BP-ANN Approach for Modeling Cd(II) Bio-Sorption from Aqueous Solutions Using *Cajanus cajan* Husk

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ABSTRACT: *This work aims at the modeling of bio-sorption of cadmium(II) onto physically and chemically activated Cajanus cajan (Pigeon pea) husks. Experimental data obtained were fitted to a number of isotherm and kinetic models, and the results interpreted. The monolayer Cd(II) bio-sorption capacities of the husk were found to considerably increase by 2.82 times due to chemical activation, for bio-sorption from a solution containing an initial Cd(II) concentration of 100 mg/L and by about 1.78 times for a solution containing an initial Cd(II) concentration of 150 mg/L. Further, BackPropagation Artificial Neural Network (BP-ANN) was applied to understand the accuracy and prediction of isotherm and kinetic data. The tangent sigmoid transfer function was used at the input to hidden layer where as a linear function was used at output layer. The isotherm and kinetic data were distributed into training (65%) and testing (35%) phase. The training, testing, and prediction by BP-ANN were found to be adequate, with an absolute relative percentage error of 2.1827 and correlation coefficient $R^2$of 0.9967 and 0.9863 at prediction for isotherm and kinetic studies, respectively. Comparison of BP-ANN and experimental results indicated that the prediction model is capable of predicting the bio-sorption effectiveness with good accuracy.*

KEYWORDS: *ANN Modeling; Biosorption; Cajanus cajan; Isotherms; Kinetics.*

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INTRODUCTION

The existence of heavy metals in the drinking water concerned ever health problems recently. Cadmium (Cd) is one of the listed heavy metal, mainly concerned because of its toxicity and carcinogenic nature [1]. Wastewaters from mining, metallurgy, electroplating, battery and accumulator manufacturing contain undesirable amounts of Cd(II). The transport of cadmium to drinking water occurs by contamination of wastewater to river water, wastewater to ground water through permeability. Cadmium is consumed by humans through intake of drinking water and food. The major health problems from cadmium poisoning are kidney failure, chronic pulmonary diseases, salivation, and skeletal deformity [2]. Cd(II) has been classified as group B1 carcinogen by USEPA. According to the World Health Organization, 0.005 mg/L and 0.01 mg/L of cadmium is permissible in the drinking water and in wastewater respectively [3], beyond this level the water is harmful for use.

Various techniques and methods are utilized for the elimination of cadmium from water are chemical precipitation, adsorption, ion-exchange, flocculation, electro-dialysis, and oxidation, etc [4-6]. Considering the above methods, adsorption / bio-sorption has been found economic suitable and efficient to remove cadmium from wastewaters.

In this present work, the husk of *Cajanus cajan*, commonly known as pigeon pea, that has no prominent utilization, has been used to remove Cd(II) from laboratory prepared solutions. India is the major producer and user of *Cajanus cajan* in the world. The husk of this pulse crop is available abundantly as a bio-waste.

The work aims at prediction of batch studies, isotherm studies and kinetic studies. To attain better removal efficiency and optimization of the removal process the modeling studies is carried out by using BP-ANN. BP-ANN provides the platform for plotting interactions between real time experimental data and prediction data through training with many functions. Over last few years ANN is used in many industrial and environmental applications for elimination of heavy metals from water [7-10]. Present objective of the work is to understand the application of physical model and mathematical models for bio-sorption of cadmium from water.

EXPERIMENTAL SECTION

Bio-sorbent

In this work the bio-sorbent used is the husk of *Cajanus cajan*, (commonly known as pigeon pea). The husk was collected from Chidri Dall Mill, Humnabad, Karnataka, India. It was ground in a mixer-grinder and boiled many times in distilled water until no color release takes place from it, dried, sorted into different size fractions, designated as CC(N) and stored in air tight polythene bags for experimental use. For chemical activation of the bio-sorbent, 1000 mL absolute ethanol, 500 mL of 0.5 mol/L of NaOH and 500 mL of 1.5 mol/L $CaCl_2$ were added to 200 g of CC(N), mixed thoroughly and kept aside for 24 h. The water was removed and the husk was thoroughly cleaned with distilled water to take away the chemicals and designated as CC(CA).

Chemicals and instruments

Cadmium nitrate [$Cd(NO_3)_2.4H_2O$] was used to prepare Cd(II) solutions in distilled water. Sodium hydroxide, hydrochloric acid, calcium chloride, and ethanol were used in the study. The chemicals were of analytical range and provided by SD Fine Chemicals, Mumbai.

An atomic absorption spectrophotometer (Elico-168 model, India), orbital shaker (Kemi, Kerala, India), hot air oven (Kemi, Kerala, India), precision electronic balance (Essae Teraoka Ltd.), pH meter (Elico-LI 612 model) and an all-glass water distillation unit (Borosil) were used in the study. All glass wares used were of Borosil make.

Analytical procedures

After the bio-sorption experiment, residual cadmium concentrations were determined by using an Atomic Absorption Spectrophotometer (AAS). Cadmium lamp was used at the wavelength of 228.8 nm for the analytical range of 0.2 to 1.8 mg/L, at which the sensitivity was 0.009 mg/L.

Isotherm studies

Batch bio-sorption experiment was carried out for solutions having initial Cd(II) concentrations of 100 and 150 mg/L in two batches using CC(N) and CC(CA) respectively. 50 mL solutions of a particular initial Cd(II) concentration were treated with different amounts

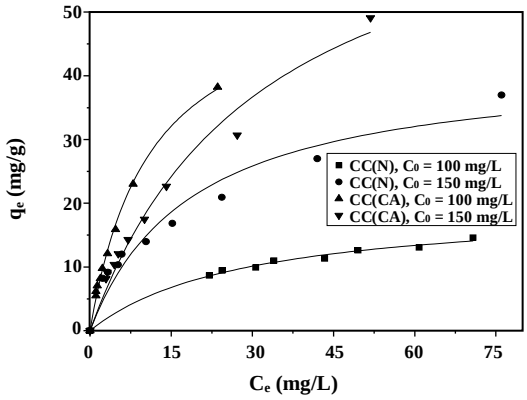


Fig. 1: Equilibrium data for the biosorption of Cd(II) onto CC husk.

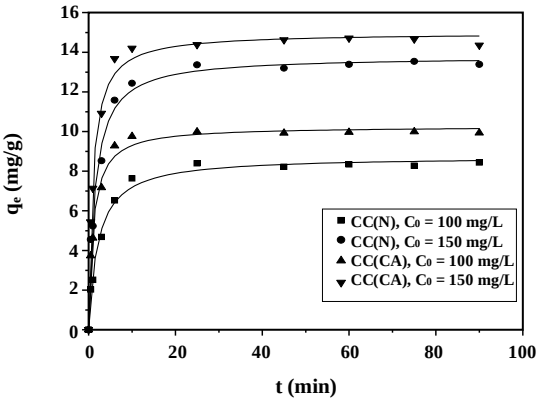


Fig. 2: Kinetic data for the biosorption of Cd(II) onto CC husk.

of the bio-sorbent according to the requirement (0.1 to 0.9 g) and shaken in an orbital flask shaker at 180 rpm for 3 h for the attainment of equilibrium at the optimum pH of 5.5±0.2. The solutions were then filtered and the left over Cd(II) concentrations were found by atomic absorption spectrophotometer.

The equilibrium metal uptake q_e (mg/g) is calculated as:

$$q_e = \frac{(C_o - C_e)}{m/V} \quad (1)$$

Where, C_0 and C_e are the initial and equilibrium Cd(II) concentration in solutions (mg/L), m is the bio-sorbent mass (g) and V is the volume of solution (L). Fig. 1 shows the experimental data.

Kinetic studies

0.5 g of CC(N) was added to a series of 250 mL glass beakers containing 50 mL of a solution containing 100 mg/L Cd(II) initial concentration, and trembled in an orbital shaker at 180 rpm. Samples were quickly vacuum filtered at time intervals of 0.5, 1, 3, 6, 10, 25, 45, 60, 75 and 90 min and the residual Cd(II) concentrations were determined by atomic absorption spectrophotometer. Similar experiments were carried out with the other initial concentration (150 mg/L) and with CC(CA).

The metal uptake q_t (mg/g) at any time t is given by:

$$q_t = \frac{(C_o - C_t)}{m/V} \quad (2)$$

Where, C_0 and C_t are initial and concentration at time t of the metal in solution (mg/L), m is the bio-sorbent mass (g) and V is the volume of (L). Fig. 2 shows the experimental data.

Origin Pro 8 software has been used for the non-linear curve fit of the experimental data to the isotherm and kinetic models at 95% confidence interval.

Back Propagation Artificial Neural Network (BP-ANN)

Increase in demand of technology globally, artificial intelligence has played an active role to forecast the difficult reactions in challenging conditions. Artificial intelligence was used when experimental faults are very high with simple mathematical and statistical tools. The bio removal process and mechanism is a complex process because of having many operating parameters. To overcome the complexion, prediction study is done by utilizing mathematical and analytical tools with enhanced accuracy.

In the present study, ANN has the capability to compare the input (experimental data) with outputs proficiently in difficult environments. Mean square error (MSE) is a significant index of the back propagation algorithm. The BP-ANN structure contains three layers, which makes the network runs by training and testing stages. The layers are (a) Input layer (I), (b) Hidden layer (H) and (c) Output layer (O).

The network structure is represented as I-H-O, where I is the input nodes (number of inputs parameter), H is hidden nodes (working node) and O is output nodes (Prediction output). Data transmissions from the first layer to the third layer moves through the second layer. The first layer (I) receives the normalized data from the real experiments and the data are hand over to the network for observation and calculation. Data observation and

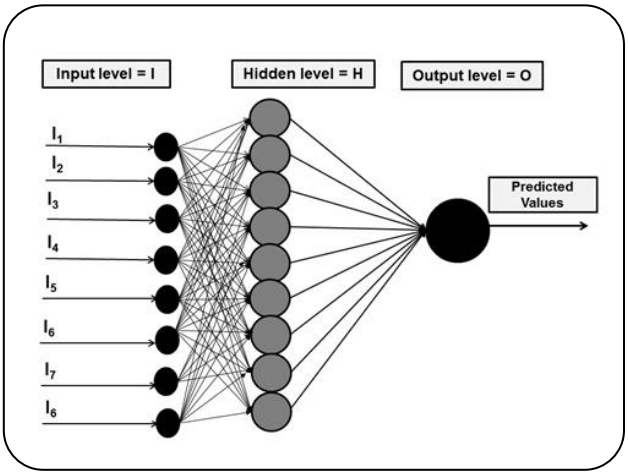


Fig. 3: ANN architecture for modeling of isotherm and kinetic studies.

the calculation is done by hidden layer (H), and finally the third layer receives all data from the second layer and transfers predicted values to the output system.

The layer of neurons available in the network is stable by its weight conditions, a preference vector and a transfer function. The calculation of neurons in the second layer is done by trial and error methodology. The input signals interconnected and reformed as weight factor (W_{ij}), which signifies the interrelationship of i^{th} node of the first layer to j^{th} node of the second layer. The start of signals is controlled by a sigmoid transfer function (f).

Likewise, outputs signal of the hidden layer is adjusted by interconnection weight (Wac) of k^{th} node of output layer to i^{th} node of hidden layer. The initiation of signals is controlled by a sigmoid transfer function (f) and output is received at final layer in the range of 0-1 and presents nonlinearity into the network, which gives the control to counter non-linear relationships between input and output data.

According to literature, several types of the transfer function are used in ANN model, such as linear (purelin) function, saturately linear (satlin) function, log sigmoid (log sid) function, and hyperbolic tangent sigmoid (tansig) function [7,10]. We have used sigmoid transfer function in the present study, which is represented as:

$$f = \frac{1}{1+e^{-x}} \quad (3)$$

The theoretical assumptions and calculation in the present study are carried out considering our previous studies [11]. The significance of sigmoid transfer function is activation in first layer and second layer, i.e. input (I) and hidden layer (H) neurons respectively. Whereas, linear function (purelin) is generally applied to get the same at output layer neurons. The multi input neurons are represented in Fig. 3. In the present study, bio-sorption isotherm and kinetics models are used as inputs to mathematical models (ANN).

Adsorption capacity is the required output from the artificial neural network. The overall experimental values are divided into two sets 65 % and 35 % data for training and testing respectively. The values are normalized to overcome the scrabbling effect according to available literature [12, 13].

RESULTS AND DISCUSSION

SEM and EDAX analysis

SEM images and EDAX spectrum of the material before and after cadmium bio-sorption was studied, and represented in Fig. 4 and Fig. 5.

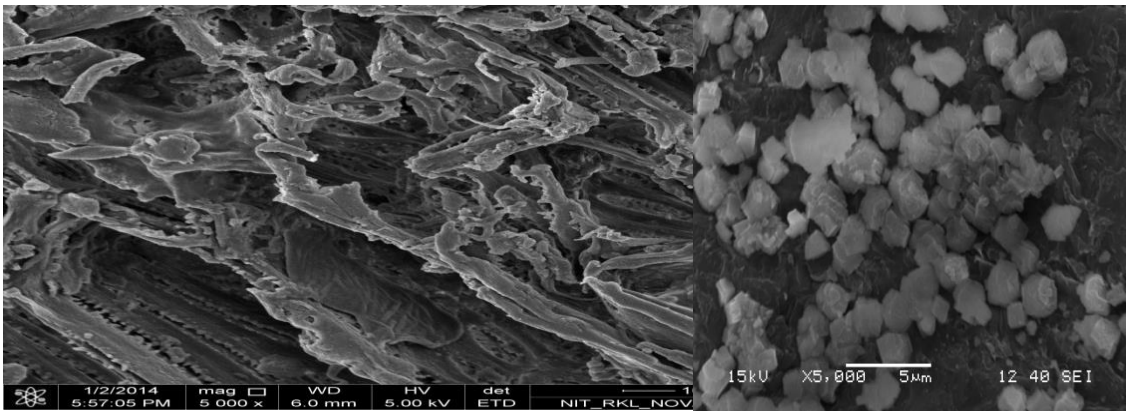
The micrograph clearly reveals that non-uniformed shaped particles are obtained having pores in between of each particle after activation. After cadmium bio-sorption, SEM images were obtained in order to understand the modification in the surface, it was observed that the pores are closed and agglomerated. EDAX spectrum, which gives direct confirmation for the presence of element in starting material and bio-sorbed material (Fig. 3). Cadmium peaks were observed at EDAX spectrums after bio-sorption of Cd (II) onto activated bio-sorbent, confirming the Cd (II) bio-sorption on bio-sorbents. It is evident from the SEM images and EDAX analysis that cadmium is biosorbed by the biomaterial.

Isotherm modeling

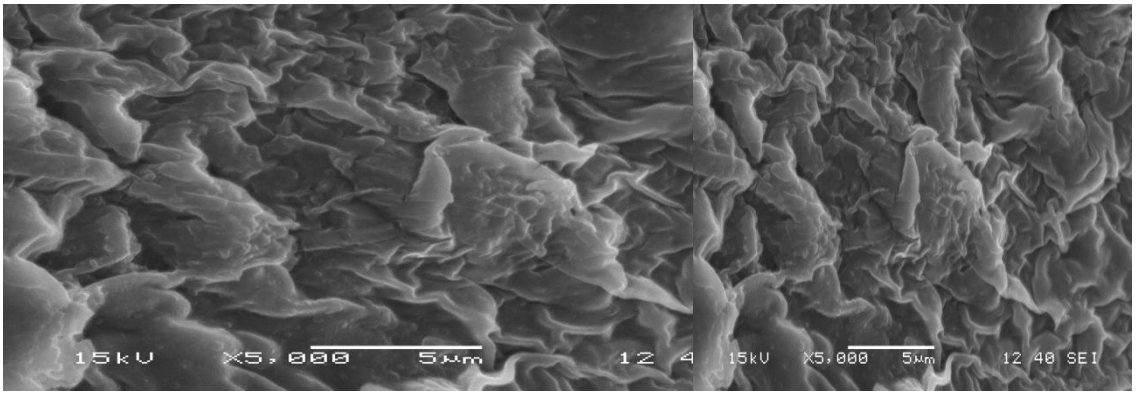
Different isotherm models tested for the data with their respective parameters are given in Table 1.

Henry model

Henry model represents the equation of a straight line. It is a linear multilayer model represented with a single and two parameters [14]. The values of the parameters of these models are given in Table 1. The Henry model with the parameter K_H (L/g), with no intercept, gave the least fit (8^{th} in order) to the experimental data (R^2 = 0.7389). This was due to the unavailability of bio-sorption data in the lower range of metal concentration. However the other



CC(N) – Before Experiment **CC(CA) – Before Experiment**



CC(N) – After biosorption Cd(II) **CC(CA) – After biosorption of Cd(II)**

Fig. 4: SEM images of CC.

CC - Before experiment **CC - After biosorption of Cd(II)**

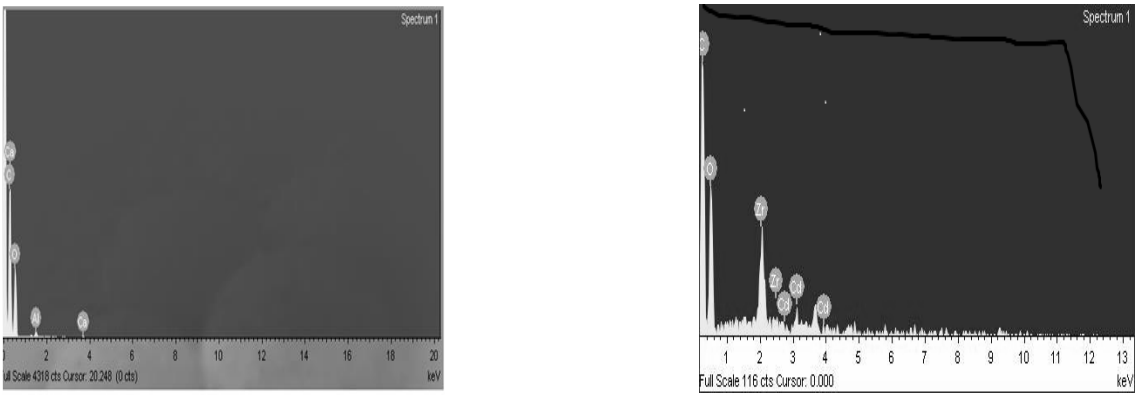


Fig. 5: EDAX images of CC.

Henry model with parameters *a* (L/g) and *b* (mg/g), that represents a straight line with an intercept gave an improved fit (5th in order) with R^2 = 0.9353. This is due to the availability of experimental data at higher concentrations.

Freundlich model

This is a multilayer empirical model generally applicable for bio-sorption on heterogeneous surfaces in which the sorption energy distribution decreases exponentially [15]. In this model, the values of K_F and *1/n* depend on the mechanism and the rate of bio-sorption. A value of *1/n* between 0.2 and 0.8 represents a good sorbent, the lower end indicating the formation of a relatively strong bond between the sorbent and the sorbate. This model gives best fit (first in order) with an R^2 = 0.9947. The values of 1/*n* (see Table 1) fall well in the range of 0.2 to 0.8 representing that the sorption of Cd(II) on the bio-sorbent is favorable.

Langmuir model

This is suitable for monolayer bio-sorption on the surface having a finite number of indistinguishable sorption spot [16]. In this model it is assumed that the monolayer bio-sorption on an energetically identical surface, where the bio-sorption process occurs only at particularly limited to small sites, and saturated layer correlates to entire possession of these spots. The parameters, q_m (mg/g) and K_L (Lg/mg) are the Langmuir parameters, linked to the greatest bio-sorption ability for an entire monolayer (mg/g), and to the resemblance between the bio-sorbent and sorbate (L/mg) respectively. This isotherm has been generally used for bio-sorption and adsorption from liquid solutions by researchers and gave the 3rd best fit with an R^2 = 0.9781. The single layer bio-sorption ability of *Cajanus cajan* husk has got to increase appreciably due to chemical activation (see Table 1). Langmuir model also defines a dimensionless parameter R_L that specifies favorable or unfavorable isotherm for its various values as defined by the following equation [17]:

$$R_L = \frac{1}{1 + K_L C_o} \quad (4)$$

Calculated values of R_L (0.2228, 0.1123, 0.0997, 0.1760) indicates that the bio-sorption isotherms for Cd(II) are all favorable.

Table 2 presents a comparison between the maximum bio-sorption capacities achieved for the bio-sorbents of this study and others found in the literature [18-37].

Tempkin model

Tempkin model takes into account the sorbate - sorbent interactions and states that the decrease in the bio-sorption heat is linear than logarithmic [38]. In this model, *R* is the Universal gas constant (J/mol.K), *T* is the absolute temperature (K), ΔQ (J/mol) is the heat of bio-sorption and K_T (L/g) is the Tempkin constant. This model gave the 4th best fit. The values of ΔQ (see Table 1) indicate that bio-sorption of Cd(II) on both CC(N) and CC(CA) is endothermic.

Dubinin - Raduskevich model

Dubinin - Radushkevich isotherm is temperature independent [39]. It predicts the strength of bio-sorption per molecule of adsorbate and highest bio-sorption ability of the bio-sorbent.

In this model, ε is the Polanyi potential and *D* is the model constant (mol^2/J^2) given by the following equations [40]:

$$\varepsilon = RT \ln\left[1 + \frac{1}{C_e}\right] \quad (5)$$

$$E = \frac{1}{\sqrt{2D}} \quad (6)$$

This model gives an estimate of the mean free energy, *E* (J/mol), of bio-sorption per molecule of sorbate, when it is transferred to the surface of the solid from infinity in the solution. The values are given in Table 1 for the experiment data. The models provide the 6th best fit with R^2 = 0.8938 for the experimental data.

Halsey model

The Halsey isotherm is a multilayer model and it confirms the hetero-porous character of the bio-sorbent [41]. This isotherm provides the best fit and hence confirms multilayer bio-sorption of Cd(II) and the hetero porous nature of CC(N) and CC(CA).

Harkins-Jura model

The Harkins – Jura isotherm with model constants *A* and *B* is suitable for multilayer bio-sorption on a sorbent

Table 1: Isotherm parameter values for the biosorption of Cd(II) on CC at 303 K.

Sl. No.	Model	Equation	C_0 (mg/L)	CC(Normal)		CC(Chemically activated)		R^2 (Global)
				Parameter values		Parameter values		
1.	Henry (1-p)	$q_e = K_H C_e$	100	K_H = 0.2493		K_H = 1.8907		0.7389
			150	K_H = 0.5879		K_H = 1.0773		
2.	Henry (2-p)	$q_e = aC_e + b$	100	a = 3.3922	b = 0.1791	a = 5.5012	b = 1.5005	0.9353
			150	a = 7.7908	b = 0.4197	a = 6.5240	b = 0.8632	
3.	Freundlich	$q_e = K_F C_e^{1/n}$	100	K_F = 2.4542	1/n = 0.4143	K_F = 6.2099	1/n = 0.5814	0.9947
			150	K_F = 4.9718	1/n = 0.4585	K_F = 4.2498	1/n = 0.6160	
4.	Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	100	q_m = 19.7674	K_L = 0.0349	q_m = 55.7780	K_L = 0.0903	0.9781
			150	q_m = 42.1614	K_L = 0.0527	q_m = 75.8072	K_L = 0.0312	
5.	Tempkin	$q_e = \frac{RT}{\Delta Q} \ln K_T C_e$	100	ΔQ = 538.5	K_T = 0.2900	ΔQ = 247.1	K_T = 1.3109	0.9421
			150	ΔQ = 322.4	K_T = 0.8096	ΔQ = 192.6	K_T = 0.5001	
6.	Dubinin – Radushkevich	$q_e = q_m \exp\left(-D\varepsilon^2\right)$	100	q_m = 17.4292	D = 0.0064	q_m = 41.4105	D = 1.6068	0.8938
			150	q_m = 32.3938	D = 0.0027	q_m = 49.3413	D = 0.0035	
7.	Halsey	$q_e = \exp\left(\frac{\ln k - \ln C_e}{n}\right)$	100	n = -2.4135	k = 0.1145	n = -1.7199	k = 0.0433	0.9947
			150	n = -2.1810	k = 0.0303	n = -1.6232	k = 0.0955	
8.	Harkins -Jura	$q_e = \sqrt{\frac{A}{B + \log C_e}}$	100	A = 63.97	B = 2.1290	A = 45.24	B = 1.0722	0.8178
			150	A = 109.05	B = 1.7317	A = 92.67	B = 1.5049	
9.	Henderson	$q_e = \sqrt[2]{\frac{-\ln(1-C_e)}{k}}$	100	k = 2624.8	n = 2.4697	k = 3.7741	n = 1.5938	0.9936
			150	k = 197.23	n = 2.3348	k = 8.1607	n = 1.6583	

with heterogeneous pore size distribution [42]. This model provides the 7th best fit.

Henderson model

This model [43] with constants *n* and *k* explains multilayer bio-sorption and gives the 2nd best fit confirming multilayer bio-sorption of Cd(II) by CC(N) and CC(CA) as indicated by the Freundlich model.

Kinetic modeling

Different kinetic models were tested for the experimental data and their respective parameters are given in Table 3.

Fractional power model

This model indicates that the metal uptake increases exponentially with time [43]. The value of ϑ less than 1 indicates that biosorption of Cd(II) onto CC is time dependent. The values of the product of model constants (k_F. ϑ),which is the specific bio-sorption rate followed the order 1.1525, CC(CA) (150 mg/L) > 1.14580, CC(N) (150 mg/L) > 0.8012, CC(CA) (100 mg/L) > 0.7510, CC(N) (100 mg/L).

First-order model

In this model, C_t and C_o are the concentration of Cd(II) at time *t* and initially (mg/L), respectively, and k_1 is the first order rate constant, (1/min.) [44]. A comparison of the results with the correlation coefficient is shown in Table 3. The influence of chemical reactions and transport phenomena are often inseparable and hence simple first or second order kinetic rate equations are not suitable for the bio-sorption process with solid surfaces [45].

Pseudo-first-order model

This model equation is based on solid capacity [46]. Here q_e (mg/g) is the equilibrium amount of Cd(II)

Table 2: Comparison of the maximum biosorption capacity of cadmium for different biosorbents.

Biosorbent	Biosorption capacity q_{max}, mg/g	pH	References
Raw pine cone	1.9	7.0	[18]
Fenton activated cone	10.7	6.0	[18]
Azadirachta indica (Neem) leaf	158.0	9.5	[19]
Hydrilla verticillata	15.0	5.0	[20]
Wheat bran	15.71	5.0	[21]
Scolymus hispanicus L.	54.05	6.5	[22]
Husk of Lathyrus sativus	53.76	6.0	[23]
Mushrooms (Pleurotus platypus)	34.96	6.0	[24]
Pycnoporus sanguineus (P. sanguineus)	3.32	6.0	[25]
Rhizopus cohnii (R. cohnii)	40.5	4.5	[26]
Acacia leucocephala bark powder	167.7	5.0	[27]
Red algae (Ceramium virgatum)	39.7	5.0	[28]
Powder of Areca catechu	10.66	6.0	[29]
Penicillium simplicissimum	52.50	4.0	[30]
NaOH treated bacterial dead Streptomyces rimosus biomass	63.3	8.0	[31]
H. Splendens	32.5	5.0	[32]
Mucor rouxii	20.31	6.0	[33]
Ulva lactuca	29.2	5.0	[34]
Eleocharis acicularis biomass	33.71	6.0	[35]
Pantoea sp.	52.0	6.0	[36]
Polymerized tamarind fruit shell	24.31	7.0	[37]
Cajanus cajan husk (Normal)	42.16	5.5	Present study
Cajanus cajan husk (Chemically activated)	75.80	5.5	Present study

bio-sorbed and k_1 (1/min) is the bio-sorption rate constant and their values are given in Table 3.

Second-order model

The rate of second-order reactions is proportional to the product of two reactant concentrations, i.e. proportional to the concentrations raised to power unity of two different reactants or to the square of the concentration of one reactant [47], C_t and C_o are the concentration of Cadmium at time t and initially (mg/L), respectively, and k_2 is the second order rate constant, (g/mg.min). Again this isotherm fails to confirm the results owing to the reason that the influence of chemical reactions and transport phenomena are experimentally inseparable.

Pseudo-second-order model

This model presumes that the driving energy for bio-sorption is proportional to the fraction of active sites available [48]. The rate constant k_2 (g/mg.min), correlation coefficient, $R^{2,}$ and the calculated uptake capacity, q_e are given in Table 3. R^2 is closer to unity for this model; as a result, the bio-sorption kinetics for Cd(II) will be approximated more satisfactorily by this model rather than the other kinetic models discussed.

Elovich model

This model assumes that the surface active sites of the bio-sorbents are heterogeneous and it is based on the sorption capacity. It is normally applied to explain

Table 3: Kinetic parameter values for the biosorption of Cd(II) on CC at 303 K.

Sl. No.	Model	Equation	C_0 (mg/L)	CC(N) Parameter values		CC(CA) Parameter values		R^2 (Global)
1	Fractional power	$q_t = k_F t^{\vartheta}$	100	k_F = 3.8356	ϑ = 0.1958	k_F = 5.9089	ϑ = 0.1356	0.8721
			150	k_F = 7.1212	ϑ = 0.1609	k_F = 8.8114	ϑ = 0.1308	
2	First-order	$C_t = C_0 \exp(-k_f t)$	100	k_f = 0.1841		k_f = 0.5688		0.9275
			150	k_f = 0.2933		k_f = 0.5770		
3	Pseudo-first-order	$q_t = q_e\left(1-e^{-k_1 t}\right)$	100	q_e = 8.2600	k_1 = 0.2963	q_e = 9.8086	k_1 = 0.6007	0.9829
			150	q_e = 13.1283	k_1 = 0.4362	q_e = 14.3170	k_1 = 0.6581	
4	Second-order	$C_t = \frac{C_0}{(C_0 - k_s t + 1)}$	100	k_s = 2.819×10^{-3}		k_s = 10.558×10^{-3}		0.9752
			150	k_s = 3.42×10^{-3}		k_s = 6.876×10^{-3}		
5	Pseudo-second-order	$q_t = \frac{q_e^2 k_2 t}{1 + k_s q_e t}$	100	q_e = 8.7388	k_2 = 0.0529	q_e = 10.2634	k_2 = 0.0938	0.9932
			150	q_e = 13.7939	k_2 = 0.0510	q_e = 14.9828	k_2 = 0.0691	
6	Elovich	$q_t = \ln(\alpha_e \beta_e t)^{1/\beta_e}$	100	α_e = 23.7259	β_e = 0.9149	α_e = 179.6267	β_e = 0.9507	0.9455
			150	α_e = 158.8234	β_e = 0.8356	α_e = 592.5716	β_e = 0.8590	
7	Ritchie	$q_t = q_e\left[1-\left(\frac{1}{\beta_r + k_r t}\right)\right]$	100	q_e = 8.7464	β_r = 1.0077 / k_r = 0.4567	q_e = 10.2667	β_r = 1.0054 / k_r = 0.9564	0.9933
			150	q_e = 13.8182	β_r = 1.0196 / k_r = 0.6831	q_e = 14.9837	β_r = 1.0012 / k_r = 1.0342	
8	Intra-particle diffusion	$q_t = k_{in}\sqrt{t}$	100	k_{in} = 2.5376		k_{in} = 3.4730		0.6298
			150	k_{in} = 3.2809		k_{in} = 5.1212		
9	Film diffusion	$\ln\left[1-\frac{q_t}{q_e}\right] = k_{fd} t$	100	k_{fd} = -0.2165		k_{fd} = -0.3316		0.9361
			150	k_{fd} = -0.2581		k_{fd} = -0.3345		

the chemisorption kinetics of gases on the heterogeneous solid [49]. It is quite limited as it only explains a limiting condition eventually attained by the rate curve.

Constant α_e is associated to the chemisorptions rate and β_e is linked to the surface coverage. The experimental kinetic data show only satisfactory agreement with the Elovich equation. This model was used for the sorption of metals by various biomaterials and is based on a mechanism of second-order reaction for heterogeneous bio-sorption operation [50,51].

Ritchie model

Ritchie's kinetic model assumes that the rate of bio-sorption at any time depends only on the fraction of unoccupied sites [52]. This is the second best fitting model to the data as evidenced by the value of R^2 = 0.9933.

Film and intra-particle diffusion models

To know the existence of intra-particle diffusion during the bio-sorption process, experimental data can be analyzed with Weber-Morris model [53]. The graph of q_t versus $t^{1/2}$ for a porous sorbent normally represents three regions: film diffusion and bio-sorption onto the surface, intra-particle diffusion, and saturation. Applicability of the above equation in the intra-particle diffusion region indicates the sorbent is porous and interconnected. Inadequate regression coefficient provides for the existence of intra particle diffusion, but it is not dominant and rate control.

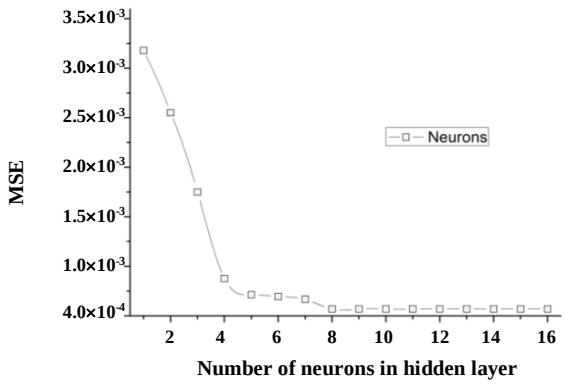


Fig. 6: Number of neurons in the hidden layer.

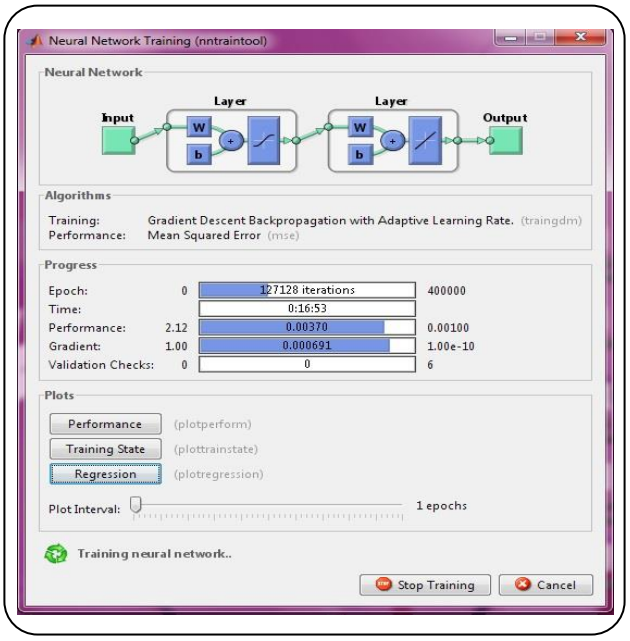


Fig. 7: ANN toolbox using MATLAB (NNTRAINTOOL).

In the film diffusion model, the slope of a linear plot of $-\ln\left[1-\left(q_t/q_e\right)\right]$ versus *t* gives an estimate of the film diffusion constant. Fitting of this model to the kinetic data indicates that film diffusion is also not a predominant mechanism for Cd(II) bio-sorption onto the husks.

Mathematical modeling of bio-sorption kinetic and isotherm studies by using artificial neural networks

This work utilizes BP-ANN to predict the bio-sorption capability. Six hundred and fifty seven combinations of bio-sorption isotherm and bio-sorption kinetic data are spread into training and testing sets respectively, 65 % (428 rows) of data were taken for the training of the prediction model and 35% (229 rows) of data were taken for testing. The present study is performed by using MATLAB software (7.6, R2008a). The number of nodes in the second layer is distinct, by the relation discussed in the literature [13] and presented in Fig. 6.

Fig. 7 represents a neural network training tool, used for training of the prediction network.

The scattering of the predicted data (training and testing) and the performance plot is represented in Fig. 8 and Fig. 9 respectively for bio-sorption equilibrium and kinetic studies. Mean Squared Error (MSE) is observed at different frequency to train the neural network and tested with different numbers of neurons In the second layer. Training ends, if the subsequent condition arises [10]:

(i) If the determined amount of periods is achieved

(ii) If training time exceeded the predetermined time value.

(iii) The decline in the performance to the objective

(iv) Validation time go beyond than definite failures,

The two important factors (Learning and momentum) are adjusted periodically in the trial to achieve better accuracy in term of Mean Squared Error (MSE) [54-56].

For the training phase, the learning and momentum parameter were adjusted to 0.45 and 0.40, respectively. Numerous repetitions (900000 times) were experimented to attain least root mean square error of 0.95 at 732010 epochs with correlation value of R^2 = 0.9968, and 0.9980, (Fig. 8 and Fig. 9), at training for isotherm and kinetic studies values respectively. At this point training of the neural network was stopped and the testing phase is investigated. A good correlation (R^2 = 0.9967 and 0.9863) is obtained at testing phase indicates better connection with the real and obtained predicted data for isotherm and kinetic modeling studies respectively. The distribution of residuals versus experimental runs for isotherm and kinetic studies are being presented in Fig. 10 and Fig. 11 respectively.

The absolute mean relative percentage error of training and predicted data were found to be 1.057 and 1.159 respectively for isotherm studies, similarly for kinetic studies the absolute mean relative percentage error of training and testing/predicted data were found to be

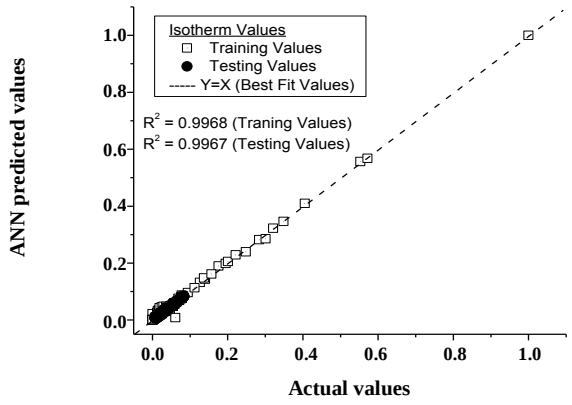


Fig. 8: Correlation of predicted and actual values of isotherm studies (training and testing data).

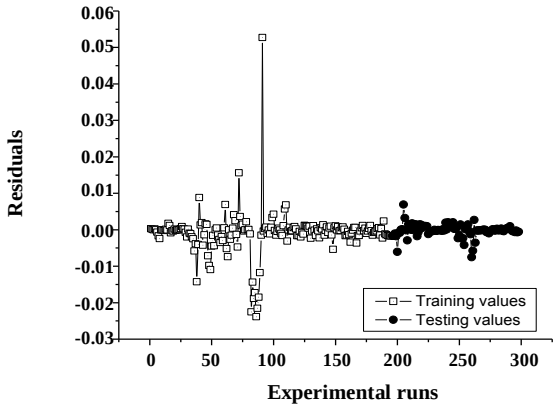


Fig. 10: Distribution of residuals versus experimental runs at training and testing (isotherm studies).

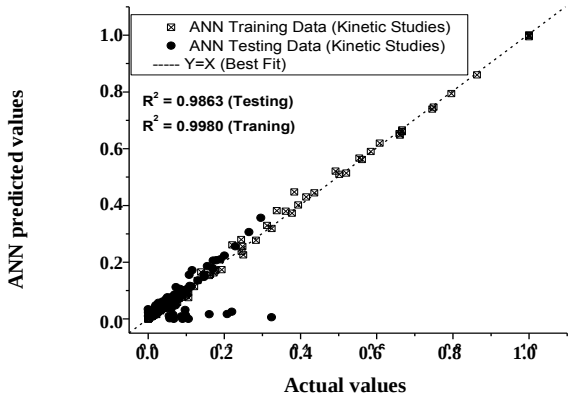


Fig. 9: Correlation of predicted and actual values of kinetic studies (training and testing data).

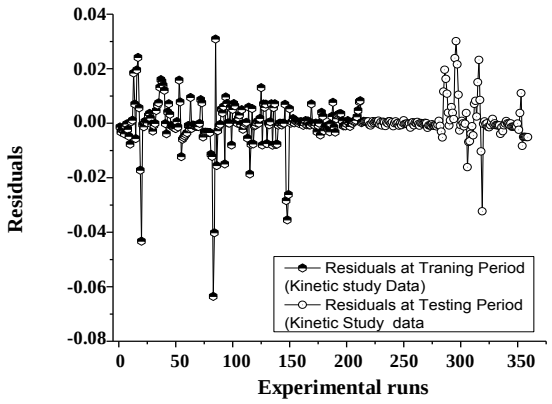


Fig. 11: Distribution of residuals versus experimental runs of kinetic studies.

1.2052 and 1.91344 respectively. The respective plots are presented in Fig. 12 and Fig. 13. It was agreed from the data received that the ANN prediction presents well, agreement with experimental values. The present studies provide a determination to develop value of scientific methodology in actual experiments [57-60]. The findings show that artificial neural network is a favorable technique for the prediction of biosorption data.

CONCLUSIONS

In the present study, modeling of the experimental data for the bio-sorption of Cd(II) from aqueous solutions by *Cajanus cajan* husk, low cost, and locally available sorbent, have been performed to know the various features of the bio-sorption process. It is found that the bio-sorption process is multilayer bio-sorption. Chemical activation leads to improvement in bio-sorption capacity of the husk. The nature of bio-sorption is endothermic process and the bio-sorbent used in the present study is of hetero porous nature. The kinetic study is best fitted to pseudo-second-order rate of bio-sorption of Cd(II) onto CC(N) and CC(CA). For prediction of bio-sorption efficiency of Cd(II) from aqueous solutions, a three layer BP-ANN is utilized. The artificial neural network study concludes effective prediction with a correlation coefficient value of R^2, 0.9967 and 0.9863 at testing phase. Hence, it is concluded from the above studies, the bio-sorbent (*Cajanus cajan* husk) can be effectively and economically used for the removal of Cd(II) from wastewater at large scale water treatment.

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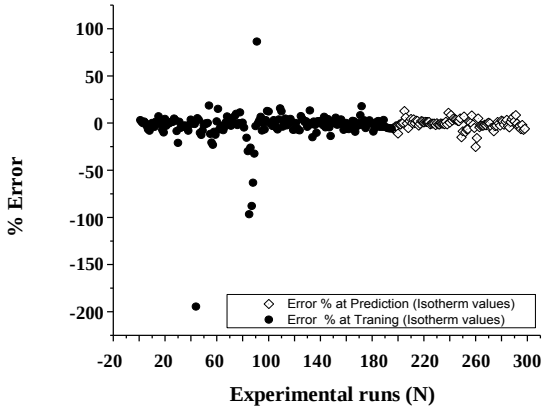

Fig. 12: Percentage relative error at training and testing (isotherm studies).

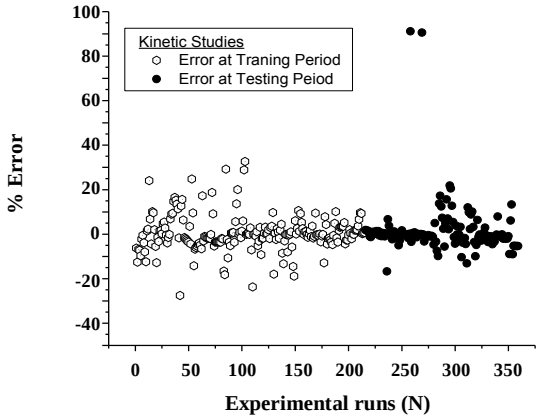

Fig. 13: Percentage relative error at prediction and training of kinetic studies.

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