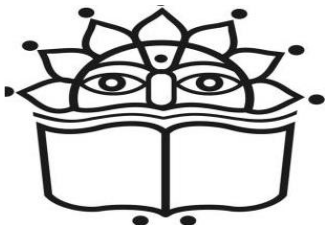

Vidya Pratishthan's Kamalnayan Bajaj Institute of Engineering and Technology, Baramati

Department of Civil Engineering

A

project report on

Prediction of Copper Ion Breakthrough Curve using Artificial Neural Network

In the partial fulfilment of the requirement for Bachelor Degree in Civil Engineering

Submitted by

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CERTIFICATE

This is to certify that the following students have satisfactorily carried out the project-I work entitled **"Prediction of Copper ion Breakthrough Curve using Artificial Neural Network".**

This work is being submitted for the award of Degree of Bachelor of Civil Engineering. It is submitted in the partial fulfillment of the prescribed syllabus of Savitribai Phule Pune University, Pune of B.E (2015 Course) for the academic year 2020-2021.

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LIST OF NOTATIONS

Influent Concentration	C_o
Effluent Concentration	C_t
Rate constant of Adams-Bohart model	K_{AB}
Linear Velocity	u_o
Bed Depth	Z
Maximum Iron Adsorbtion Capacity Per Unit Volume of Adsorbent Column	N_o
Thomas Rate Constant	K_{th}
Equilibrium uptake per g of adsorbent	q_o
Mass of Adsorbent	w
Flow rate	v
time	t

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ABSTRACT

Adsorption kinetic, equilibrium and column studies are used to investigate removal of metal ions from aqueous phase. The adsorption column data in the form of breakthrough curve is used for the design of adsorption column for industrial/domestic water/wastewater treatment. Several mathematical models which are available to predict the experimental breakthrough curve data, do not describe the data all the time. Hence, present work aims at investigating the suitability of backpropogation artificial neural network technique (BP-ANN) to predict Cu^{2+} breakthrough curve. It was observed that predicted values using BP-ANN method are closely matching with the experimental data. Higher R^2 value of 0.996 and lower RMSE value of 0.011 further justified the suitability of BP-ANN method to predict the Cu^{2+} breakthrough curve.

CHAPTER 1
INTRODUCTION

1.1 General

Water in its purest form is tasteless, colorless and odour less liquid and is regarded as a universal solvent. It has the ability to dissolve more substances than any other liquid. Owing to this single most attribute of water, it tends to easily become polluted with numerous substances that makes it unfit for many beneficial uses in day-to-day life (Hegazi, 2013).

Heavy metals are of environmental concern because of adverse effects they cause to human health and the environment. These are released into the environment by both natural and anthropogenic activities. The natural sources are dominated by parent rocks and metallic minerals, while the anthropogenic sources are agricultural activities, metallurgical activities, energy production and transportation and so on (Celik and Demirbas, 2005; Kjellstrom et al., 1977; Pastircakova, 2004). Heavy metals exist in aqueous waste streams of many industries like metallurgical and metal manufacturing, electroplating, chemical manufacturing, printing, dye and paint industry, paper, textile, refinery and petrochemicals, leather goods manufacturing, fertilizer and pesticides industry and so on. The heavy metals find their way into the aquatic bodies along with the wastewater effluent released by industries without adequate or no treatment at all. The presence of heavy metals may pose a great environmental hazard if it enters the freshwater sources used for domestic purposes (Celik and Demirbas, 2005; Kjellstrom et al., 1977; Pastircakova, 2004). Moreover, heavy metal accumulated in soil over a long period of time when washed off by rain may dissolve in the irrigation water and ultimately enter the food chain through consumable crops.

In the recent past years, different treatment techniques have been developed to remove heavy metals from aquatic systems. Although various treatments such as chemical precipitation, coagulation–flocculation, flotation, ion exchange and membrane filtration can be employed to remove heavy metals from contaminated wastewater, they have their inherent advantages and disadvantages in application (Kurniawan et al., 2006).

Owing to growing interest in the development of novel and innovative treatment processes, adsorption has emerged as one of the most promising techniques due to their proven efficiency in the removal of heavy metals from the water/wastewater present in trace level (Choy et al., 2000; Febrianto et al., 2009; Gupta et al., 2001). The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. In addition, adsorbents can be regenerated by suitable desorption process (Fu and Wang, 2011). The adsorption separation is based on two distinct mechanisms: Equilibrium, and kinetic mechanisms. The equilibrium mechanism is based on the solid having different abilities to accommodate different species, that is the stronger adsorbing species is preferentially removed by the solid. The kinetic mechanism is based on the different rates of diffusion of different species into the pore; thus by controlling the time of exposure the faster diffusing species is preferentially removed by the solid (Do, 1998).

Several authors have investigated adsorption of single metal ion from solution using different types of adsorbents (Ayoob & Gupta, 2008; Febrianto et al., 2009; Gupta et al., 2001; Kadirvelu et al., 2001; Mohan & Singh, 2002). These studies have tried to investigate potential of various adsorbent to remove single metal ion from the aqueous phase by carrying out experiments with different environmental/operational conditions such as effect of pH, agitation/mixing, dose of adsorbent, initial concentration of adsorbate, variation in temperature etc. in batch mode studies as well as continuous mode column studies.

Although batch adsorption studies provide useful information on the application of adsorption to the removal of specific waste constituents, continuous column studies provide the most practical application of this process in wastewater treatment. In batch mode adsorption studies, the same solution remains in contact with a given quantity of the adsorbent. The adsorption process continues, however, till equilibrium between the solute concentration in solution, and the solute adsorbed per unit weight of the adsorbent is reached. This equilibrium established is static in nature, as it does not change further with time. In dynamic column adsorption, solution continuously enters and leaves the column, so that the complete equilibrium is never established at any stage between the solute in solution and the amount adsorbed. Equilibrium has to be continuously established, as each time, it meets the fresh concentrations,

and hence, equilibrium in column mode is termed as dynamic equilibrium. Additional information on the efficiency of the treated adsorbent in the column mode has been gathered in order to ascertain the practical applicability of the adsorbent for real industrial wastewaters (Dwivedi et al., 2008).

The continuous mode column adsorption study generally involves the application of mechanistic and phenomenological models such as mass transfer equations (Moreno-Pérez et al., 2018). These models are developed considering certain assumptions and may show some limitations for the simulation of adsorption breakthrough curves in multicomponent solutions (Moreno-Pérez et al., 2018; Jani et al., 2017). The application of alternate models is an option for the breakthrough analysis especially in multi-component adsorption. Artificial neural networks (ANNs) are reliable and flexible alternative models that can be used to simulate challenging processes (Moreno-Pérez et al., 2018; Jani et al., 2017). This type of models is able to model multivariable systems and can be used to identify non-linear relationships between independent and dependent variables.

1.2 Problem Statement

Adsorption is widely used technique for the removal of heavy metal ions and data obtained under continuous mode column studies is used to design adsorption columns for industrial applications. Several mathematical models are used to predict the breakthrough curves of metals ions and consequently required design parameters. However, these models are suitable to describe all the experimental breakthrough data. Hence, present work investigates the suitability of Artificial Neural Network technique to predict the breakthrough curve.

1.3 Objectives of the work

Adsorption is widely used technique for the removal of heavy metal ions. In the recent past years, the artificial intelligence field have gained favour to model the adsorption column breakthrough data. The Artificial Neural Network (ANN) is inductive approach able to establish non-linear connections between a set of input data and its output, without needing sophisticated theory. Therefore, present work aims at:

- predicting adsorption breakthrough curve for the removal of selected metal ion using the Artificial Neural Network (ANN) technique.

1.4 Expected outcome

Available mathematical models are not suitable to describe obtained breakthrough curve for metal ions adsorption onto adsorbent. Artificial Neural Network may be used as efficient and precise technique for the prediction of metal adsorption breakthrough curve.

CHAPTER 2
LITERATURE REVIEW

2.1 Heavy metals in environment

All industrial operations dealing with heavy metals either as raw materials or finished products produce wastewater containing dissolved heavy metal ions as one of the prime contaminants. If dissolved heavy metals are not separated from the waste stream, it may find its path to the environment – a matter of serious concern. The prime heavy metals in the wastewater of some of the important industries are listed in Table 2.1.

Table 2.1: Heavy metal ions in industrial wastewater (Bradl, 2005; Tchobanoglous et al., 2003)

Industries	Heavy metals
Battery Recycling Units	Lead, Arsenic, Cadmium
Lead Smelting	Lead, Mercury, Cadmium
Mining and Ore processing	Lead, Mercury, Cadmium, Chromium, Arsenic
Tanneries	Chromium
Industrial/Municipal dumpsite	Lead, Chromium
Industrial Estates	Lead, Chromium
Artisanal Gold Mining	Mercury
Product Manufacturing	Lead, Chromium, Cadmium, Arsenic, Mercury
Chemical Manufacturing	Arsenic, Chromium, Mercury, Cadmium, Lead
Dye Industry	Chromium, Lead, Cadmium, Arsenic
Petrochemical Processing	Lead, Chromium, Cadmium
Electronic Waste Recycling	Lead, Chromium, Cadmium
Electroplating	Cadmium, Lead, Nickel
Heavy Industries	Chromium, Cadmium, Arsenic

2.2 Removal of heavy metals

The conventional processes for removing heavy metals from wastewater include many processes such as chemical precipitation, flotation, adsorption, ion exchange, and electrochemical deposition (Fu and Wang, 2011). Precipitation is the most commonly applicable technique and is considered to be the most economical. It is widely used for heavy metal removal from inorganic effluent (Ghosh et al., 2011). In precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates. The forming precipitates can be separated from

the water by sedimentation or filtration, the treated water is then decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation and sulfide precipitation (Fu and Wang, 2011). However, precipitation is accompanied by formation of large amounts of sludge contaminated with toxic heavy metals. Metal bearing sludge–especially metal-hydroxide sludge is inherently susceptible to leaching into groundwater when sludge is disposed of in landfills.

Ion exchange processes have been widely used in the treatment of industrial wastewater due to their many advantages, such as high treatment capacity, high removal efficiency, and fast kinetics (Kang et al., 2004). The most common cation exchangers are strongly acidic resins with sulfonic acid groups (–SO_3H) and weakly acid resins with carboxylic acid groups (–COOH). Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations. As the solution containing heavy metal passes through the cations column, metal ions are exchanged for the hydrogen ions on the resin (Fu and Wang, 2011). Most of the ion exchange resins are expensive and release other cations such as H^+ or Na^+ in aqueous solution. Process efficiency is strongly pH dependent as most metals bind better at higher pH, due to less competition from protons for adsorption sites (Tchobanoglous et al., 2003). High concentrations of influent total suspended solids can plug the ion exchange bed and cause high head loss and inefficient operation. The exhausted ion-exchange medium is highly concentrated with toxic heavy metal ions and requires careful disposal. Presence of oxidants, particles, solvents and polymers may affect the performance of ion-exchange resins.

Membrane filtration technologies with different types of membranes show great promise for heavy metal removal for their high efficiency, easy operation and space saving. The membrane processes used to remove metals from the wastewater are ultra-filtration, reverse osmosis, nano-filtration and electro-dialysis (Fu and Wang, 2011). These membrane processes are expensive, as high capital and operating costs are required by the higher energy input to develop pressure needed for operation (Tchobanoglous et al., 2003). Other recognizable limitations include membrane fouling and deterioration with time resulting from deposition of soluble materials, organic materials, suspended and colloidal particles and other contaminants thus requiring high level of pre-treatment.

Coagulation and flocculation followed by sedimentation and filtration is also employed to remove heavy metal from wastewaters (Fu and Wang, 2011). The removal of heavy metals by coagulation using coagulants such as ferric chloride and poly-aluminium chloride (PAC) etc. have yielded excellent heavy metal removal from effluent (El Samrani et al., 2008).

The methods described previously to remove heavy metals from water/wastewater are expensive or ineffective, especially when the metal concentration is less than 100 ppm (Miretzky et al., 2006; Schiewer and Volesky, 1995). The sludge generated in the precipitation method poses challenges in its handling, treating and land-filling. Ion exchange usually requires a high capital cost of the equipment as well as a high operational cost due to the use of chemicals for resin regeneration. Electrolysis allows the removal of metal ions from the solution in a solid metallic form for recycling. The advantage of this method is that there is no need for additional chemicals, and hence, there is no sludge generation. However, it is inefficient at a low metal concentration. Membrane processes such as reverse osmosis and electro-dialysis tend to suffer from the instability of the membranes in salty or acidic conditions and fouling by inorganic and organic substances present in wastewater (Doan et al., 2008).

The advantage and disadvantages of various physico-chemical methods for treatment of heavy metal in wastewater are presented in Table 2.2. Among these processes adsorption is the most commonly used technique for the removal of heavy metal ions due to easy availability of adsorbent material and its high efficiency for the removal of metal ions at trace level present in solution.

2.3 Adsorption

Although all the above methods have been applied for the removal of heavy metals from wastewater, most of the techniques have some limitations such as requirement of several pre-treatments as well as additional treatments. In addition; some of them are less effective and require high capital cost (An et al., 2001). Among all the above techniques, adsorption is most commonly adopted due to easy availability of good adsorbent, low cost and their removal efficiency of metal even at very low concentration (Srivastava et al., 2007). Adsorption is a

process that occurs when a solute accumulates from the liquid phase to the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (Kumar and Awasthi, 2009).

The key point of adsorption process is to use an adsorbent with sufficiently high selectivity, capacity and re-generativity. Some of the major industrially used adsorbents are activated alumina, activated carbon, zeolite, silica gel, molecular sieve carbon, molecular sieve zeolites and polymeric adsorbents. Attention has been given on the various adsorbents, which have metal-binding capacities and are able to remove unwanted heavy metals from contaminated water at low cost. Because of their low cost and local availability, natural materials such as chitosan, zeolites, clay, or certain waste products from industrial operations such as fly ash, coal, and oxides are classified as low-cost adsorbents (Babel and Kurniawan, 2003).

2.3.1 Batch adsorption studies

Adsorption is one of the most widely used techniques for pollutant removal from contaminated systems. The process of adsorption as a metal removal technique is understood by carrying out batch kinetics and equilibrium studies.

Kinetic mechanism:

In the past decades, several mathematical models have been proposed to describe adsorption data, which can generally be classified as adsorption reaction models and adsorption diffusion models. At present, adsorption reaction models have been widely developed to describe the kinetic process of adsorption (Srivastava et al., 2007). Among these models, the most commonly used are pseudo-first and pseudo-second-order kinetic models.

Equilibrium Mechanism

Proper analysis and design of adsorption processes requires relevant adsorption equilibria as one of the vital information. In equilibrium, a certain relationship prevails between solute concentration in solution and adsorbed state (i.e., the amount of solute adsorbed per unit mass of adsorbent). Their equilibrium concentrations are a function of temperature. Therefore, the adsorption equilibrium relationship at a given temperature is referred as adsorption isotherm.

Table 2.2: Advantages and disadvantages of various physico-chemical methods used for removal of heavy metals from wastewaters (Sources: Fu and Wang, 2011).

Sr. No.	Removal Process	Advantages	Disadvantages
1	Chemical precipitation (when metal conc. more than 1000 mg/l)	Metals are precipitated as sulfides, hydroxides and carbonates. Low-cost process. Simple process, inexpensive equipment requirement, and convenient and safe operations.	Chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Other drawbacks are its excessive sludge production that requires further treatment, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal. Ineffective when metal ion concentration is low.
2	Ion exchange method	It is environment friendly, can provide high flow rate of treated water and has low maintenance cost.	It cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids present in the wastewater. Ion exchange is nonselective and is highly sensitive to pH of the solution. Ion-exchange resins must be regenerated by chemical reagents when they are exhausted and the regeneration can cause serious secondary pollution. It is expensive, especially when treating a large volume of wastewater containing heavy metal in low concentration, hence limits its use at large scale.
3	Electrolytic recovery or electro-winning	Metal deposited on electrodes are strippable and recoverable. Require fewer chemicals, provide good reduction yields and produce less sludge.	Corrosion could become a significant limiting factor, where electrodes would frequently have to be replaced. High initial capital investment and the expensive electricity supply.
4	Membrane filtration	High efficiency since it is capable of removing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals.	High cost, process complexity, membrane fouling and low permeate flux limits their use in heavy metal removal.
5	Floatation	High metal selectivity, high removal efficiency, high overflow rates, low detention periods, low operating cost and production of more concentrated sludge.	High initial capital cost, high maintenance and operation costs.
6	Adsorption	Low-cost, easy operating conditions, having wide pH range, high metal binding capacities.	Low selectivity, production of waste products.

Several adsorption isotherms originally used for adsorption are available and readily adopted to correlate adsorption equilibria in heavy metals adsorption. Some well-known ones are Freundlich, Langmuir, The Temkin and Sips equation (Srivastava et al., 2007). The most widely used among them are Freundlich and Langmuir equations (Febrianto et al., 2009).

2.3.2 Column studies

Although batch adsorption studies provide useful information on the application of adsorption to the removal of specific waste constituents, continuous column studies provide the most practical application of this process in wastewater treatment. In batch mode adsorption studies, the same solution remains in contact with a given quantity of the adsorbent. The adsorption process continues, however, till equilibrium between the solute concentration in solution, and the solute adsorbed per unit weight of the adsorbent is reached. This equilibrium established is static in nature, as it does not change further with time. In dynamic column adsorption, solution continuously enters and leaves the column, so that the complete equilibrium is never established at any stage between the solute in solution and the amount adsorbed. Equilibrium has to be continuously established, as each time, it meets the fresh concentrations, and hence, equilibrium in column mode is termed as dynamic equilibrium. Additional information on the efficiency of the treated adsorbent in the column mode has been gathered in order to ascertain the practical applicability of the adsorbent for real industrial wastewaters (Dwivedi et al., 2008).

As the adsorbate solution passes through column, the adsorption zone (where the bulk of adsorption takes place) starts moving out of the column and the effluent concentration start rising with time. This is termed as break point. The time taken for the effluent concentration to reach a specific breakthrough concentration of interest is called the breakthrough time (Goel et al., 2005). For most adsorbent–pollutant systems, the breakthrough curve is obtained after an effluent concentration of 50% has been reached. To facilitate the calculations of the bed adsorption capacity, the breakthrough curve is often fixed at 50 %, sometimes at 10 % of the inlet concentration according to the target quality of the final effluent (Tchobanoglous et al.,

2003). The point of the column exhaustion is the point where the effluent concentration reaches 95 % of its influent value.

Many mathematical models have been proposed for the evaluation of efficiency and applicability of the column models for large scale operations. Some of the well known models are Adams-Bohart, BDST, Thomas, and Yoon-Nelson.

The Adams–Bohart model: Adams–Bohart model (Bohart & Adams, 1920) based on the surface reaction theory assumes that equilibrium is not instantaneous; therefore, the rate of the adsorption is proportional to the adsorption capacity which still remains on the sorbent. This model established the fundamental equations describing the relationship between C_t/C_o and t in a continuous system. The Adam's–Bohart model is used for the description of the initial part of the breakthrough curve and is expressed as:

$$\frac{C_t}{C_o} = \exp\left(k_{AB} C_o t - k_{AB} N_o \frac{z}{u_o} \right) \tag{2.1}$$

where, C_o and C_t (meq/L) are the influent and effluent concentrations respectively, k_{AB} [L/(meq.min)] is rate constant of Adams-Bohart model, u_o (cm/min) is the linear velocity calculated by dividing the flow rate by the column section area, z (cm) is the bed depth of column and N_o (meq/L) is maximum ion adsorption capacity per unit volume of adsorbent column. The linear form of Adams-Bohart model is expressed as:

$$\ln\left(\frac{C_t}{C_o} \right) = k_{AB} C_o t - k_{AB} N_o \frac{z}{u_o} \tag{2.2}$$

Thomas model: The basic assumptions of Thomas model are: (i) negligible axial and radial dispersion in the fixed bed column (ii) the adsorption is described by a pseudo-second-order reaction rate principle which reduces a Langmuir isotherm at equilibrium (iii) constant column void fraction (iv) constant physical properties of the biomass (solid-phase) and the fluid phase (v) isothermal and isobaric process conditions (vi) the intra particle diffusion and external resistance during the mass transfer processes are considered to be negligible (Dolphen et al., 2007). The linearized form of Thomas model can be expressed as follows:

$$\ln\left(\frac{C_o}{C_t}-1\right)=\frac{k_{Th}q_o w}{\nu}-k_{Th}C_o t \qquad (2.3)$$

where, k_{Th} [mL/(min.meq)] is the Thomas rate constant; q_o (meq/g) is the equilibrium uptake per g of the adsorbent; C_o (meq/L) is the influent concentration; C_t (meq/L) is the effluent concentration at time t; w (g) the mass of adsorbent and ν (mL/min) the flow rate. A linear plot of $\ln[(C_o/C_t)-1]$ against time (t) was employed to determine values of q_o and k_{Th} from the intercept and slope of the plot. The column data were fitted to the Thomas model to determine the Thomas rate constant (k_{Th}) and maximum solid phase concentration (q_o).

Adsorption column studies:

Fixed bed columns are commonly used in large-scale wastewater treatment because of their maximum application in adsorption capacity with high effluent quality. Adsorption only occurs in a particular region of the bed, known as the mass transfer zone (MTZ), which moves through the bed. Applications of fixed bed adsorption, also called percolation, include the removal of dissolved anions and cations from water. Adsorbent particles have finite capacity for fluid phase molecules. Packed-bed column is the common process configuration used for the adsorption of pollutants from industrial streams, groundwater and wastewaters in large-scale applications. The determination of several operating parameters of adsorption columns implies the analysis of breakthrough curves. In particular, the modeling of packed-bed adsorption of water pollutants is challenging due to the nonlinear behavior of the adsorption process that depends on the number of adsorbates, pH, temperature, feed flow and column characteristics. Furthermore, the mathematical models which are developed considering certain assumptions have some limitations for the simulation of adsorption breakthrough curves (Moreno-Pérez et. al, 2018). Mass transfer equations also require different parameters that are usually obtained from empirical correlations. As an alternative, the use of intelligent algorithms can be used to predict these adsorption data. The artificial intelligence field allowed the development of information processing systems based on human brain structures. The Artificial Neural Network (ANN) is inductive approach able to establish non-linear connections between a set of input data and its output, without needing sophisticated theory. In this context, the present work investigates the capability of ANN in predicting the breakthrough curves of Cu^{2+} adsorbed onto activated alumina.

CHAPTER 3
MATERIAL AND METHODS

3.1 Experimental copper breakthrough data

The experimental copper (Cu^{2+}) breakthrough data has been taken from the Ph.D thesis (Patil and Jawed, 2016) for investigating the suitability of Artificial Neural Network technique to describe the Cu^{2+} breakthrough curve. The Cu^{2+} breakthrough data has been obtained by passing 0.60 meq/L of Cu^{2+} solution through granular activated alumina (GAA) bed depth of 3 cm with flow rate of 2 mL/min.

3.2 Artificial neural network (ANN)

The neural network is a mathematical method for learning based on biological nervous systems. The neuron is the basic (fundamental) unit in the ANN and interacts with other neurons by means of connections. The input of the neuron is given by weighted sum output of the previous layer (Padhila et al., 2015). An artificial neural network is a computer model derived from a simplified concept of the brain. It is a parallel distribution processing system composed of nodes (neurons) and connections (weights), and is based on the principle that a highly interconnected system of simple processing elements that can learn complex interrelationships between independent and dependent variables. Neurons are single processing elements, which connected to neurons in the next layer and therefore forming different types of ANNs. The most popular ANN is the back-propagation ANN (BP-ANN), which belongs to the class of supervised learning techniques because the method consists in comparing the response of the output units to the desired responses via an iterative process in which an error term is calculated and used to readjust the weights in the network in order to obtain network responses close to the desired responses. Its most important feature is the ability to learn from examples and to generalize, since the learnt information is stored across the network weights. Neural networks do not require the explication of a mathematical model. The final model is built through a continuous and iterative adjustment of weights which, in fact, reflect the relationship of input variables and output variables that are the parameters and results in our experiments. Thus, it is not surprising that BP-ANN has gained momentum in numerous industrial and scientific areas.

3.2.1 ANN topology

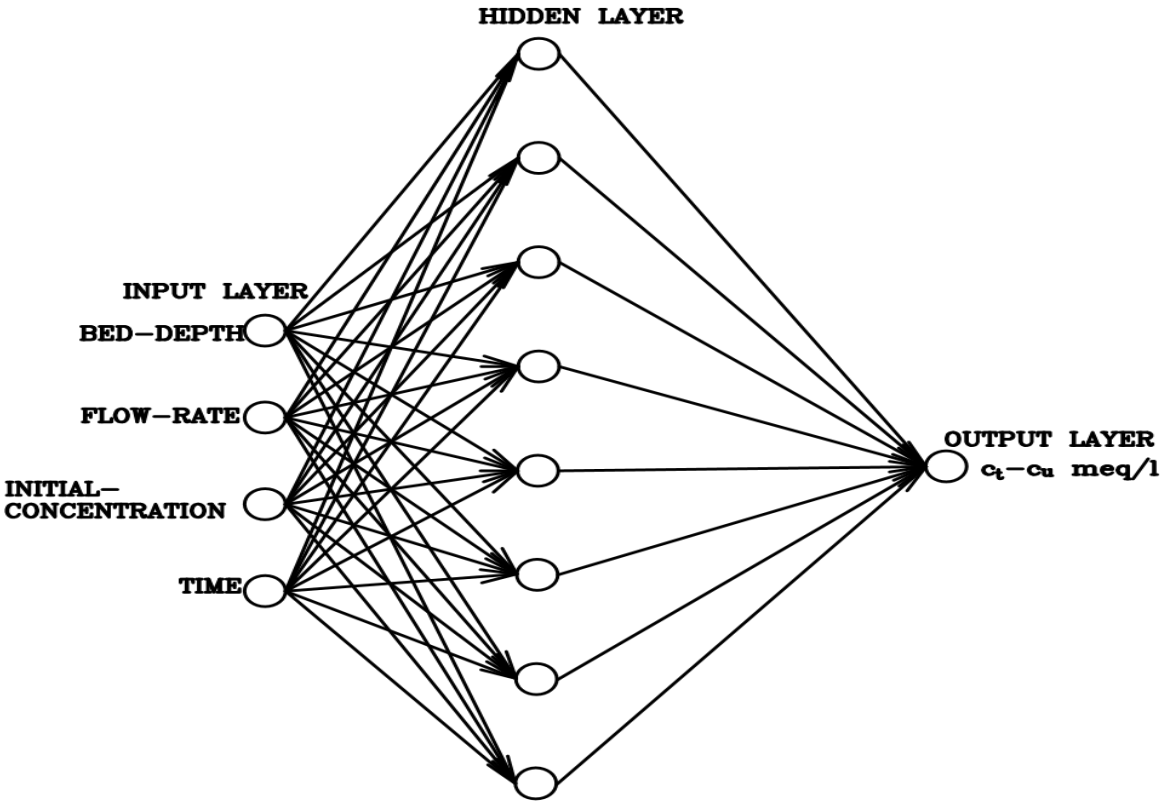

Fig. 3.1: Structure of the BP-ANN model used for the prediction of Cu^{2+} metal ion breakthrough curve.

Fig. 3.1 shows the BP-ANN topology which depicts three types of layers: one input layer, one hidden layer and one output layer. The universal approximation theorem suggests that a network with one hidden layer with a sufficient number of neurons can in principle relate any given set of inputs to a set of outputs to an arbitrary degree of accuracy. As a result, the neural network used in this work is equipped with one hidden layer. The action of the neurons in hidden and output layers is summing weighted inputs and produces an output signal through a transfer function (activation function) and for the neurons in input layer the input is directed to the output. As is the usual practice, an additional neuron, called the bias neuron, which do not take any input and they emit a constant output value of 1 to the neurons in the next layer, is added to the input and hidden layers in order to meet the universal approximation property of the network (relating inputs to outputs).

3.2.2 ANN flowchart

Fig. 3.2 shows the flowchart of BP-ANN method used to predict the breakthrough curve of selected Cu^{2+} metal ion. In this input parameters are bed depth, flow rate, initial concentration of selected Cu^{2+} metal ion and time. And output parameter is effluent concentration of selected Cu^{2+} metal ion. Thereafter data is split into two different sets. These two sets are the training set and the testing set. The training set is used for training the model and the testing set is used for testing the accuracy of the model. Out of the total data available, 100% data is used for training the model and 100% data is used for testing the model. Then data is preprocessed using standard scalar class in python. it will transform your data such that its distribution will have a mean value 0 and standard deviation of 1. Thereafter, using sequential model, data is processed with the help of 4 input neurons, 1 output neuron and 1 hidden layer which consists of 8 neurons and activation (Sigmoid). Activation function decides, whether a neuron should be activated or not by calculating weighted sum and further adding bias with it. The purpose of the activation function is to introduce non-linearity into the output of a neuron. Then this data is fitted into model as train and test data. Furthermore, training process is done using 700 epochs and 1 batch size. For the optimization purpose, Adam optimizer is used. Thereafter, weights are updated using root mean square error function and improve accuracy. In this method, 700 iterations are done to arrive at minimal root mean square value and maximum accuracy. Then the graph is plotted between experimental and predicted values.

3.3 Mathematical Model

3.3.1 Artificial Neural Network

A network consists of just one hidden layer containing eight neurons. The single neuron receives input from the prior input layer, does computations, and sends the result away. We have four inputs here, X_1, X_2, X_3, X_4, with weights W_1 to W_{40} respectively. The neuron applies a function f to the dot-product of these inputs, which is $W_1X_1 + W_2X_2 + ... + W_nX_n + b$. Besides the four numerical input values, there is one input value 1 with weight b, called the Bias. The main function of bias is to stand for unknown parameters or unforeseen factors.

In the input layer, we send four numerical inputs through 4 units

$$X = X_1, X_2, ..., X_n \mid X \in R \text{ and } R=4$$

Randomly assign weights for them at the first place

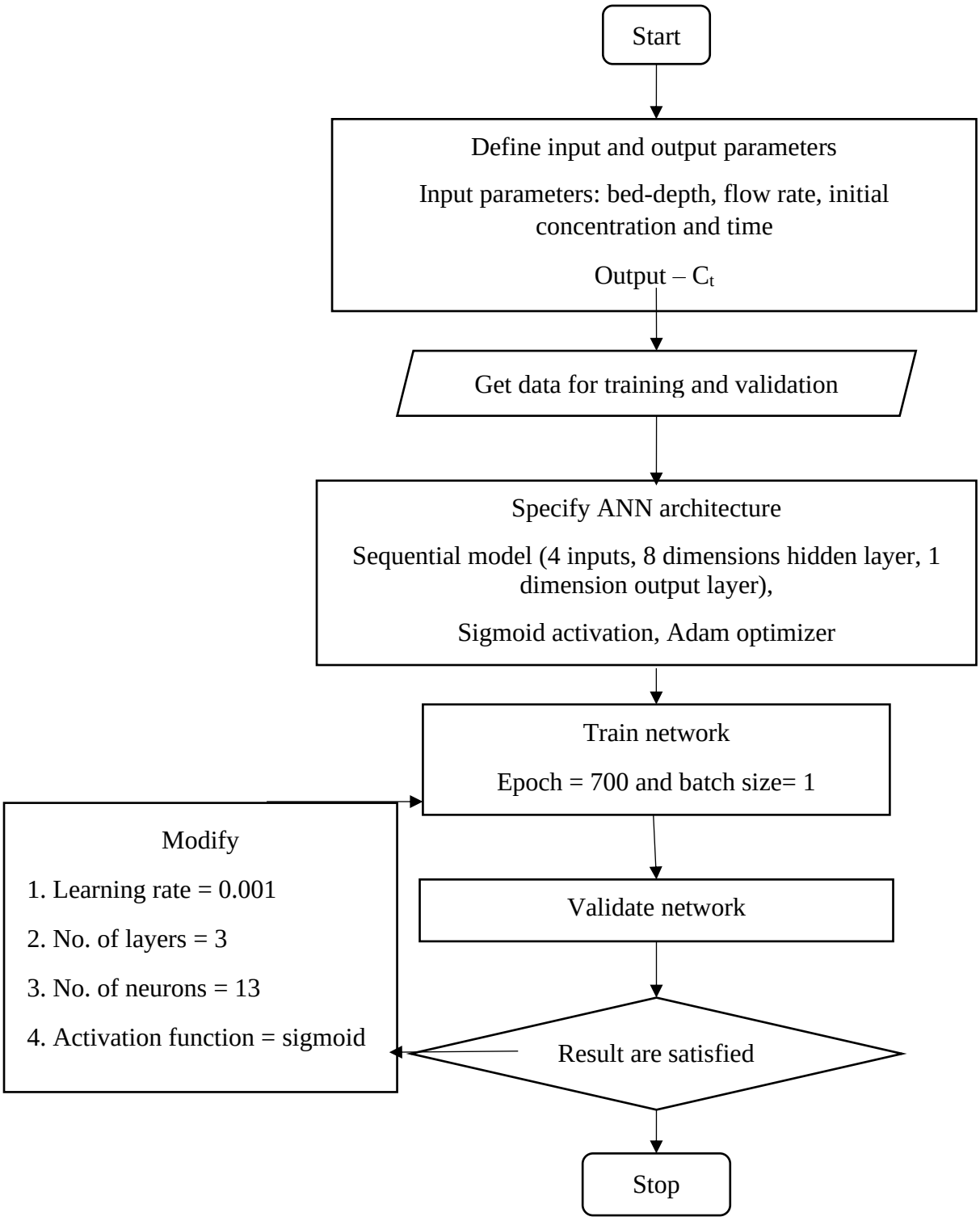

Table 3.2: Flow chart of BP-ANN used to predict breakthrough curve of Cu^{2+} adsorption onto GAA.

$W = W_1, W_2, ..., W_{40}$

The values for weights will be adjusted later in the training process

$$Z = W_1 \cdot X_1 + W_2 \cdot X_2 + ... + W_n \cdot X_n + b$$

$$Z = \sum_{i=1}^{n} XiWi + b \qquad \text{……(Input for neurons)}$$

Activation Function:

An activation function in a neural network defines how the weighted sum of the input is transformed into an output from a node or nodes in a layer of the network. If the output range of the activation function is limited, then it may be called a "squashing function." Many activation functions are nonlinear and may be referred to as the "nonlinearity" in the layer or the network design. The choice of activation function has a large impact on the capability and performance of the neural network, and different activation functions may be used in different parts of the model. The activation function is used within or after the internal processing of each node in the network, although networks are designed to use the same activation function for all nodes in a layer. A network may have three types of layers: input layers that take raw input from the domain, hidden layers that take input from another layer and pass output to another layer, and output layers that make a prediction. Activation functions are also typically differentiable, meaning the first-order derivative can be calculated for a given input value. This is required given that neural networks are typically trained using the backpropagation of error algorithm that requires the derivative of prediction error in order to update the weights of the model.

Sigmoid function:

Activation functions is the sigmoid function which is defined as: $\mathbf{f(x) = 1/ 1 + e^{-x}}$

Sigmoid function outputs in the range (0, 1), it makes it ideal for linear regression problems where we need to find the probability of the data belonging to a particular class.

$$a = \text{sigmoid}(Z)$$

$$a = \text{sigmoid}\left(\sum_{i=1}^{n} XiWi + b\right)$$

$$a = \mathbf{1/ 1 + e^{-}}\left(\sum_{i=1}^{n} XiWi + b\right)$$

Training model:

Training an Artificial Neural Network. Once a network has been structured for a particular application, that network is ready to be trained. To start this process the initial weights are chosen randomly.

Epoch:

An epoch refers to one cycle through the full training dataset. Usually, training a neural network takes more than a few epochs. An epoch means training the neural network with all the training data for one cycle. In an epoch, we use all of the data exactly once. A forward pass and a backward pass together are counted as one pass. If the batch size is 1, we can complete an epoch with a 700 iteration. Simply, for each epoch, the required number of iterations times the batch size gives the number of data points. We can use multiple epochs in training. In this case, the neural network is fed the same data more than once. In this training process weight updated and improve accuracy.

Calculate loss (MSE):

Mean Squared Error loss, is calculated as the average of the squared differences between the predicted and actual values.

$$\text{MSE} = (\text{Actual value} - \text{Predicted value})^2$$

Calculate Error gradient:

An error gradient is the direction and magnitude calculated during the training of a neural network that is used to update the network weights in the right direction and by the right amount. the gradient as the multi-variable derivative of the loss function with respect to all the network parameters(weights).

$$\text{Gradient} = \frac{\partial\,(Loss)}{\partial(weight)}$$

3.3.2 Backpropagation

Optimizer:

Loss tells us how poorly the model is performing at that current instant. Now we need to use this loss to train our network such that it performs better. Essentially what we need to do is to

take the loss and try to minimize it, because a lower loss means our model is going to perform better. The process of minimizing (or maximizing) any mathematical expression is called optimization. Optimizers are algorithms or methods used to change the attributes of the neural network such as weights and learning rate to reduce the losses. Optimizers are used to solve optimization problems by minimizing the function.

Update Weight:

Consider W_{1old} and W_{1new} weights are non-updated and updated respectively,

$$W_{1new} = W_{1old} - \alpha \text{ (Gradient)}$$

$$W_{1new} = W_{1old} - \alpha \left(\frac{\partial\ (Loss)}{\partial (weight)}\right)$$

W_{1new} updated weight

α = Learning rate (0.001 for ADAM)

Update the weights using gradient descent. It calculates the gradient of the error function with respect to the neural network's weights. The calculation proceeds backwards through the network.

Adam:

Adaptive Moment Estimation is an algorithm for optimization technique for gradient descent. Adam optimizer is algorithms or methods used to change the attributes of the neural network such as weights and learning rate to reduce the losses.

Root Mean Square Error:

RMSE is a frequently used measure of the differences between values predicted by a model and the values observed. RMSE is the square root of the average of squared errors and is given by

$$\text{RMSE}=\sqrt{\frac{\sum_{i=1}^{N}(x_i-\hat{x}_i)^2}{N}}$$

x_i = actual observation value

$\hat{x}_i$= predicted value

N= number of non-missing data points

i = variable i

Coefficient of Determination:

The coefficient of determination is a measurement used to explain how much variability of one factor can be caused by its relationship to another related factor. This correlation, known as the "goodness of fit," is represented as a value between 0.0 and 1.0.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Implementation of Artificial neural network using python

Python programming language was utilized for the prediction of breakthrough curve using artificial neural network technique. Following are the various library functions that are used for the programming purpose.

```
import pandas as pd
```

Pandas is an open-source library that is built on top of NumPy library. It is a Python package that offers various data structures and operations for manipulating numerical data and time series. It is mainly popular for importing and analyzing data much easier. Pandas is fast and it has high-performance & productivity for users.

```
cols = ['bed_depth','flow_rate','initial_concetration','time','ct_cu_meql']
```

cols = Create a list_cols with features and labels name.

```
list_dp = []
```

list dp = Initialise empty list as list_dp**.** Append the data set value into this list using List inbuilt function append.

```
df2 = pd.DataFrame(list_dp, columns=cols)
```

Crate this data like csv file using Data Frame in pandas.

Pandas Data Frame is two-dimensional size-mutable, potentially heterogeneous tabular data structure with labelled axes (rows and columns). A Data frame is a two-dimensional data structure, i.e., data is aligned in a tabular fashion in rows and columns.

```
from sklearn.preprocessing import StandardScaler

sc = StandardScaler()

X = sc.fit_transform(X)
```

Pre-process data using Standard scaler:

Standard Scaler is that it will transform your data such that its distribution will have a mean value 0 and standard deviation of 1.

```
import keras
from tensorflow.keras.models import Sequential
from tensorflow.keras.layers import Dense
```

Keras is an open-source software library that provides a Python interface for artificial neural networks. Keras acts as an interface for the TensorFlow library. From tensorflow.keras import Sequential model . And import Dense layer.

```
model = Sequential()
model.add(Dense(8,input_dim=4, activation='sigmoid'))
model.add(Dense(1, activation='sigmoid'))
```

Define model:

1) Sequential model
2) First input layer of dimension 4 and hidden layer of 8 neurons and sigmoid activation function
3) 1 output layer of 1 neuron

```
model.compile(loss='mean_squared_error', optimizer='adam',metrics =["m
ean_squared_error"])
```

Compile Model:

Loss:

In machine learning, Loss function is used to find error in the learning process. **Keras** requires loss function during model compilation process.

Keras provides quite a few loss function in the losses module and they are as follows −

- mean_squared_error
- mean_absolute_error

All above loss function accepts two arguments

1) true labels as tensors

2) prediction with same shape

Optimizer: Optimization is an important process which optimize the input weights by comparing the prediction and the loss function.

Adam − Adam optimizer.

keras.optimizers.Adam , learning rate = 0.001

Metrices: Metrics is used to evaluate the performance of your model. It is similar to loss function, but not used in training process.

Compile the model: Keras model provides a method, compile() to compile the model.

```
model_fn=model.fit(X, y, epochs=700, batch_size=1)
```

Model Training: Models are trained by NumPy arrays using *fit()*. The main purpose of this fit function is used to evaluate your model on training.

- X, y − It is a tuple to evaluate your data.
- epochs − no of times the model is needed to be evaluated during training.
- Batch size − training instances. Then Prediction value

```
import numpy as np
from sklearn.metrics import mean_squared_error
from math import sqrt
pred_train= model.predict(X)
print(np.sqrt(mean_squared_error(y,pred_train)))
```

Then Prediction value And mean square error print.

```
import matplotlib.pyplot as plt
import matplotlib.pyplot as plt
```

```
plt.scatter(m,y,color='red')
plt.plot(m,pred_train,color='blue')
plt.xlabel('Time')
plt.ylabel('cu-ct concentration')
```

Using matplotlib model in python plot graph. Visualization of data is done by matplotlib library. On x axis Time (min) is plotted and on Y axis ct_cu_meq/l is plotted. The Scatter () function plots one dot for each observation. Hence, plt.Scatter () function is used for plotting the graph.

4.2 Prediction of Cu^{2+} breakthrough curve using artificial neural network method

Breakthrough occurs when adsorbate reaches the end of the column and leaves with the column effluent. Breakthrough curve is plot of the adsorbate concentration in the column effluent as a function of time. ANN model was selected for breakthrough curve modelling. To validate the predictive power of the model, the database was randomly divided into a training subset (100%) and testing subset (100%) for estimation of the parameters and assessment of the model predictions, respectively. The coefficient of determination (R^2) and root mean square error (RMSE) were employed to evaluate the accuracy of the models.

Fig. 4.1 compares the experimental and predicted C_t values of Cu^{2+} metal ion in the effluent solution with the time. It can be observed that predicted values are closely matching with

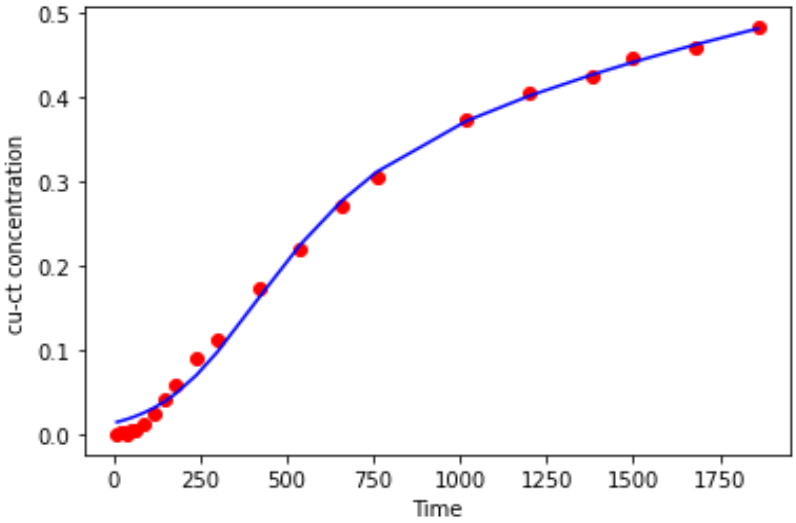

Fig. 4.2: BP-ANN predicted breakthrough curve data for the adsorption of Cu^{2+} metal ion onto GAA column bed.

the experimental data. This observation is further justified with R^2 value of 0.996 and RMSE value of 0.011. This indicates that BP-ANN method can be effectively used for the prediction of breakthrough curve of Cu^{2+} metal adsorption onto GAA.

CHAPTER 5
CONCLUSIONS

BP-ANN technique was used for the prediction of Cu^{2+} breakthrough curve. Following are the major observations from the study conducted:

1. Predicted values are closely matching with the experimental data.
2. R^2 value of 0.996 and RMSE value of 0.011 further justified the suitability of BP-ANN method to predict the Cu^{2+} breakthrough curve.
3. This indicates that BP-ANN method can be effectively used for the prediction of breakthrough curve of Cu^{2+} metal adsorption onto GAA.

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ANNEXURE

Program:

```
import pandas as pd

cols = ['bed_depth','flow_rate','initial_concetration','time','ct_cu_meql']
list_dp = []
list_dp.append([3,2,0.6,10,0.001])
list_dp.append([3,2,0.6,20,0.004])
list_dp.append([3,2,0.6,30,0.003])
list_dp.append([3,2,0.6,40,0.002])
list_dp.append([3,2,0.6,50,0.005])
list_dp.append([3,2,0.6,60,0.005])
list_dp.append([3,2,0.6,90,0.012])
list_dp.append([3,2,0.6,120,0.024])
list_dp.append([3,2,0.6,150,0.042])
list_dp.append([3,2,0.6,180,0.060])
list_dp.append([3,2,0.6,240,0.092])
list_dp.append([3,2,0.6,300,0.113])
list_dp.append([3,2,0.6,420,0.173])
list_dp.append([3,2,0.6,540,0.221])
list_dp.append([3,2,0.6,660,0.271])
list_dp.append([3,2,0.6,760,0.305])
list_dp.append([3,2,0.6,1020,0.374])
list_dp.append([3,2,0.6,1200,0.405])
list_dp.append([3,2,0.6,1380,0.426])
list_dp.append([3,2,0.6,1500,0.448])
list_dp.append([3,2,0.6,1680,0.458])
list_dp.append([3,2,0.6,1860,0.483])
df2 = pd.DataFrame(list_dp, columns=cols)
df2

X = df2.iloc[:,:4].values
y = df2.iloc[:,4].values
m = df2.iloc[:,3].values

import matplotlib.pyplot as plt
plt.scatter(m,y,color='red')
plt.show()

y.shape

from sklearn.preprocessing import StandardScaler
sc = StandardScaler()
```

```
X = sc.fit_transform(X)

import keras
from tensorflow.keras.models import Sequential
from tensorflow.keras.layers import Dense

model = Sequential()
model.add(Dense(8,input_dim=4, activation='sigmoid'))
model.add(Dense(1, activation='sigmoid'))
model.compile(loss='mean_squared_error', optimizer='adam',metrics =["mean_squared_error"])

model_fn=model.fit(X, y, epochs=700, batch_size=1)


import numpy as np
from sklearn.metrics import mean_squared_error
from math import sqrt
pred_train= model.predict(X)

print(np.sqrt(mean_squared_error(y,pred_train)))
print(pred_train)

import matplotlib.pyplot as plt

plt.scatter(m,y,color='red')
plt.plot(m,pred_train,color='blue')
plt.xlabel('Time')
plt.ylabel('cu-ct concentration')
plt.show()
```