ARTIFICIAL NEURAL NETWORK BASED MODELING OF THE SUPPORTED LIQUID MEMBRANE FOR SIMULTANEOUS EXTRACTION AND RECOVERY OF CADMIUM AND LEAD FROM WASTE WATER

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CANDIDATE'S DECLARATION

We, Sugandh Luthra, 2k21/MSCCHE/60 and Arvind yadav, 2k21/MSCCHE/07 of MSc. Chemistry, hereby declare that the project Dissertation titled "Artificial neural network based modeling of the supported liquid membrane for simultaneous extraction and recovery of cadmium and lead from waste water" which is submitted by us to the Department of Applied Chemistry, Delhi Technological University, Delhi in partial fulfillment of the requirement for the award of the degree of Master of Science, Chemistry is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any Degree, Diploma Associate ship, Fellowship or other similar title or recognition.

Place: Delhi **SUGANDH LUTHRA**

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CERTIFICATE

I hereby certify that the Project Dissertation titled "Artificial neural network based modeling of the supported liquid membrane for simultaneous extraction and recovery of cadmium and lead from waste water" which is submitted by Sugandh Luthra, 2k21/MSCCHE/60 and Arvind yadav, 2k21/MSCCHE/07 of Department of Applied Chemistry, Delhi Technological University, Delhi in partial fulfillment of the requirement for the award of the degree of Master of Science, Chemistry, is a record of the project work carried out by the students under my supervision. To the best of my knowledge this work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere.

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ABSTRACT

With the exponential popularization of modern industries, more products are being produced, leading to water wastage and chemical disposal. These toxic chemicals are submerged in clean water resources, resulting in increased drinkable water toxicity. Separation of poisonous substances from wastewater is a pressing requirement to adopt the proof of concept of clean industrialization. Supported liquid membrane (SLM) is a popular and widely adopted non-dispersive membrane for the recovery and extraction of solutes from aqueous solution. The efficiency of cadmium and lead separation increases with the use of SLM. In this study, we have adopted an ANN-based approach to predict the results related to the recovery and extraction of cadmium and lead using the MATLAB deep learning toolbox. The experimental results are predicted by modeling the experimental data and analyzing the effect of the operating parameter. The accuracy of the predicted model is validated with experimental results, and the variation in the features helped in optimizing the study.

ACKNOWLEDGEMENT

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CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS, ABBREVIATIONS AND NOMENCLATURE

mg – milligram

L - litre

y_{exp} - experimental output

y_{model} - model predictions

M – Molar

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Population growth and urbanization have led to an increase in demand for industrialization, agriculture, etc. This has led to the establishment of various industries and the use of pesticides and fertilizers to increase crop yield due to which many toxic materials enter the water bodies and create them unfit for consumption. The rise in different water usage caused by the growing global population has resulted in not only a reduction in the amount of accessible renewable freshwater but also contamination and a decline in the quality of freshwater reservoirs.

Cadmium and lead are among those creating toxicity in the water bodies. They can enter into the environment through natural or artificial discharge and get accumulated in air, water, or soil. Metals transfer from one constituent to another constituent has been spotted after the initial accumulation into any of the constituents [1].

According to the guidelines set forth by the World Health Organization (WHO), the acceptable range for cadmium levels in drinking water is between 0.003 and 0.005 mg/L, while a recommended safe limit of 0.003 mg/L is advised for wastewater[2] and for lead in drinking water advisable level is < 0.01 mg/L and for wastewater is 0.01 mg/L [2], [3].

1.2 USES OF CADMIUM AND LEAD

Lead and its compounds are primarily found in occupations associated with lead, along with diverse sources such as the use of leaded gasoline, industrial activities like lead smelting and combustion, pottery making, boat construction, lead-based painting, the presence of lead-containing pipes, battery recycling, grid manufacturing, the arms industry, pigments, and the printing of books. Despite, the usage being discontinued in some countries it is still used in several industries such as car repair, battery production, recycling, refining, smelting, etc. [4]

Cadmium has been used widely in Nickel-Cadmium batteries as electrodes. Its application holds good in the pigment industry, as stabilizers in plastic, and in the plating and coating industries. It is also used in electrical appliances as semiconductors and as an alloying element. Cadmium alloys can be categorized into three groups: alloys that exhibit higher electrical conductivity, alloys that have enhanced heat conductivity and alloys specifically engineered for electrical contact purposes.

1.3 CAUSES OF CADMIUM AND LEAD

The release of cadmium and lead is due to discharge from various industries like steel works, electroplating, electrolytic depositing, conversion-coating, anodizing-cleaning, milling, and etching industries[5]. Corrosion of pipes and plumbing fixtures, leaching from landfills, hazardous waste sites, and other waste disposal can cause entry of cadmium and lead into water bodies. Some prevalent contributors to the presence of cadmium and lead are the dyes industry, pesticide industry, paper mill industry [6], pharmaceuticals [7].

1.4 NEGATIVE IMPACTS OF CADMIUM AND LEAD

Once these toxic metals enter the water bodies, they get accumulated into the food chain, potentially posing risks to human health [8] and harming aquatic life. [9] They can potentially cause adverse effects on bones and can be the root cause of cancer in the kidneys, and liver due to their accumulation as carcinogenic pollutants [10]. Its retention in the soil is less efficient so, it seeps down the groundwater and enters the food web [11]. The intake of vegetables containing high levels of heavy metals can significantly reduce essential nutrients in the body. This depletion can lead to decreased immune defenses, disabilities associated with malnutrition, and a higher occurrence of upper gastrointestinal cancer [8], [12], [13].

1.5 PREVENTION METHODS

To prevent the harmful effects, water should be treated and toxic metals should be removed from waste water before disposing. There are several traditional methods used for removing Cadmium and Lead from wastewater including the activated charcoal method, ion exchange method [14]–[17], _chemical_precipitation [18]–[20] ,reverse_osmosis [21], ion_flotation [22], [23] _Coagulation/flocculation [24], [25] , adsorption [26], and electrochemical removal[27]. Conventional methods have certain disadvantages as compared to more advanced or alternative techniques. They lack selectivity leading to low purity in the separation or incomplete separation for some metals. They suffer from low efficiency and yield leading to incomplete removal. The inefficiency can result in significant metal losses or require multiple treatment steps, leading to increased costs and waste generation like sludge or precipitates that require further treatment for disposal. Some conventional methods use harmful chemicals, reagents, and high energy consumption which can add to expenses and pose environmental risks. To overcome these demerits modern techniques are used like absorption, chemical hydrogels, membrane separation, biosorption, photo catalysis, electro dialysis, nanotechnology and nanoparticles.

CHAPTER 2

THEORY

2.1 LIQUID MEMBRANE

Liquid membrane technology is a specialized separation technique that involves the transport of specific molecules or ions across a liquid membrane to separate them from a mixture. In this process, a liquid membrane acts as a selective barrier that allows the passage of certain species while blocking others, based on their chemical or physical properties.

2.1.1 USES OF LIQUID MEMBRANE

Liquid membrane technology has been widely used in various fields, including chemical, pharmaceutical, environmental, and biotechnological industries, for the separation, extraction, concentration, and recovery of specific components from complex mixtures.

2.1.2 ADVANTAGES OF LIQUID MEMBRANE

Liquid membrane technology is highly efficient, allowing for continuous and simultaneous extraction and transport of target components, resulting in reduced processing time and increased productivity. The operating system of liquid membrane technology is insensitive, making it robust and stable in various operating conditions, reducing the chances of system failures and downtime. Compared to other separation methods, liquid membrane technology is a less costly affair in terms of capital investment, making it economically viable for industrial applications. One of the advantages of liquid membrane technology is the minimal production of secondary sludge, reducing the generation of waste and the need for additional disposal or treatment. Liquid membrane technology is characterized by low energy and solvent consumption, making it an environmentally friendly option for separation processes, and reducing the overall environmental impact. This technology allows for high-concentration factors, enabling the extraction and recovery of target components at higher concentrations, which can be beneficial in various applications. The high flux of liquid membrane technology enables the efficient mass transfer of gases, ions, and molecules through the permeation and transport process, ensuring effective separation and extraction. Liquid membrane technology offers selective mass transfer, allowing for precise separation of specific components from complex mixtures, based on their chemical or physical properties, leading to high selectivity and purity of the extracted components.

2.1.3 CLASSIFICATION OF LIQUID MEMBRANE

Liquid membranes can be classified into different types, including emulsion liquid membranes (ELMs), supported liquid membranes (SLMs), bulk liquid membranes (BLMs), strip dispersion membranes (SDMs), solvent-impregnated membranes (SIMs), polymer inclusion membranes (PIMs), and liquid membrane extraction modules (LMXMs).
These types of liquid membranes differ in their composition and mode of operation.

- ELMs – They use emulsifying agents to stabilize droplets of a carrier phase. Emulsion liquid membranes have a low thickness and a very large surface area per unit of volume, which makes the separation and accumulation process very quickly in the emulsion vehicle . In order to remove the transported species, the vehicles must be created prior to the operation; they must be stable enough to minimise leakage to a minimum but not so stable that they can be destroyed after separation. As a result, the process requires several unit operations and isn't very attractive technologically.

- SLMs immobilize a liquid phase on a porous support material.
- BLMs have a liquid phase between two membranes. A water-immiscible liquid membrane phase is used in a U-tube that generally separates the aqueous feed and stripping phases of bulk liquid membranes. BLMs are frequently employed to determine the transport characteristics of new carriers, however they aren't very attractive technologically due to their small membrane surface area[28].
- SDMs use a continuous phase with a dispersed phase of stripping agent.
- SIMs impregnate a solvent into a polymeric membrane.
- PIMs contain an extractant in a polymeric membrane.
- LMXMs are modular systems for selective mass transfer.

2.2 SUPPORTED LIQUID MEMBRANE

Supported Liquid Membrane (SLM) is a liquid membrane-based separation technology that uses a nondispersive membrane to selectively transport a target substance from a mixture. The supported liquid membrane (SLM) is a type of membrane that consists of a supported liquid layer sandwiched between two solid layers. The liquid layer contains a selective solvent that can selectively transport a target molecule from one side of the membrane to the other. The working of supported liquid membrane is represented diagrammatically in Figure 2.1.

The feed solution containing the target molecule is introduced on one side in the membrane is usually an organic solvent that can selectively transport certain molecules or ions across the membrane. This process occurs in three main steps:

1. Absorption: The feed solution containing the target molecules or ions is contacted with the liquid membrane. The target species selectively absorb into the liquid membrane through various mechanisms such as diffusion, complexation or ion-pairing.

2. Transport: The absorbed species are transported across the liquid membrane by diffusion. The rate and selectivity of transport depends on the properties of the liquid membrane, such as its viscosity, polarity and affinity for the target species.

3. Desorption: The target species are desorbed from the liquid membrane into the receiving solution on the other side of the membrane. This can occur spontaneously, or by addition of a desorbing agent.

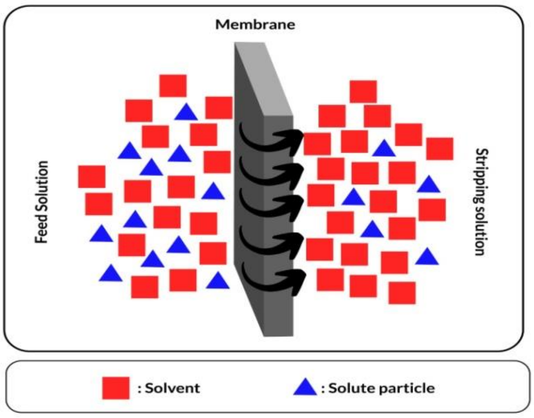

Figure 2.1 Separation process using supported liquid membrane

2.2.1 USES OF SLM

It is widely used for the simultaneous extraction and recovery of toxic metals like cadmium and lead from wastewater. Membrane-based separation is used for extraction and recovery of cadmium and lead that are more efficient, cost-effective, low energy consumption, and environmentally friendly. The process works by the selective partitioning of metal ions into a liquid membrane, which is then recovered and concentrated. The metal ions in the liquid membrane are then concentrated into a separate fraction, leaving the remaining metal ions in the solution. The process is effective in removing cadmium and lead from a solution of metal ions since they have a higher partition coefficient than other metals.

2.2.3 TYPES OF SLM

SLM is divided into two types:

2.2.3.1 FLAT SHEET SUPPORTED LIQUID MEMBRANE (FSSLM):

It is the simplest form of the liquid membrane which uses a microporous solid support for the liquid membrane. The solid support is treated with the extractant and clamped between two half cells using gaskets to create two compartments. The feed solution is stored in one compartment, and the strip solution is kept in the other and stirred by mechanical stirrers [29].

2.2.3.2 HOLLOW FIBRE SUPPORTED LIQUID MEMBRANE (HFSLM):

It is used to extract metal ions. The outer cell of the module is made up of a single nonporous substance, which prevents the solution from moving through the material. Many thin fibres are arranged in neat rows inside the shell [30]. With the help of pumps, the source phase travels through the fibres and the receiving phase travels through the shell side.

2.3 ARTIFICIAL NEURAL NETWORK

ANN is a popular and flexible machine learning algorithm for modeling and predicting complex systems between input and output variables [31]. It is suitable for predicting many experimental data. MATLAB provides a comprehensive set of functions and tools for creating, training, and evaluating ANN. ANN consists of multiple layers of interconnected nodes, also called neurons. Each neuron receives one or more inputs, performs a mathematical operation on those inputs, and produces an output [31], [32]. The output of one neuron can be connected to the input of another neuron, forming a network of interconnected neurons. In Neural networks, the connections between their inputs and outputs are called architecture or topology. The architecture can be varied by changing the number of hidden layers or the number of neurons in the hidden layer. Each node processes the signal, operates on the data to produce the output, and has a variable magnitude associated with it called weight.
The network can identify certain patterns in the dataset and then uses them for prediction, function estimation, etc.

The neural network is composed of multiple layers that work together to process and transform input data into meaningful output. It is broadly divided into three layers:

INPUT LAYER: The input layer neurons take in the input data, process it, and then send it on to the hidden layers for further processing. The number of neurons in the input layer corresponds to the number of parameters of input data.

HIDDEN LAYER: These layers are located between the input and output layers. The number of hidden layers and the number of neurons in each layer depends on the complexity of the problem and the architecture of the network. Each neuron in the hidden layer performs a weighted sum of its input, applies an activation function, and passes the result to the next layer.

OUTPUT LAYER: this layer provides the final output of the neural network. The number of neurons in the output layer depends on the nature of the task.
To measure the deviation between generated results and experimental results, we define a function called Mean Squared Error (M.S.E.).

Mean squared error (MSE) is a function used to evaluate the performance of the network's predictions. It measures the average squared difference between the predicted output and actual output for a given input data set. The lower value of MSE indicates that prediction is closer to the actual output.

$$\text{Mean square error} = \frac{1}{n}\sum_{i=1}^{n}(y_{exp} - y_{model})^2 \qquad (2.1)$$

where, n is the number of the data point. y_{exp} and y_{model} represent the experimental output and model predictions, respectively

2.3.1 LEVENBERG-MARQUARDT ALGORITHM

The Levenberg-Marquardt algorithm is an optimization method commonly used for solving nonlinear least squares problems, particularly in the context of training neural networks or fitting mathematical models to data. The Levenberg-Marquardt algorithm is known for its efficiency in finding the minimum of the objective function. It provides fast convergence for well-behaved problems and is less sensitive to the initial parameter estimates compared to other optimization techniques. It enhances the algorithm's robustness, convergence speed, applicability, stability, and user-friendliness, making it a popular choice for solving nonlinear least squares problems in various fields. Levenberg-Marquardt algorithm application extends beyond neural network training and is commonly used in various fields, including computer vision, robotics, and scientific data analysis.

CHAPTER 3

PROCEDURE

Data on the simultaneous extraction and recovery of cadmium and lead from wastewater was derived from relevant scholarly sources[8] that investigated the potential use of environment-friendly vegetable oils as solvents in liquid membrane separation techniques for transporting solutes.

The experiment performed by [2] used N-Methyl-N,N-dioctyloctan-1-ammoniumchloride (Aliquat-336) as carrier agent, ethylenediaminetetraacetic acid (EDTA) as a stripping agent, polyvinylidene fluoride (PVDF) as a supporter and coconut oil-based flat sheet supported liquid membrane. They used the data to investigate the selectivity of individual metals with varying molar ratios in the feed solution.

In this study, the extraction and recovery data were used to carry out the training of ANN. An evaluation of the experimental data from [8] and ANN assumptions are reported in Table 1. ANN model used a neural network fitting toolbox in MATLAB which uses a multi-layer network. Neurons in the hidden layer were optimized to layer size 7 to find the minimum MSE for the set of 41 experimental data points which was randomly divided into 3 sets to train, validate and test ANN.

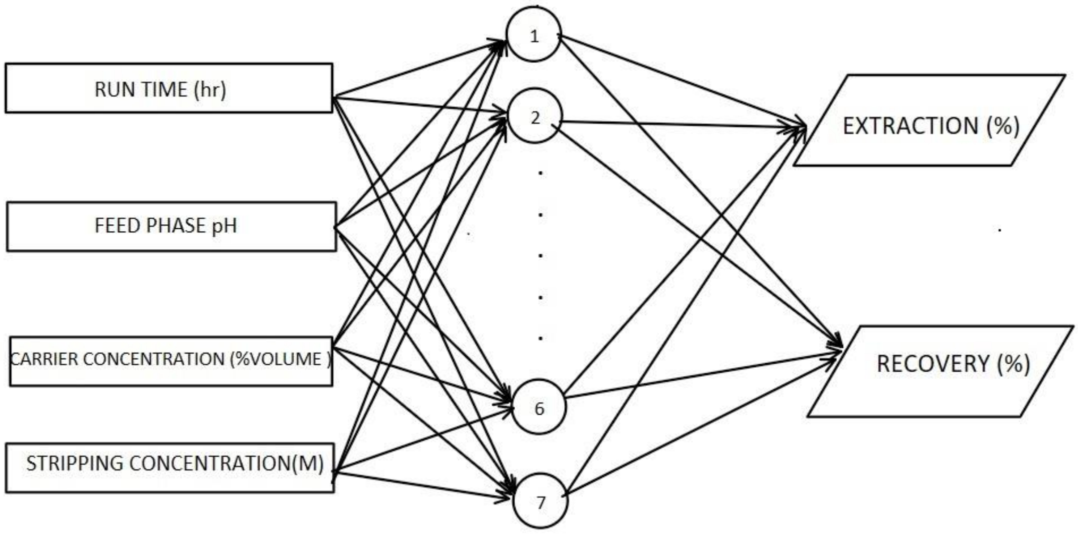

Figure 3.1 Architecture of ANN

The upper and lower range of the operating parameter is reported in Table 2. Using the same range, the data was simulated using Levenberg-Marquardt Algorithm in the feedforward approach. A surface graph was created by conducting simulations where two input parameters were changed within the range as reported in Table 2. One of the input parameters is considered as run time, varying the other parameter to plot the surface graphs. This allowed for an analysis of its effect on the separation of cadmium and lead, and how the variations in these two parameters interacted with each other.

Table 2 - Inputs used for training the ANN model

Input Parameters	Range
Run time (hr)	0.5-10
Feed phase pH	3-7
Carrier concentration (volume %)	0.25-1.0
Stripping concentration (M)	0.01-0.05

CHAPTER 4

RESULT AND DISCUSSION

4.1 Artificial Neural Network Training and Validation:

On Training, testing, and validating the data from experimental results of [8], a random selection of 70% of data was used for training, 15% was used for testing and 15% was used for validation. During training, the model learns from a labelled dataset, also known as the training dataset. The model adjusts its internal parameters through an optimization algorithm to minimize the difference between the predicted outputs and the true labels. The training dataset is typically divided into batches or mini-batches, and the model updates its parameters by computing gradients and propagating them through the network. No. of neurons in the hidden layer were optimized to layer size 7 as it achieved the minimum MSE. The MSE and Correlation coefficients between experimental result and model prediction (R) of the trained data is reported in Table 3. The regression plot depicts the relationship between experimental data and predicted data in Fig 4.1 which indicated the validation of the ANN model to predict the data by fitting with the experimental results. A correlation factor of more than 0.98 depicts the accuracy of predicting the data using the ANN model.

On comparing the experimental results and predicted results, we found a maximum relative error of 15.7%. The absolute error is reported in Table 1.

Table 3 – MSE and R value in training, validation and testing

Steps	No. of data points	MSE	Correlation coefficients between experimental result and model prediction (R)
Training	29	7.7629	0.98531
Validation	6	8.1126	0.98001
Testing	6	8.6819	0.99172

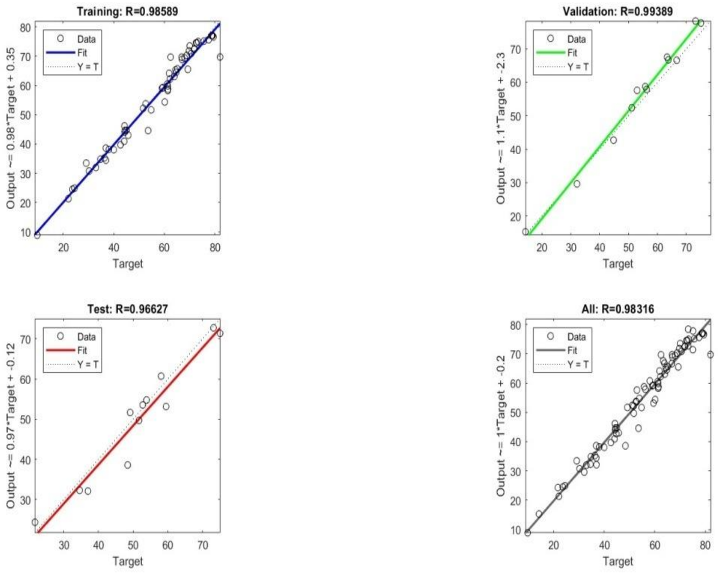

Figure 4.1 Regression plots of experimental results and predicted results

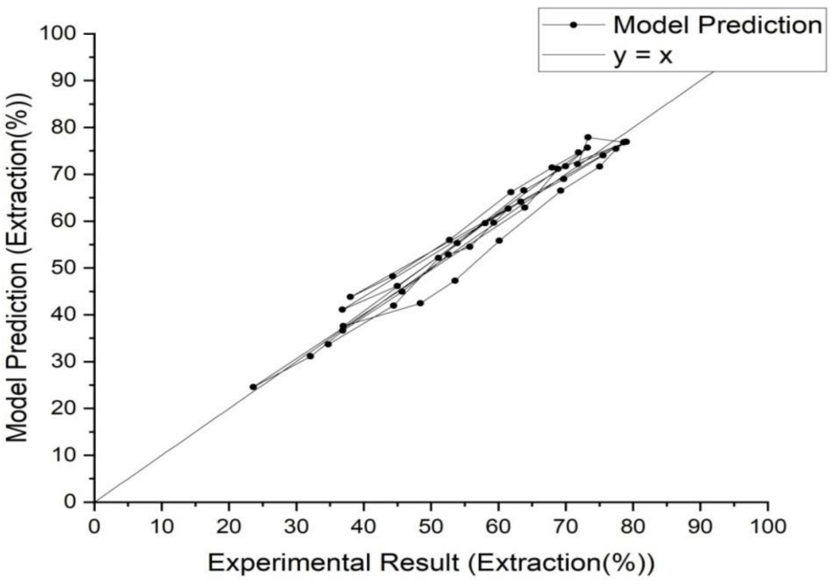

Figure 4.2 Experimental results vs. model predictions

4.2 Effect of feed phase pH: Fig 4.3 and 4.4 depict the effect of feed phase pH and run time on percentage extraction and recovery of cadmium and lead. The value of percentage extraction and recovery increased with increasing pH and run time. At low pH the cadmium and lead complex remain undissociated in the solvent inhibiting the extraction.

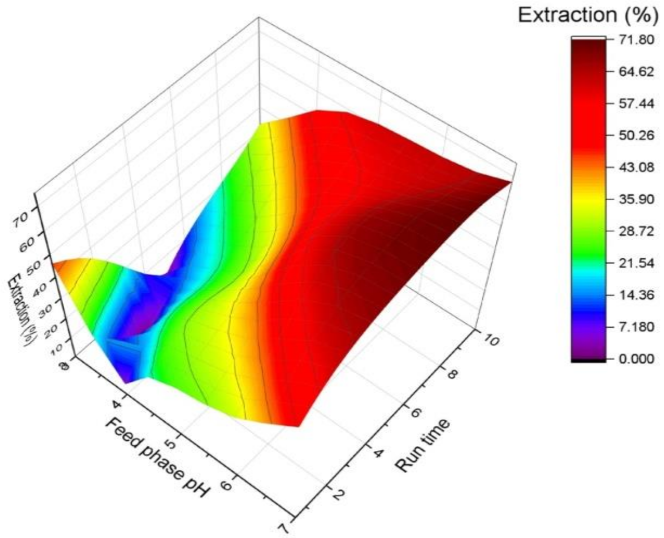

Figure 4.3 Effect of feed phase pH and run time on extraction

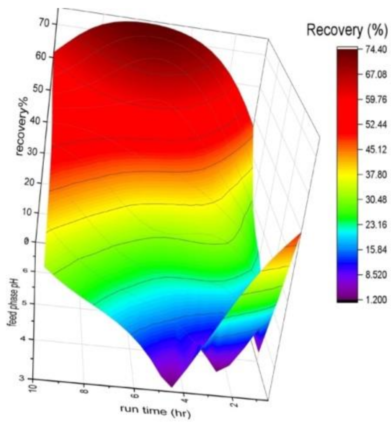

Figure 4.4 Effect of feed phase pH and run time on recovery

4.3 Effect of carrier concentration:

The increase in the transportation of cadmium and lead is dependent on the rate of complex formation, which increases with the rise in no. of carrier. Fig 4.5 and 4.6 depict that on increasing in carrier concentration, percentage extraction and recovery increases but to a certain extent. An excessive rise in the concentration of carrier creates hindrance to the complex which decreases the rate of transport of cadmium and lead due to an increase in viscosity of the membrane phase which results in a low rate of diffusion.

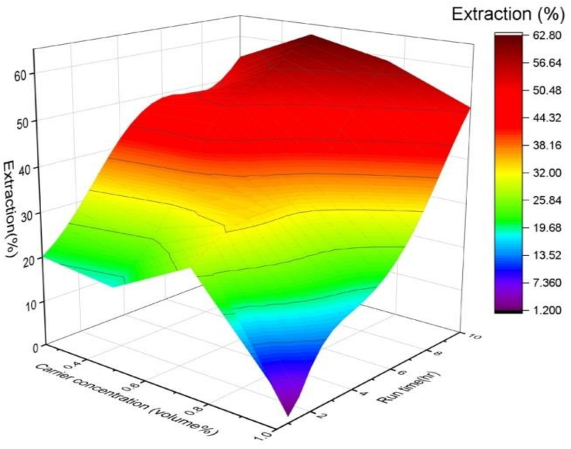

Figure 4.5 Effect of carrier concentration and run time on extraction

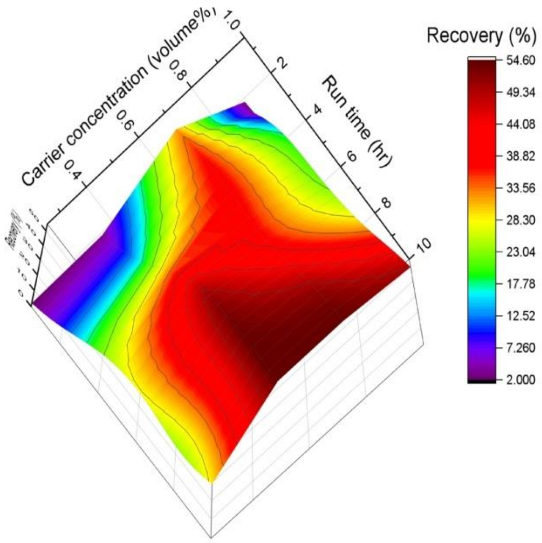

Figure 4.6 Effect of carrier concentration and run time on recovery

4.4 Effect of stripping concentration:

Fig 4.7 depicts the effect of stripping concentration on the percentage extraction of cadmium and lead. The graph shows the high rate of extraction during the initial hours with a low concentration of stripping agent. With increasing time and stripping concentration the percentage extraction reduces. This is caused by forming a saturated solution of stripping agent in the strip phase.

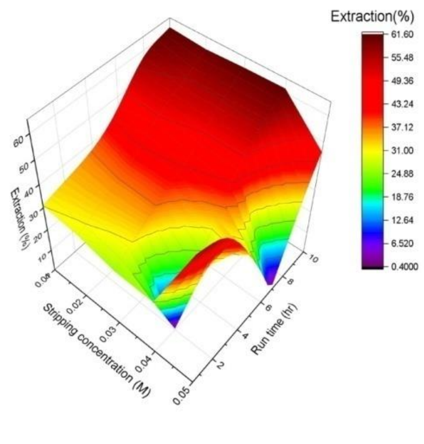

Figure 4.7 Effect of stripping concentration and run time on extraction

Fig 4.8 depicts the effect of stripping concentration on the percentage recovery of cadmium and lead. The graph shows the low rate of recovery during the initial hours and eventually, recovery increases with increasing time and later decreases. The concentration of the stripping agent does not hold much impact on recovery as it impacts the extraction of cadmium and lead.

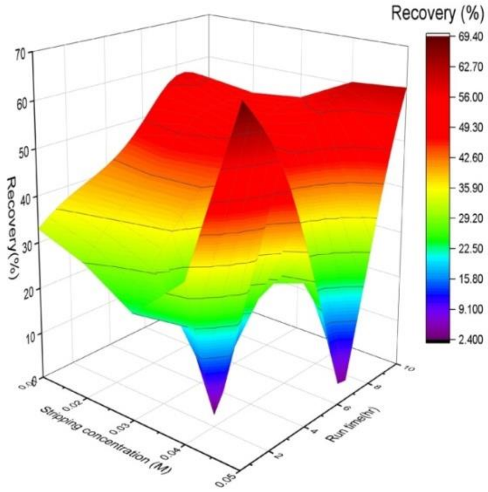

Figure 4.8 Effect of stripping concentration and run time on recovery

CHAPTER 5

CONCLUSION

In this study, the artificial neural network approach successfully helped in modeling the separation of cadmium and lead using supported liquid membrane. The minimum mean squared error was found with seven nodes in the hidden layer with a correlation factor of 0.98.

For a short run time, extraction increases with low stripping concentration. However, for longer run time, high feed phase pH, and high carrier concentration lead to a high percentage of extraction and recovery.

We could conclude that optimum conditions for maximum extraction and recovery of cadmium and lead are high run time (9-10 hr), high feed phase pH (6-7), moderate carrier concentration (0.5% (v/v)) and low stripping concentration (0.1-0.2M).

APPENDICES 1

Table 1 Comparison of experimental results and model prediction (Experimental data has been taken from *[8]*

S.No.	Initial feed sol. conc. (PPM)	Volume of feed phase (ml)	Volume of stripping phase (ml)	Run time (hr)	Feed phase pH	Carrier conc. (Vol. %)	Stripping Cons. (M)	Experimental Result (%Extraction)	Experimental Result (%Recovery)	Model Prediction (%Extraction)	Model Prediction (%Recovery)	Absolute error (% Extraction)	Absolute error(% Recovery)
1	5	200	200	10	3.00121	0.5	0.015	34.7222	24.4895	33.66638076	24.63620226	3.040761368	-0.599041475
2	5	200	200	10	3.49838	0.5	0.015	44.4444	36.2885	41.95294941	32.74844273	5.605769426	9.755314414
3	5	200	200	10	3.98482	0.5	0.015	51.1111	44.78	52.12063582	43.12461824	-1.975179201	3.696698884
4	5	200	200	10	4.49443	0.5	0.015	58.0555	49.1323	59.56851296	50.83921522	-2.606149225	-3.474120327
5	5	200	200	10	5.00452	0.5	0.015	63.3333	56.2418	64.12065554	55.69391969	-1.243193607	0.974151458
6	5	200	200	10	5.50266	0.5	0.015	69.7222	61.1472	68.98010661	61.03892169	1.064357395	0.177078121
7	5	200	200	10	6.00097	0.5	0.015	75.5555	64.3962	74.05040169	66.67204565	1.992043348	-3.534130348
8	5	200	200	10	6.47683	0.5	0.015	78.6111	66.8175	76.82135352	69.79368232	2.276709623	-4.454195859
9	5	200	200	10	7.00162	0.5	0.015	73.3333	65.1011	77.87441668	71.04223601	-6.192434656	-9.126014782
10	5	200	200	10	6.5	0.247239	0.015	71.7799	51.623	72.1753291	51.25266368	-0.550891133	0.717386287
11	5	200	200	10	6.5	0.498732	0.015	79.0145	62.455	76.92068876	69.88423835	2.649907605	-11.89534601
12	5	200	200	10	6.5	0.74612	0.015	68.8255	66.9448	71.13496139	67.12501826	-3.355531587	-0.26920427
13	5	200	200	10	6.5	0.998409	0.015	63.9388	61.3211	62.86747074	60.98628522	1.675554222	0.546002574
14	5	200	200	1	6.5	0.5	0.05	23.6264	9.74102	24.5957971	8.595332503	-4.103025019	11.76147361
15	5	200	200	1.5	6.5	0.5	0.05	32.1096	14.2356	31.13089132	15.70017298	3.048025136	-10.2881015
16	5	200	200	2	6.5	0.5	0.05	36.8868	22.0844	36.6263741	21.86555999	0.706013806	0.990925786
17	5	200	200	3	6.5	0.5	0.05	45.7006	32.9406	44.92217407	31.93015489	1.703316645	3.067476351
18	5	200	200	5	6.5	0.5	0.05	52.5874	44.2378	52.84550685	45.25047297	-0.490815	-2.289157622
19	5	200	200	7	6.5	0.5	0.05	55.7746	52.939	54.50592213	52.10904761	2.274651666	1.567752305
20	5	200	200	9	6.5	0.5	0.05	59.3282	59.0358	59.65428235	59.19852304	-0.549624552	-0.27563452
21	5	200	200	10	6.5	0.5	0.05	61.4774	61.3438	62.67396246	62.07227782	-1.946345265	-1.187532917
22	5	200	200	1.5	6.5	0.5	0.01	36.8268	29.1078	41.07637128	33.67001362	-11.53934438	-15.6735089
23	5	200	200	2	6.5	0.5	0.01	45	44.0912	46.14072707	40.66066433	-2.534949041	7.780545032
24	5	200	200	3	6.5	0.5	0.01	53.8754	59.4818	55.30077087	53.39430273	-2.645680349	10.23421832
25	5	200	200	5	6.5	0.5	0.01	63.805	66.696	66.55789583	68.53672082	-4.314545609	-2.759866886
26	5	200	200	7	6.5	0.5	0.01	69.9968	72.7906	71.69736148	72.85775335	-2.429484599	-0.092255523
27	5	200	200	9	6.5	0.5	0.01	73.2058	75.0966	75.67361393	72.38808945	-3.371063395	3.606701967
28	5	200	200	1	6.5	0.5	0.015	36.9598	21.6912	37.56984602	26.954559	-1.650566333	-24.26495076
29	5	200	200	1.5	6.5	0.5	0.015	48.4038	34.5588	42.45368816	33.55917721	12.29265437	2.892527496
30	5	200	200	2	6.5	0.5	0.015	53.5514	42.647	47.28253732	40.23501895	11.70625358	5.655687506
31	5	200	200	3	6.5	0.5	0.015	60.145	54.7794	55.83469209	52.44298393	7.16652741	4.265136292
32	5	200	200	5	6.5	0.5	0.015	69.2562	64.7058	66.50443722	67.69110687	3.973308937	-4.613661942

33	5	200	200	7	6.5	0.5	0.015	75.036	73.1618	71.65066515	72.47010987	4.511614221	0.945425243
34	5	200	200	9	6.5	0.5	0.015	77.4784	79.4118	75.4438878	71.90816338	2.625908897	9.449019698
35	5	200	200	10	6.5	0.5	0.015	78.8806	81.9854	76.90140904	69.88558622	2.509097248	14.7584982
36	5	200	200	1.5	6.5	0.5	0.02	38.0376	30.263	43.79693825	33.52502843	-15.14117151	-10.7789328
37	5	200	200	2	6.5	0.5	0.02	44.2922	40.004	48.22298195	39.65128783	-8.874659543	0.881692265
38	5	200	200	3	6.5	0.5	0.02	52.7356	51.6728	55.98728947	51.00848503	-6.166023471	1.285618297
39	5	200	200	5	6.5	0.5	0.02	61.8446	62.2308	66.1833777	66.41028375	-7.015612839	-6.716101593
40	5	200	200	7	6.5	0.5	0.02	67.999	70.5602	71.4594659	71.86209203	-5.088995273	-1.84507984
41	5	200	200	9	6.5	0.5	0.02	71.9208	72.4944	74.65768124	70.8036486	-3.805409898	2.332251042

CHAPTER 6

REFERENCES

[1] B. M. Kaličanin, “Determination of very toxic metal — Cadmium in natural water samples,” *Desalination*, vol. 249, no. 1, pp. 58–62, Nov. 2009, doi: 10.1016/j.desal.2009.03.006.

[2] J. A. Cotruvo, “2017 WHO Guidelines for Drinking Water Quality: First Addendum to the Fourth Edition,” *J. AWWA*, vol. 109, no. 7, pp. 44–51, Jul. 2017, doi: 10.5942/jawwa.2017.109.0087.

[3] G. K. Kinuthia, V. Ngure, D. Beti, R. Lugalia, A. Wangila, and L. Kamau, “Levels of heavy metals in wastewater and soil samples from open drainage channels in Nairobi, Kenya: community health implication,” *Sci. Rep.*, vol. 10, no. 1, p. 8434, May 2020, doi: 10.1038/s41598-020-65359-5.

[4] A. L. Wani, A. Ara, and J. A. Usmani, “Lead toxicity: a review,” *Interdiscip. Toxicol.*, vol. 8, no. 2, pp. 55–64, Jun. 2015, doi: 10.1515/intox-2015-0009.

[5] C. F. Carolin, P. S. Kumar, A. Saravanan, G. J. Joshiba, and M. Naushad, “Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review,” *J. Environ. Chem. Eng.*, vol. 5, no. 3, pp. 2782–2799, Jun. 2017, doi: 10.1016/j.jece.2017.05.029.

[6] T.-K. Tran, H.-J. Leu, K.-F. Chiu, and C.-Y. Lin, “Electrochemical Treatment of Heavy Metal-containing Wastewater with the Removal of COD and Heavy Metal Ions,” *J. Chinese Chem. Soc.*, vol. 64, no. 5, pp. 493–502, May 2017, doi: 10.1002/jccs.201600266.

[7] A. Bielen *et al.*, “Negative environmental impacts of antibiotic-contaminated effluents from pharmaceutical industries,” *Water Res.*, vol. 126, pp. 79–87, Dec. 2017, doi: 10.1016/j.watres.2017.09.019.

[8] K. K. Bhatluri, M. S. Manna, P. Saha, and A. K. Ghoshal, “Supported liquid membrane-based simultaneous separation of cadmium and lead from wastewater,” *J. Memb. Sci.*, vol. 459, pp. 256–263, 2014, doi: 10.1016/j.memsci.2014.02.019.

[9] C. V. Bhaskar, K. Kumar, and G. Nagendrappa, “Assessment of Heavy Metals in Water Samples of Certain Locations Situated Around Tumkur, Karnataka, India,” *E-Journal Chem.*, vol. 7, no. 2, pp. 349–352, 2010, doi: 10.1155/2010/415150.

[10] P. Joseph, “Mechanisms of cadmium carcinogenesis☆” *Toxicol. Appl. Pharmacol.*, vol. 238, no. 3, pp. 272–279, Aug. 2009, doi: 10.1016/j.taap.2009.01.011.

[11] S. Mashhadikhan, A. Ebadi Amooghin, H. Sanaeepur, and M. M. A. Shirazi, “A critical review on cadmium recovery from wastewater towards environmental sustainability,” *Desalination*, vol. 535, p. 115815, Aug. 2022, doi: 10.1016/j.desal.2022.115815.

[12] G. V. Iyengar and P. P. Nair, “Global outlook on nutrition and the environment: meeting the challenges of the next millennium,” *Sci. Total Environ.*, vol. 249, no.

1–3, pp. 331–346, Apr. 2000, doi: 10.1016/S0048-9697(99)00529-X.
[13] P. K. Rai, S. S. Lee, M. Zhang, Y. F. Tsang, and K.-H. Kim, "Heavy metals in food crops: Health risks, fate, mechanisms, and management," *Environ. Int.*, vol. 125, pp. 365–385, Apr. 2019, doi: 10.1016/j.envint.2019.01.067.
[14] A. Bashir *et al.*, "Removal of heavy metal ions from aqueous system by ion-exchange and biosorption methods," *Environ. Chem. Lett.*, vol. 17, no. 2, pp. 729–754, Jun. 2019, doi: 10.1007/s10311-018-00828-y.
[15] C. Zhao *et al.*, "A hybrid process of coprecipitation-induced crystallization-capacitive deionization-ion exchange process for heavy metals removal from hypersaline ternary precursor wastewater," *Chem. Eng. J.*, vol. 378, p. 122136, Dec. 2019, doi: 10.1016/j.cej.2019.122136.
[16] M. Alonso, A. López-Delgado, A. M. Sastre, and F. J. Alguacil, "Kinetic modelling of the facilitated transport of cadmium (II) using Cyanex 923 as ionophore," *Chem. Eng. J.*, vol. 118, no. 3, pp. 213–219, May 2006, doi: 10.1016/j.cej.2006.02.006.
[17] N. H. 1531-1541. Park, K. H., Parhi, P. K., & Kang, "Studies on removal of low content copper from the sea nodule aqueous solution using the cationic resin tp 207.," *Sci. Technol.*, vol. 47, pp. 1531–1154, 2011.
[18] M. M. Matlock, B. S. Howerton, and D. A. Atwood, "Chemical precipitation of heavy metals from acid mine drainage," *Water Res.*, vol. 36, no. 19, pp. 4757–4764, Nov. 2002, doi: 10.1016/S0043-1354(02)00149-5.
[19] Q. Wang *et al.*, "Non-thermal plasma oxidation of Cu(II)-EDTA and simultaneous Cu(II) elimination by chemical precipitation," *J. Environ. Manage.*, vol. 248, p. 109237, Oct. 2019, doi: 10.1016/j.jenvman.2019.07.008.
[20] F. Fu, L. Xie, B. Tang, Q. Wang, and S. Jiang, "Application of a novel strategy-Advanced Fenton-chemical precipitation to the treatment of strong stability chelated heavy metal containing wastewater," *Chem. Eng. J.*, vol. 189–190, pp. 283–287, 2012, doi: 10.1016/j.cej.2012.02.073.
[21] K. P. Lee, T. C. Arnot, and D. Mattia, "A review of reverse osmosis membrane materials for desalination-Development to date and future potential," *J. Memb. Sci.*, vol. 370, no. 1–2, pp. 1–22, 2011, doi: 10.1016/j.memsci.2010.12.036.
[22] F. S. Hoseinian, B. Rezai, E. Kowsari, and M. Safari, "A hybrid neural network/genetic algorithm to predict Zn(II) removal by ion flotation," *Sep. Sci. Technol.*, vol. 55, no. 6, pp. 1197–1206, Apr. 2020, doi: 10.1080/01496395.2019.1582543.
[23] H. Saleem, P. Pal, M. A. Haija, and F. Banat, "Regeneration and reuse of bio-surfactant to produce colloidal gas aphrons for heavy metal ions removal using single and multistage cascade flotation," *J. Clean. Prod.*, vol. 217, pp. 493–502, Apr. 2019, doi: 10.1016/j.jclepro.2019.01.216.
[24] Y. Sun, S. Zhou, S.-Y. Pan, S. Zhu, Y. Yu, and H. Zheng, "Performance evaluation and optimization of flocculation process for removing heavy metal," *Chem. Eng. J.*, vol. 385, p. 123911, Apr. 2020, doi: 10.1016/j.cej.2019.123911.
[25] Q. Zhang *et al.*, "Cumulative effects of pyrolysis temperature and process on properties, chemical speciation, and environmental risks of heavy metals in magnetic biochar derived from coagulation-flocculation sludge of swine

wastewater," *J. Environ. Chem. Eng.*, vol. 8, no. 6, p. 104472, Dec. 2020, doi: 10.1016/j.jece.2020.104472.

[26] U. Upadhyay, I. Sreedhar, S. A. Singh, C. M. Patel, and K. L. Anitha, "Recent advances in heavy metal removal by chitosan based adsorbents," *Carbohydr. Polym.*, vol. 251, p. 117000, Jan. 2021, doi: 10.1016/j.carbpol.2020.117000.

[27] T. Wu *et al.*, "Amidoxime-Functionalized Macroporous Carbon Self-Refreshed Electrode Materials for Rapid and High-Capacity Removal of Heavy Metal from Water," *ACS Cent. Sci.*, vol. 5, no. 4, pp. 719–726, Apr. 2019, doi: 10.1021/acscentsci.9b00130.

[28] N. M. Kocherginsky, Q. Yang, and L. Seelam, "Recent advances in supported liquid membrane technology," *Sep. Purif. Technol.*, vol. 53, no. 2, pp. 171–177, 2007, doi: 10.1016/j.seppur.2006.06.022.

[29] P. K. Parhi, "Supported liquid membrane principle and its practices: A short review," *J. Chem.*, vol. 2013, 2013, doi: 10.1155/2013/618236.

[30] A. Gabelman and S.-T. Hwang, "Hollow fiber membrane contactors," *J. Memb. Sci.*, vol. 159, no. 1–2, pp. 61–106, Jul. 1999, doi: 10.1016/S0376-7388(99)00040-X.

[31] E. Alpaydin, "Introduction to Machine Learning (Adaptive Computation and Machine Learning series)," *MIT Press Cambridge*, p. 584, 2009, [Online]. Available: http://www.amazon.com/Introduction-Machine-Learning-Adaptive-Computation/dp/026201243X

[32] D Hammerstrom, "Neural networks at work," *IEEE Spectr.*, 1993.