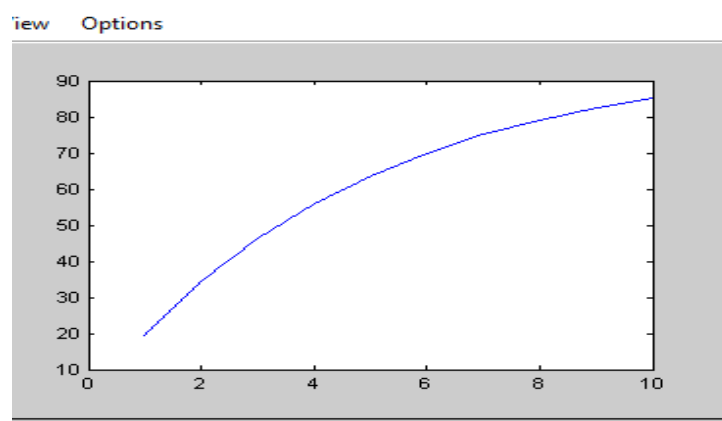
```

1 function [cf, cs] = css(cf)
2     co=5;
3     k1=0.2691;
4     k2=0.6939;
5     for t=1:10
6         cf(t)=co*exp(-k1*t)
7         cs(t)=(cf(t)/exp(-k1*t)) * (1 - (k2*exp(-k1*t) / (k2-k1)) + (k1*exp(-k2*t) / (k2-k1)))
8     end
9
10    Ef=( (co-cf) / co) *100;
11    Sf=(cs / (co-cf)) *100;
12    result=[cf' cs' Ef']
13
14
15
16
  
```

a) Equations codes



b) Extraction%



c) Stripping%

Figure 3: Equation code, Extraction and stripping of Cd⁺² at carrier conc.= 10%, C₀ = 0.4 ppm , feed pH=5 and stripping with pH=8 for 10 hr.

Fuzzy Logic

With a variety of manipulation techniques, fuzzy common sense structures are employed as controllers. Figure (4) shows the structure which was used in this work (Mamdani fuzzy inference). Each rule in the Mamdani machine produces a fuzzy set as its output. Mamdani structures are rather suitable for specialist device functions the place regulations are set up based totally on human specialist knowledge, such as engineering procedures, due to the fact their rule basis is extra intuitive and easier to grasp.

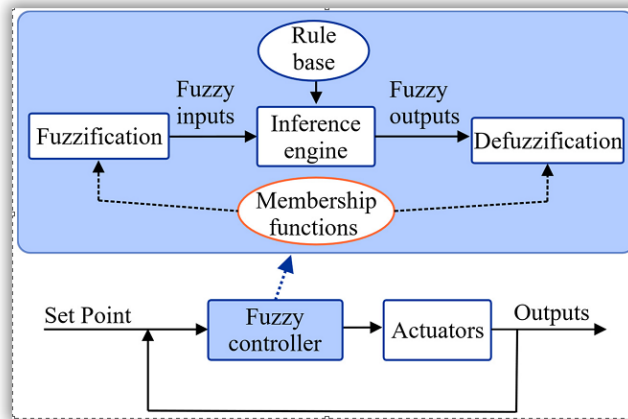


Figure 4: Control System Structure with a Fuzzy Controller.

The fuzzy inference device graph seems in Fuzzy Logic Designer, with the names of every enter variable is on the left and the names of every output variable is on the right. This study, employed six input (carrier conc. , initial conc. , pH strip , pH feed , temp. and rpm) and two output (E% and S%), as shown in figure (5).

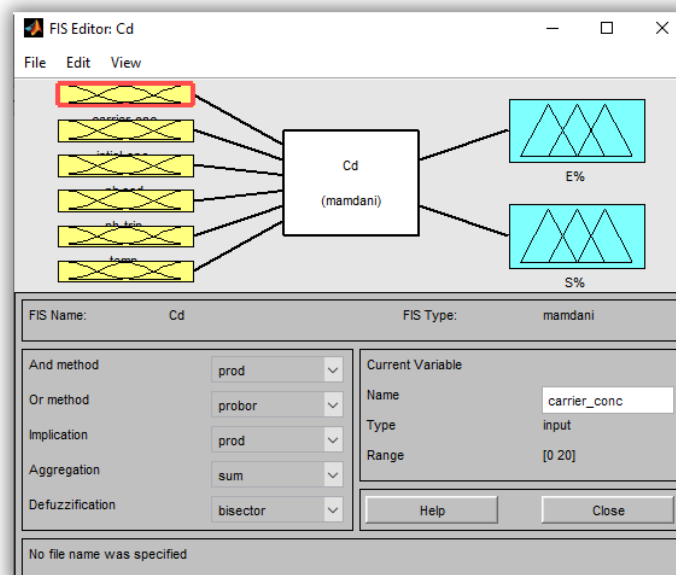


Figure 5: Fuzzy Logic Designer - FIS editor (Build mamdani system of fuzzy logic) , the number of input and output variables , method and defuzzification.

The affiliation feature editor is a device that indicates and updates all of the affiliation features related to all of the fuzzy inference systems enter and output variables. A function of membership, known as

(MF) is truly a curve which effectively describes how every factor in the enter area corresponds to a price of affiliation (or affiliation degree). In this study, employed for six input and two output functions of gaussian curve membership (gaussmf): (NB), (NS), (Z), (PS), as well as (PB) for the fuzzy controller output, as well as five affiliation functions: (NB), (NS), (Z), (PS), as well as (PB), as indicated in figure (6).

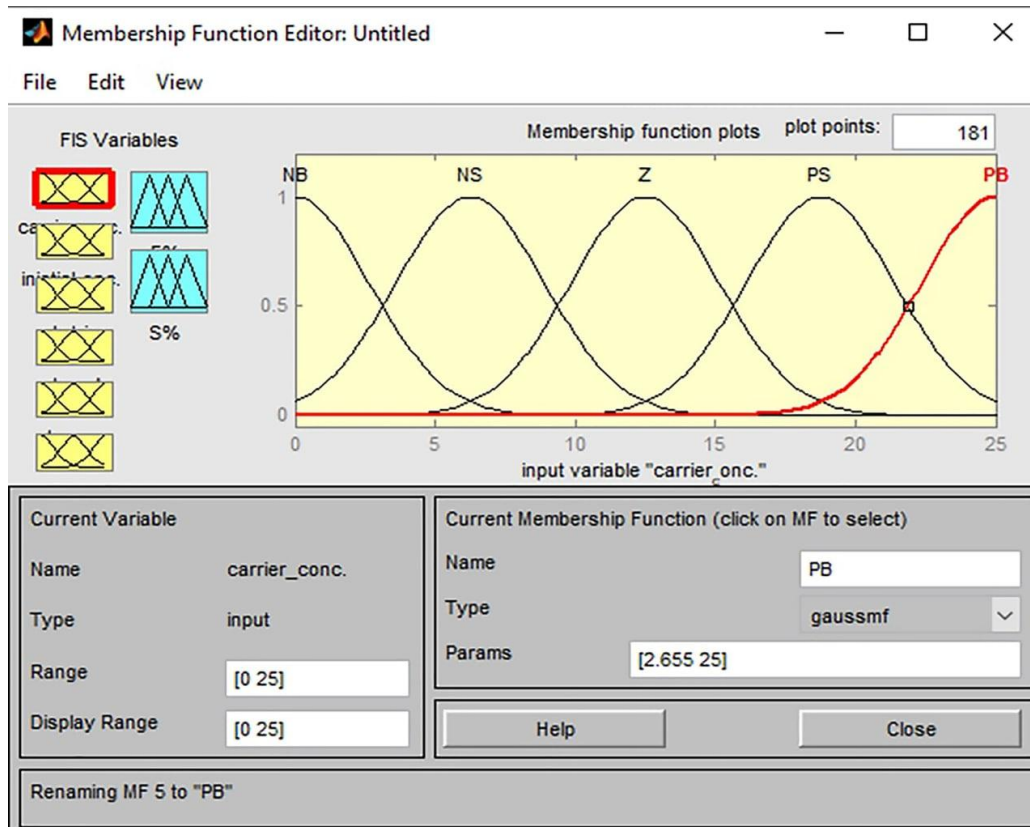


Figure 6: Membership Function (gaussmf) For Input and Output.

To whole manipulate tasks, fuzzy manage employs selection policies primarily based on fuzzy logic. Inference regulations are normally used in decision-making. Constructing regulations the use of a graphical rule editor interface is self-explanatory. The rule editor lets in the automatic introduction of rule statements primarily based on the fuzzy common sense designer's description of entering and output variables. Rules are constructed on the foundation of actual results in this study, however on a higher scale. Tables (1) and (2) display how the inputs and outputs are related via fifty-six policies (2). "Prod-probor" inference is used to decide the output of every rule. Where, "prod" is product of fuzzified input values and "probor" is used as an aggregation operator when combining the output fuzzy sets from all the input rules.

In each of the input and output variable boxes, choose one item, choose a connection item, and then click on **Add Rule** to set up a rule. Figure (7) depicts the resultant rule.

Table 1: Fuzzy logic controller rules (5 MF)

Variables	E % - S %					
	MF	NB	NS	Z	PS	PB
Carrier conc.	NB	NB	NS	~	~	~
	NS	NS	NS	Z	~	~
	Z	~	~	~	PS	PB

	PS	~	~	Z	PS	~
	PB	NB	NS	~	~	~
Initial conc.	NB	NB	NS	~	~	~
	NS	~	NS	Z	~	~
	Z	~	~	Z	PS	~
	PS	~	~	~	PS	~
	PB	~	~	~	~	PB
Temp.	NB	~	NS	Z	~	~
	NS	~	~	Z	~	~
	Z	~	~	Z	PS	~
	PS	~	~	~	PS	PB
	PB	~	~	~	PS	PB
pH feed	NB	NB	~	~	~	~
	NS	~	NS	Z	~	~
	Z	~	~	Z	PS	~
	PS	~	~	~	~	PB
	PB	~	~	Z	PS	~
pH strip	NB	NB	~	~	~	~
	NS	~	NS	Z	~	~
	Z	~	~	Z	~	~
	PS	~	~	~	~	PB
	PB	~	~	Z	PS	~
rpm	NB	~	NS	Z	~	~
	NS	~	~	Z	~	~
	Z	~	~	~	PS	PB
	PS	~	~	~	~	PB
	PB	~	~	Z	PS	~

Table 2: Range of variables used in

experimental the model

Inputs parameters		Minimum	Maximum
Carrier concentration		1%	25 %
Initial concentration of feed	Cd ⁺²	0.1	5
	Cu ⁺²	2	20
pH strip		2	12
pH feed		2	10
Temperature		10	50
Speed rate		0	250

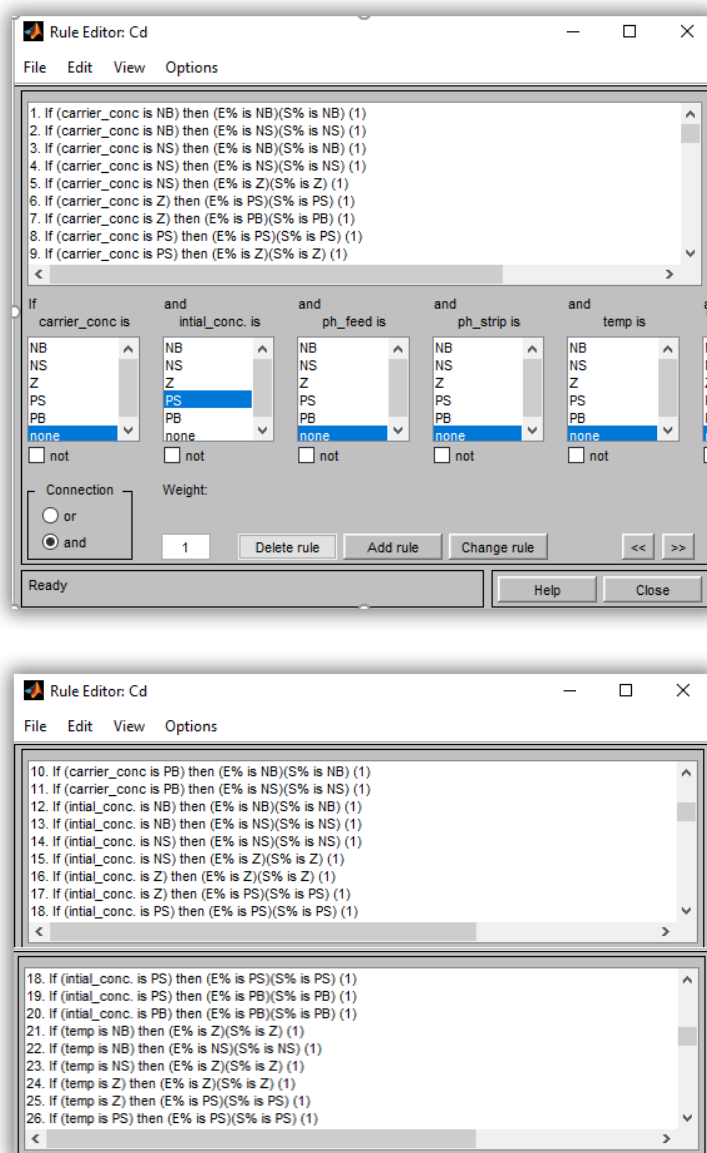


Figure 7: Rule editor (delete, add and change rule)

See the notably compressed model of the guidelines if altering the structure to index. The fuzzy inference gadget is now totally developed, with all variables, affiliation functions, and regulations in the vicinity to compute the ticks. Symbolics of Mamdani fuzzy system in workspace as file in a programming language by MATLAB obtained are presented in figure (8) .

```

1 - [System]
2 - Name='Cd'
3 - Type='mamdani'
4 - Version=2.0
5 - NumInputs=6
6 - NumOutputs=2
7 - NumRules=56
8 - AndMethod='prod'
9 - OrMethod='probor'
10 - ImpMethod='prod'
11 - AggMethod='sum'
12 - DefuzzMethod='bisector'
13
14 - [Input1]
15 - Name='carrier_conc'
16 - Range=[0 20]
17 - NumMFs=5
18 - MF1='NB': 'gaussmf', [2.124 0]
19 - MF2='NS': 'gaussmf', [2.124 5]
20 - MF3='Z': 'gaussmf', [2.17947657745867 10]
21 - MF4='PS': 'gaussmf', [2.124 15]
22 - MF5='PB': 'gaussmf', [2.12 19.9]
23
24 - [Input2]
25 - Name='intial_conc.'

```

Figure 8: System codes of Mamdani fuzzy logic control for input as well as output variables in cadmium system.

As tested in figure (9), the viewer's rule provides a roadmap concerning the entire process of fuzzy inference. Each rule appears in the form of a row of graphs, with every column representing one variable. Each row's rule range is listed on the left side. One by way of one, the computations are displayed in element in the rule viewer. It offers a microscopic photograph of the fuzzy inference gadget in this way.

- Yellow plots: demonstrates the affiliation function mentioned in the preceding section.
- Blue plot: suggests the affiliation feature referenced by using the result.

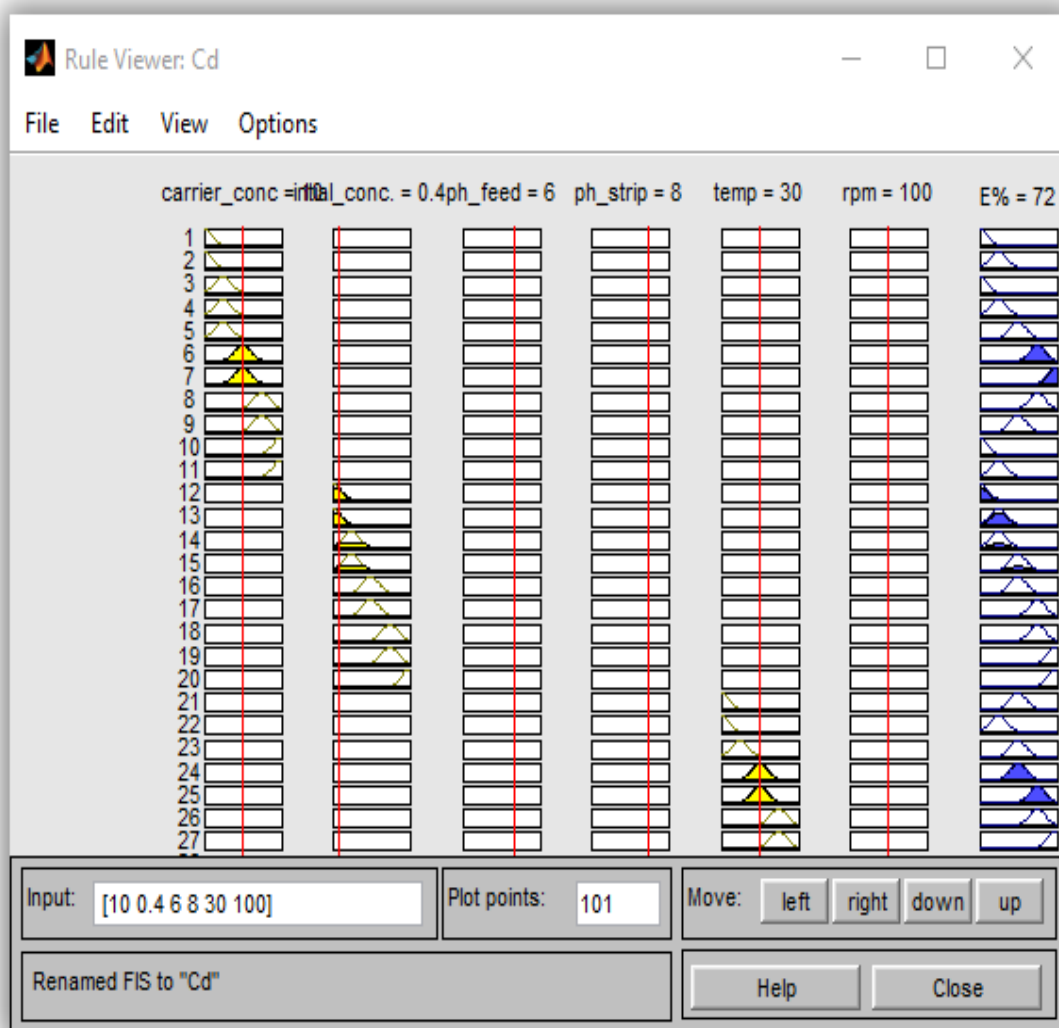


Figure 9: Rule viewer of fuzzy logic control for input and output variables.

Select Surface from the View menu in the Surface viewer. This viewer is the ultimate of the 5 primary Fuzzy Logic Toolbox UI tools. When the Surface Viewer is opened, you can see a 3D curve representing the inputs and outputs. The complete mapping can be proven in one layout considering the curve represents the state of affairs of two inputs as well as one output. As a result, Surface Viewer ultimately has drop-down picks for X (input), Y (input), as well as Z (output) that permit you to map any two inputs to any output. Below these options are the X-grid and Y-grid enter boxes, which determine how many x-axis as well as y-axis grid traces to include. This function lets in to preserve a life-like calculation time for complicated problems. The Surface Viewer obtained are presented in figure (10).

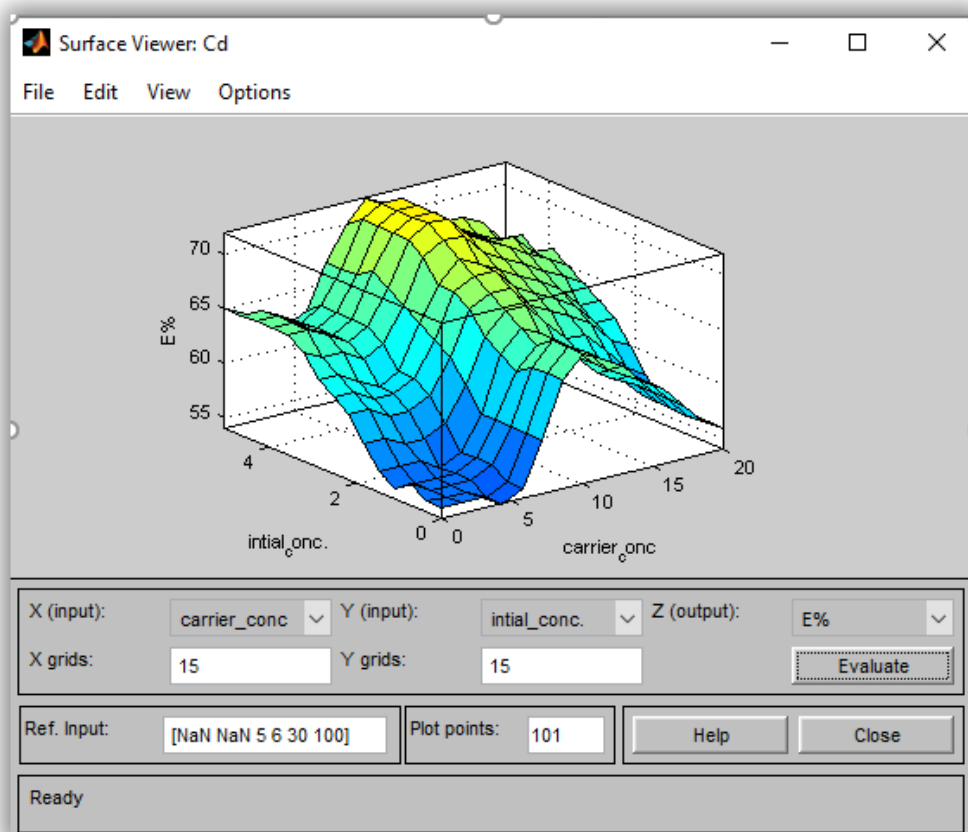


Figure 10: Surface viewer of fuzzy logic control for input (carrier conc. , initial conc.) and output (Extraction %) variables in cadmium system.

Design of Zainab_gui

In order to save time, effort, to make the most of the simulation and control system, a special program was designed for the BLM system to remove all kinds of pollutants, whether they are heavy elements, organic materials or toxic dyes. Because the mathematical model and equations are fixed for the BLM system, but the operating conditions are different, so this program is comprehensive for all operational conditions. Researchers can only change their conditions and press on **Calculate** to show the results. This program was formulated in a programmatic way by writing special codes in MATLAB, then the interface was designed that contains the conditions of the system and controls the final result, which appears in the form of graphics on the interface of the program. In addition to that, the results appear in the form of an Excel file on the Workspace in the interface of the MATLAB program. Figure (10) shows the beginning of writing the code to create the program and choosing the name where it was named (**Zainab_gui**), While figure (11),(12) and (13) show the inputs and outputs that have been programmed to appear on the front of the program.

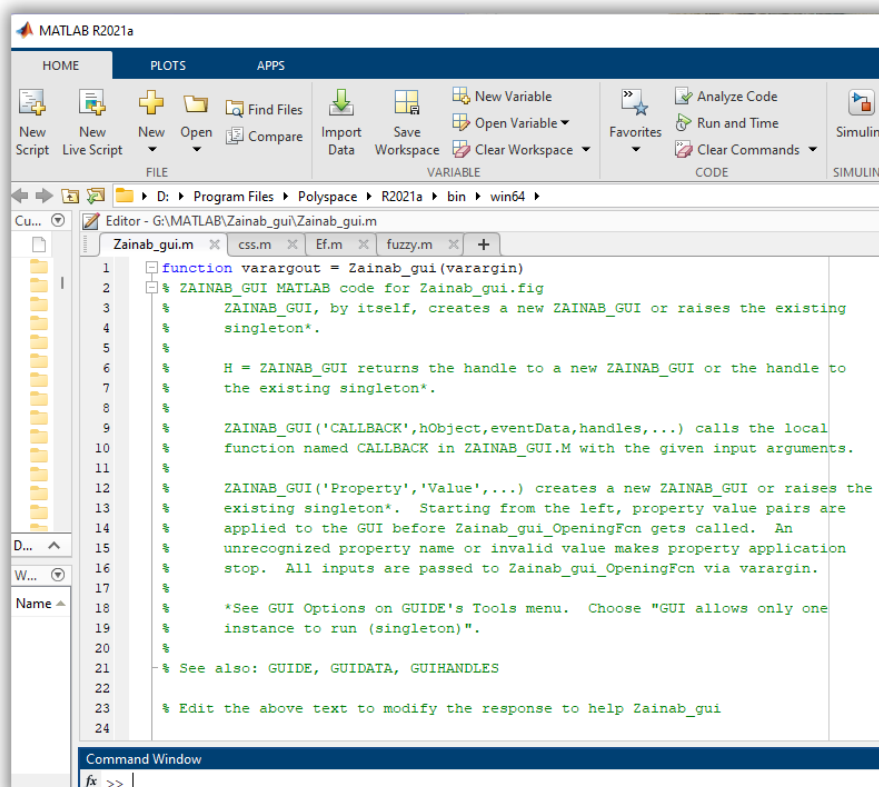


Figure 11: MATLAB code for Zainab_gui.

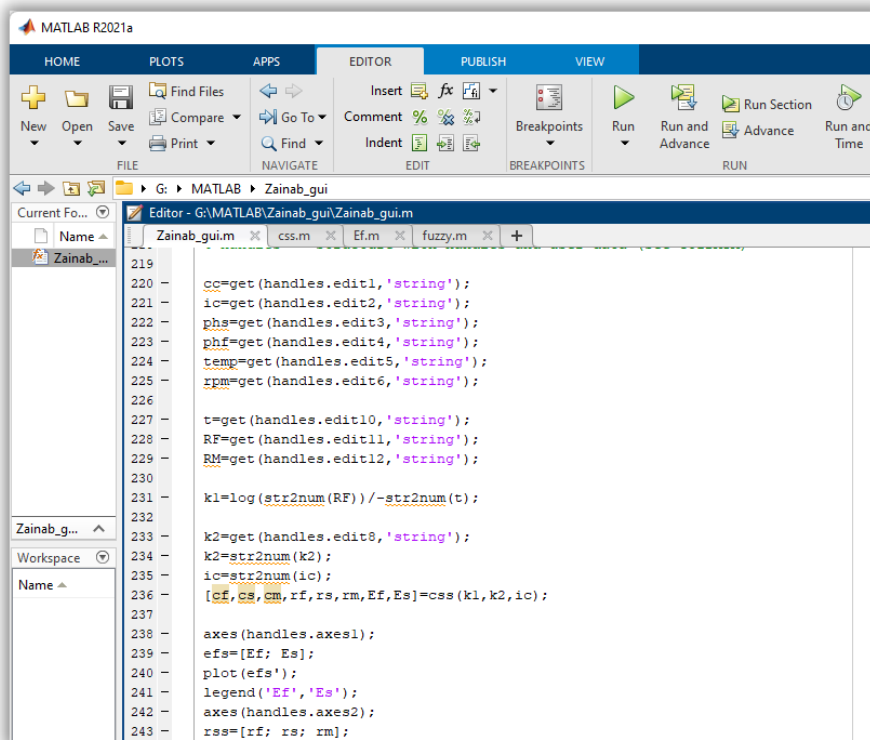


Figure 12: structure with handles and user data.

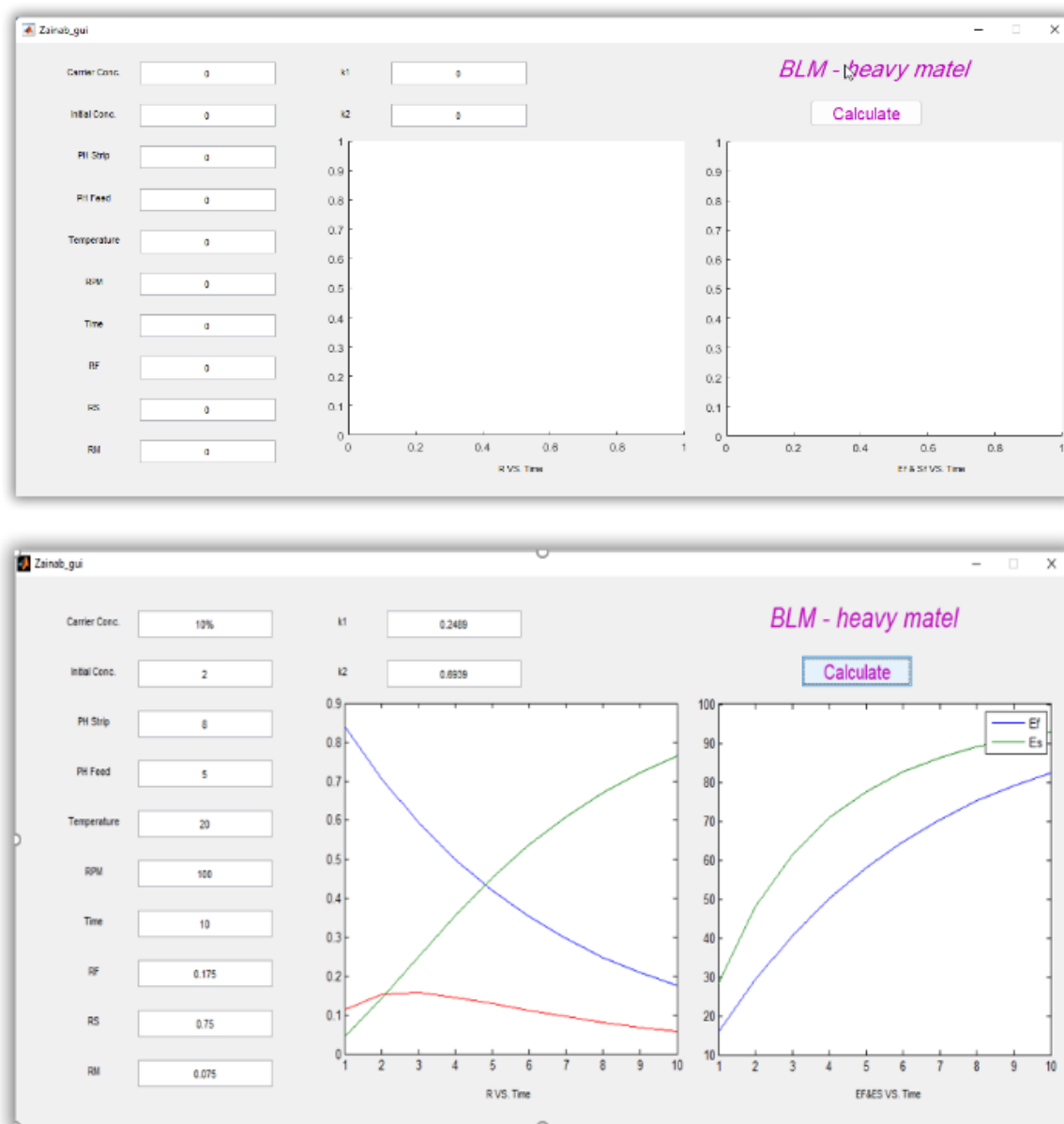


Figure [13]: Zainab_gui. Program.

Conclusion

This study presented the kinetics of transport mechanisms of heavy metals, and a mathematical model explains the behaviour of bulk liquid membrane a simulation has made on the results of practical experiments, but with wider limits, and a control system was built in a fuzzy logic control method, design and programming a software interface that includes the process of separating heavy metals by bulk liquid membrane and includes all the variables that affect the separation by using MATLAB.

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