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BIOSORPTION OF CU(II) IONS FROM INDUSTRIAL EFFLUENTS BY RICE HUSK: EXPERIMENT, STATISTICAL, AND ANN MODELING

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Highlights

▶ Removal of Cu(II) from wastewater is reported.

▶ Rice husk is used as adsorbent.

▶ Artificial neural network has predicted the percentage removal better than MLR.

Abstract. Heavy metal removal from wastewater is a significant research area and recommends sustainable development. The heavy metals cause harmful health effects, increase environmental toxicity. Adsorption is a very effective method for heavy metal removal. A fixed bed for Cu(II) removal using rice hush, an agricultural waste, is reported in this paper. The study was carried out to determine the breakthrough curves with varying operating variables like influent concentration (10–30 mg/L), flow rate (10–40 ml/min), and bed height (4–10 cm) at pH 6. The variation of the process variables like influent concentration, flow rate, and bed height were investigated. The experimental data shows that adsorption capacity increases with the rise of influent concentration. The maximum value of adsorption capacity is 10.93 mg/g at a flow rate of 10 ml/min, bed height 4 cm, and influent concentration 30 mg/L. The applicability of the MLR and ANN modeling has also been successfully carried out. ANN has better predictability than MLR. The findings revealed that rice husk could be used to treat copper-containing industrial effluents.

Keywords: wastewater management, water pollution, environmental sustainability.

Introduction

Wastewater containing toxic, hazardous heavy metal ions discharged by several industries is a global problem today (Kumar et al., 2019). Wastewater management is essential for reducing water pollution. Environmental sustainability is dependent on it. This water stream associated with metal ions is mixed with freshwater bodies and makes the new system polluted. These are like Pb(II), Cu(II), Cr(VI), Ni(II), Zn(II), can entered into the functional parts of the living beings through the water bodies and damage these vital parts of the body. Like all other metal ions, Cu(II) ions are also necessary for human health trace amounts. Still, an excessive amount can damage vital organs such as the nervous system, digestive system, excretory system, etc. (Mitra & Das, 2020). On the other hand, water is also required for living organisms. So, it is required to make

the water-bodies metal ions free within the permissible limit. Several technologies are present to treat these wastewaters like membrane separation, ion exchange, precipitation, coagulation, adsorption using the activated carbon, and adsorption using bio-sorbent (Aydin et al., 2008). Several industries, like the battery electroplating industries, manufacturing industries, smelting and metal finishing industries, etc. (Tumin et al., 2008) discharged Cu(II) ion-containing wastewater in rural areas. According to the Govt. norms, most of these industries in rural areas are small and medium-sized and cannot treat the wastewater due to financial constraints. Hence, the development of a low-cost economic process is necessary. Other processes like membrane separation, ion exchange are not economical, and precipitation, coagulation (Gayathri et al., 2011) are not efficient for industrial-scale treatment. World Health Organization (1993), Environmental Protection

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Agency (1990), Bureau of Indian standards (1991) recommended the Cu(II) ions discharging limit to the water body(s). These are 2.0, 3.0, 0.25 mg. L^{-1} respectively. Activated carbon as adsorbent is a very efficient process, and activated carbon is too much effective adsorbent but not recommended for small and medium-sized industrial treatment due to its high cost. So, searching for low-cost, economical, easily-available adsorbents is the basic need for the current situation. Hyacinth root, blackberry leaves, guava leaves, rice husk, rice bran, coconut shell, neem leaves, etc., are available locally and used as adsorbent without any treatment or modification. So, the preparation cost of these adsorbents is negligible. Rice husk is one such green natural adsorbent used to treat Cu(II) ions in the column mode without any modification or treatment.

Data modeling has been performed using multiple linear regression (MLR) (Nag et al., 2020; Das et al., 2020; Mandal et al., 2020) and Artificial Neural Network (ANN) (Kumar et al., 2019; Mitra et al., 2014; Das et al., 2015; Maiti et al., 2018) with success for the last few years. Proper analysis of data produces beneficial results if interpreted correctly using a statistically approved process like MLR. MLR can show the relationship between the independent and dependent variables. When it is extremely complicated to get any statistical/mathematical relationship between the variables, then ANN is the tool that has successfully produced the desired results.

Physical characterization was made to identify rice husk's physical properties, and the experiment was done to check the suitability of rice husk to remove Cu(II) ions. Experimental data was used to predict the Empirical/semi-empirical model. Artificial neural network prediction was made to compare with the experimental data to check the rice husk capacity, and MLR analysis was also made in the study.

1. Materials and method

1.1. Adsorbent preparation

Rice husk is used as an adsorbent and collected from Bandel, Hooghly. It is washed with and dried under the sun for a few days and finally dried in the oven for 7–8 hrs. at 60 °C. Dried adsorbents are crushed and sieved for the particle size of about 290 to 350 μm and then kept within a desiccator.

1.2. Cu(II) ion solution preparation and analysis

The Cu(II) ions stock solution of 1000 mg/L is made by dissolving 3.93 gm of copper sulfate pentahydrate in 10^3 ml of distilled water and diluted for the required standard solution. Influent and effluent Cu(II) ion concentration is measured in an Atomic absorption spectrophotometer (Model: AA 240 VARIAN, Australia). Analytical grade from E. Merck Ltd., Mumbai, India are used.

1.3. Characterization of rice husk

BET (Novawin 1000, Quantachrome, USA) was used to determine rice husk BET's surface area. The pH_{PZC} of rice husk was measured by the solid addition method. The surface morphology of rice husk was obtained from SEM (Scanning Electron Microscope) (EVO-Q400++, from ZEISS, Germany) image. The rice husk has a surface area of 0.54 m^2/g, and its Point of zero charge (pH_{PZC}) is 6.05. Figure 1 shows the SEM image of the rice husk.

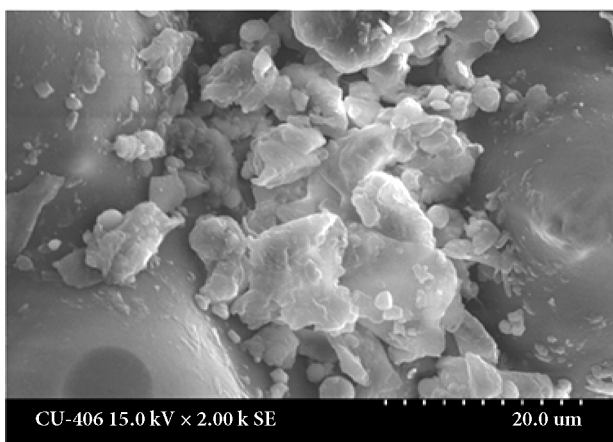CU-406 15.0 kV × 2.00 k SE   20.0 um

Figure 1. SEM image of the rice husk

1.4. Column process

The columns are made of glass (ID 1.8 cm and length 50 cm), The Cu(II) ion solution is introduced from the top of the column by peristaltic pump. The adsorbent was then placed in the column at the desired height, and water was added to settle down the adsorbent. A metal sieve plate and glass wool is placed just above to provide the mechanical support, and adsorbent loss. The solution was collected from the column bottom, and the concentration of the effluent solution was measured in AAS. Figure 2 is the schematic diagram representing the experimentation of the continuous process.
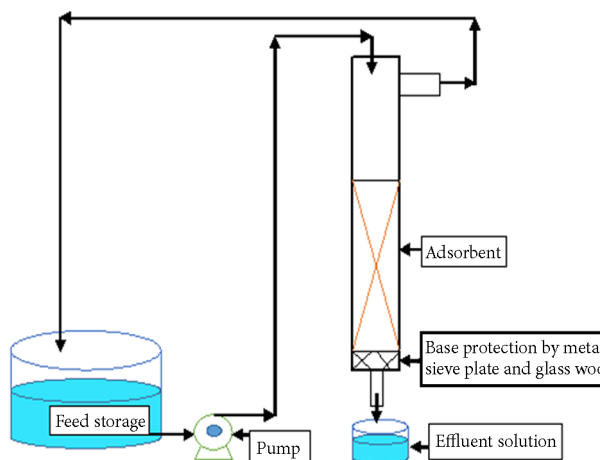

Figure 2. Experimental set-up (schematic presentation)

2. Results and discussion

2.1. Variation of process parameters

Batch experiment was done at different pH (2–8), and pH 6 was found to be the optimum (Singha & Das, 2013). At lower pH, the H_3O^+ ion concentration is more at and around the adsorbent and the diffusion of the Cu(II) ion is difficult, hence the Cu(II) ions removal is less. Also, at pH higher than 6, precipitation of $Cu(OH)_2$ makes the process a type of combination of the precipitation and adsorption, hence reducing the removal efficiency. The highest removal has been observed at a pH value of 6. Figure 3 shows the solution pH effect for removing Cu(II) ions using rice husk.
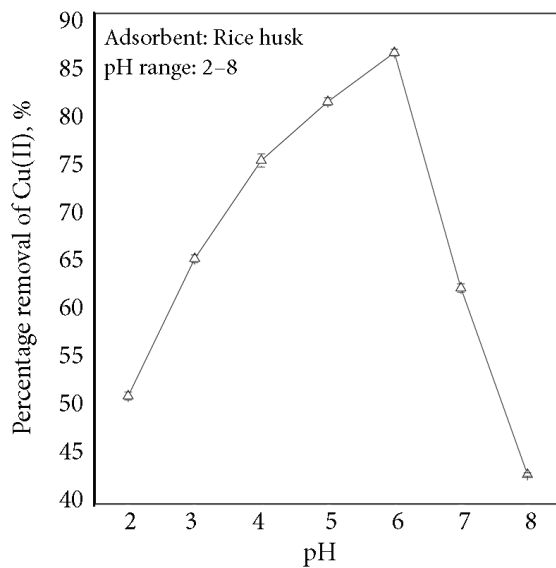

Figure 3. Effect of pH

In this study, the experiment was done using different bed depths (4 cm, 6 cm, and 10 cm) to determine the process's optimum condition. The highest bed depth (10 cm) was found as the optimum as higher removal was observed at bed depth 10 cm. The higher bed depth provides the more free adsorption sites, making more metal ions to adsorb the blank sites and making the more significant adsorption of metal ions (Mitra & Das, 2020). Figure 4 is the figure depicting the effect of bed depth on this study.

Figure 5 is the representative figure of the variation of the flow rate (10 ml/min – 40 ml/min). It is observed that with the increasing flow rate, the breakthrough time decreases rapidly (Banerjee et al., 2019). The adsorbent surface gets less time to get in touch with metal ions to adsorb less and forms a sharp breakthrough curve at increasing flow rate. Hence, the lowest flow rate (10 ml. min^{-1}) is useful for the process.

Figure 6 explains the variation of influent metal ion concentration at constant bed depth to the flow rate. It is shown from the figure that, at higher Cu(II) ion concentration, the breakthrough time becomes less (Kumar et al., 2019). More Cu(II) ions adsorb into the free adsorption

sites at a higher concentration. The rice husk is getting saturated by adsorbing more metal ions in a short time and lost its capacity for further adsorption.

2.2. Kinetic model

2.2.1. Thomas model (Thomas, 1948)

Thomas model is used to study the breakthrough performance in the continuous process. The linearized model equation is as follow:

$$\ln\left(\frac{C_0}{C_t}-1\right) = \frac{k_{th}q_0 x}{v} - k_{th}C_0 t . \qquad (1)$$
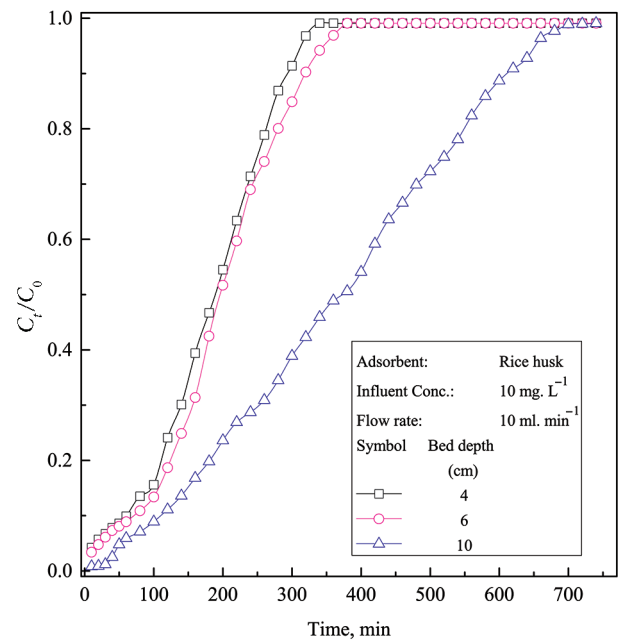

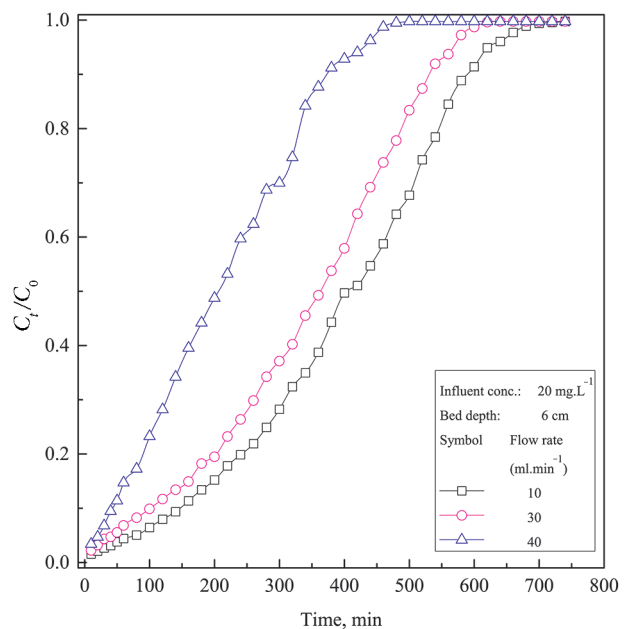Figure 4. Effect of the bed depth

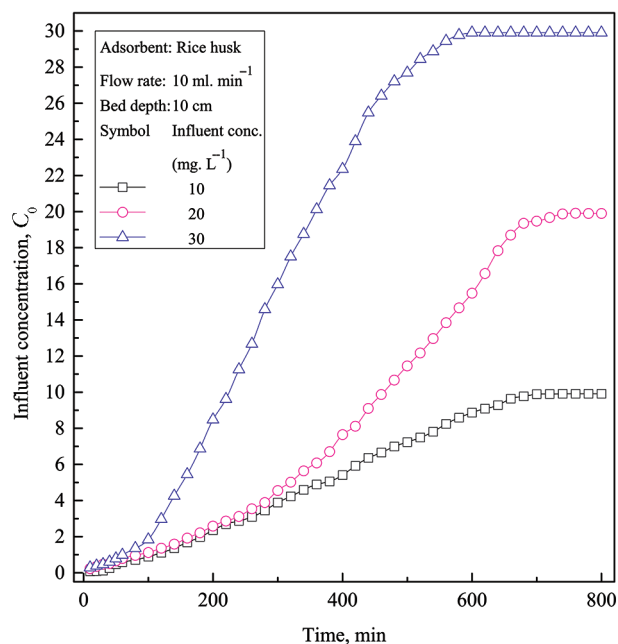Figure 5. The effect of the flow rate

Figure 6. Effect of the influent concentration

Table 1. Thomas model parameters

Variation of the bed depth The flow rate is 10 ml/min, and the inlet conc. is 10 mg/L			
Bed depth Z (cm)	The model rate constant, $k_{th} \times 10^3$ (L/mg/min)	The maximum metal uptake capacity, q_0 (mg. g^{-1})	Correlation coefficient R^2
4	1.63	5.09	0.9821
6	1.54	4.24	0.9737
10	1.64	3.86	0.8841
Variation of the rate of flow The bed depth is 4 cm and the inlet conc. is 20 mg/L			
Flow rate v (ml/min)	The model rate constant, $k_{th} \times 10^3$ (L/mg/min)	The maximum metal uptake capacity, q_0 (mg/g)	Correlation coefficient R^2
10	0.64	7.70	0.9962
30	0.84	5.58	0.9868
40	1.77	2.61	0.9493
Variation of influent concentration The rate of the flow is 10 ml/min, and the bed depth is 4 cm			
Influent conc., C_0 (mg/L)	The model rate constant, $k_{th} \times 10^3$ (L/mg/min)	The maximum metal uptake capacity, q_0 (mg/g)	Correlation coefficient R^2
10	1.63	5.09	0.9821
20	0.64	7.70	0.9962
30	0.99	10.93	0.9487

The k_{th} and q_0 are obtained from $\ln\left(\dfrac{C_0}{C_t}-1\right)$ vs. t plot. The representative value of model parameters with the value of R^2 is shown in Table 1, and Figure 7 is the representative figure for the model plot. With the increase of flow rate and bed height, adsorption capacity (q_0), decreases, whereas, with the rise of influent concentration, it increases. No trend of k_{th} on the operating variables is observed. The correlation coefficient, R^2 varies from 0.8841 to 0.9962 and indicates s statistically acceptable model. The maximum Cu(II) adsorption capacity is 10.93 mg/g at $z = 4$ cm, $v = 30$ mg/L, and $C_0 = 30$ mg/L.
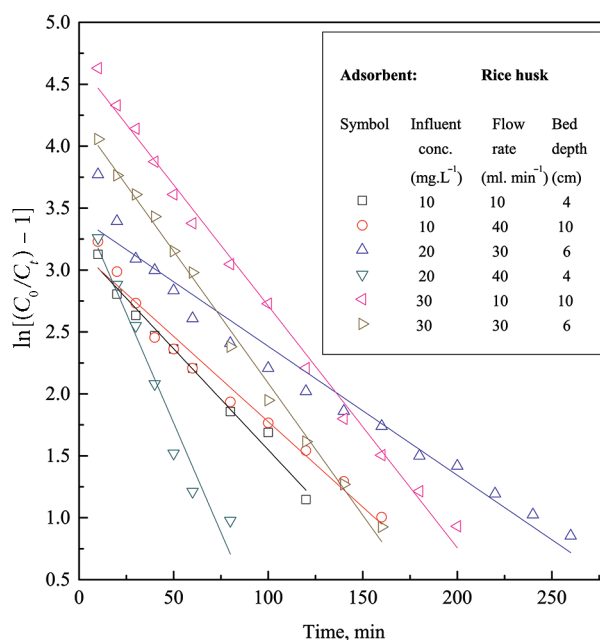

Figure 7. Thomas model graph

2.2.2. Bohart-Admas model (Bohart & Admas, 1920)

The fixed-bed column performance is described by the Bohart-Admas model also. The linear form of equation is as below:

$$\ln\left(\frac{C_t}{C_0}\right) = K_{AB}C_0 t - K_{AB}N_0\left(\frac{z}{u_0}\right). \qquad (2)$$

The K_{AB} and N_0 are determined from linearized plotting of $\ln\left(\dfrac{C_t}{C_0}\right)$ and t. Table 2 present the model parameters along with R^2 value, and Figure 8 is the model plot for the Cu(II) ions removal using rice husk. The K_{AB} value increases with the rise v and decreases with z, but no trend is observed on the increase of influent concentration. The N_0 value decreases with v and z. The R^2 value varies from 0.8413 to 0.9914 and indicates the acceptable model.

Table 2. Bohart-Admas model parameters

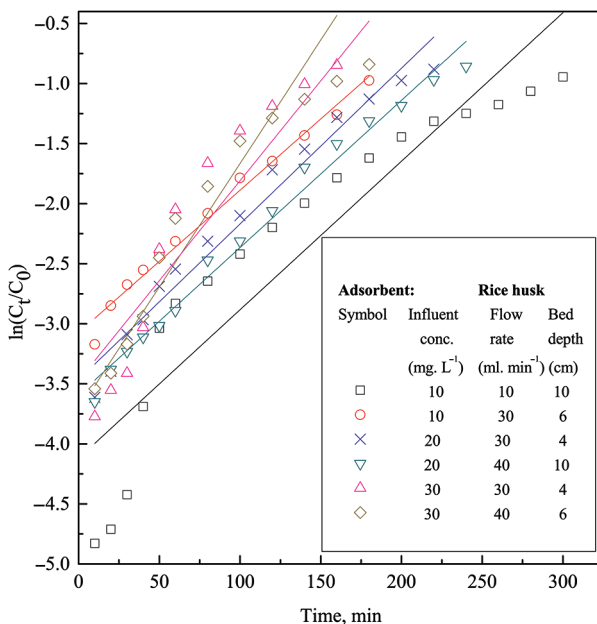| Variation of the bed depth The flow rate is 10 ml/min, and the inlet conc. is 10 mg/L			
Bed depth Z (cm)	The model rate constant, $K_{AB} \times 1000$ (L/mg)	Saturation conc., N_0 (g/L)	Correlation coefficient R^2
4	1.42	28.01	0.9914
6	1.35	20.30	0.9773
10	1.24	16.65	0.8482
Variation of the rate of flow The bed depth is 4 cm and the inlet conc. is 20 mg/L			
Flow rate v (ml/min)	The model rate constant, $K_{AB} \times 1000$ (L/mg)	Saturation conc., N_0 (g/L)	Correlation coefficient R^2
10	0.49	92.71	0.9740
30	0.65	66.81	0.9696
40	0.91	41.63	0.8413
Variation of the influent conc. The rate of the flow is 10 ml/min, and the bed depth is 4 cm			
Influent conc., C_0 (mg/L)	The model rate constant, $K_{AB} \times 1000$ (L/mg)	Saturation conc., N_0 (g/L)	Correlation coefficient R^2
10	1.42	28.01	0.9914
20	0.49	92.71	0.9740
30	0.70	68.04	0.9071

Figure 8. Bohart-Admas model graph

By comparing the two models mentioned above, we can conclude that the Thomas model is slightly better than the Bhart-Admas model.

2.3. Treatment of the industrial effluent water

Industrial effluent water has been collected from a small-sized electroplating industry close to the city of Kolkata. Adsorption of the industrial effluent is conducted after the pH has been adjustment to 6 and using a bed height of 4 cm with a 10 ml/min flow rate. The composition of the treated effluent is shown in Table 3 at the breakthrough point. It is observed that the performance of rice hush is suitable for Cu(II) containing wastewater.

Table 3. Composition of untreated and treated wastewater

Parameters (mg/L)	Untreated wastewater	Treated wastewater at breakthrough point(t_b) (mg/L)
pH	5.62	5.74
Cu(II)	7.51	0.85
Cr(VI)	43.60	34.80
Ca(II)	25.25	24.10
Na(I)	160.26	122.50
K(I)	2.15	1.43
Zn(II)	1.67	1.56
TDS	815.0	676.00

2.4. MLR model

For the study using regression to predict the percentage removal as dependent variable (y), the independent variables for consideration are temperature (x_1), bed depth (x_2), flow rate (x_3), influent concentration (x_4), and effluent concentration (x_5). The variables with their range have been shown in Table 4.

Table 4. Range of the variables

Variables (independent)		Range
Adsorbent		Rice husk
Time (min)	x_1	10 to 780
Flow rate (ml/min)	x_2	10 to 40
Bed depth (cm)	x_3	4 to 10
Influent concentration (mg/L)	x_4	10 to 30
Effluent concentration (mg/L)	x_5	0.08 to 29.91
Variable (dependent)		
The removal percentage	y	0.25 to 99.20
Number of data		755

The equation for calculation of removing efficiency of the Cu(II) ions is:

$$y = 0.905666 - 0.664508 \times x_1 - 0.072669 \times x_2 + 0.082284 \times x_3 + 0.245618 \times x_4 - 0.769871 \times x_5. \quad (3)$$

The variance, mean squared error, and the correlation coefficient obtained from Eq. (1) are 0.077854, 0.006061, and 0.961296. Here, this t-value is 1.963 for 749 degrees of freedom, and the confidence range has been 95%. Figure 9 shows the correlation plot.
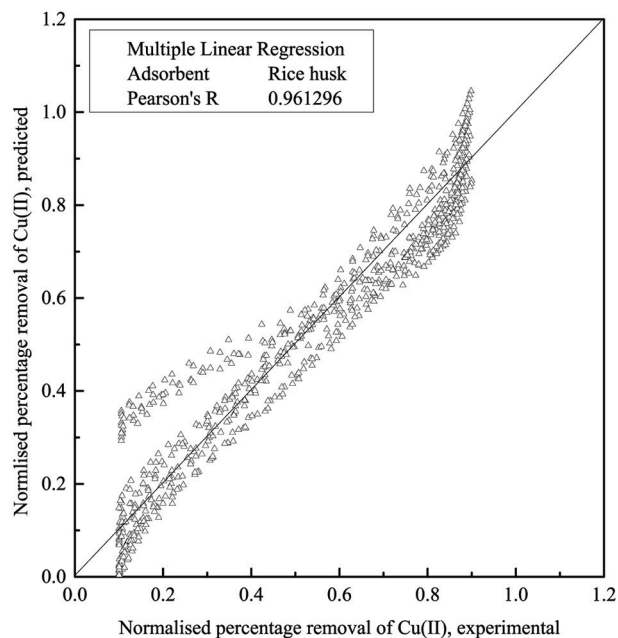
Figure 9. MLR plot for rice husk used as adsorbent

2.5. Neural Network processing

Initially, the data set is randomized 3 times and generate 3 independent data set for ANN analysis. The Levenberg-Marquardt algorithm has been applied with a hidden layer along with a output layer. Hyperbolic tangent (tanh) (Bar et al., 2011; Singha et al., 2015; Nag et al., 2017; Maiti et al., 2019) transfer function is used in the hidden and output layer. The input parameters have been described in the Table 3. 70% of the data used for training. The training process is a complex statistical or mathematical information that is applicable towards the task of updating the weights concerning all the different synapses that are connected with the nodes of the hidden layer and the input and output layers. The algorithm is responsible for making changes to the weights after the calculation of the overall error regarding the training during each epoch. For each epoch, these weight values are changed by a small amount that is randomly chosen either by subtraction or by addition with the preceding value of weights that are recorded as well as stored for each synapse. As a result of which if the corresponding error value has been found to be improved, then this process of addition and/or subtraction continues. Here, the stopping criteria presents us with an excellent solution for stopping this training at a moment when this error value reaches its optimised magnitude. From the Figure 10, it can be clearly observed from the green curve for S_3.

The use of the optimised value has been achieved after calculating the corresponding cross-validation (MSE) during any particular moment when the weights have been changed or updated simultaneously during the training process. The choice of cross-validation MSE for the application of the stopping criterion has been a good practice due to the fact that it eliminates nearly all possibility

of overtraining. Therefore, each sample's 20% data kept separately for cross-validation (Holdout method) plays a vital role. Here, the processing elements number is optimized with the evaluation of this cross-validation error. This optimum value of processing elements number is 25, 25, and 22 for the sample S_1, sample S_2 and sample S_3. This application can be visually observed in Figure 10. The cross-validation curve for sample number 2 is presented in Figure 10. The rest 10% of the data was used for the final prediction.
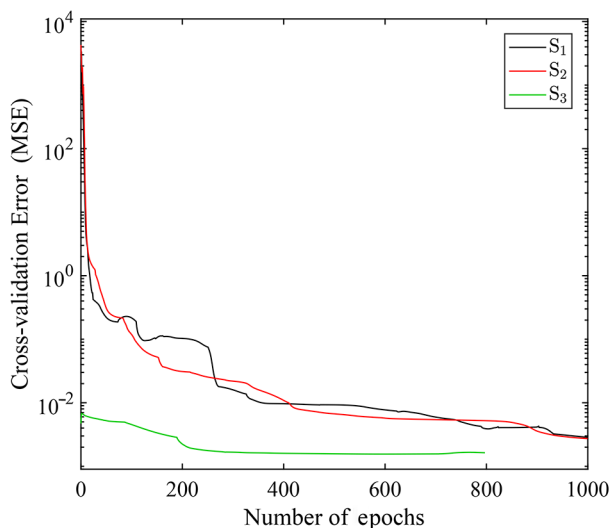

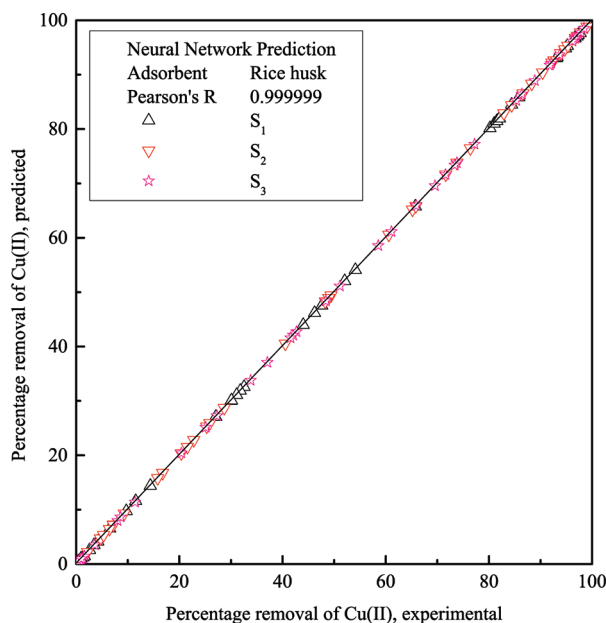Figure 10. Cross-validation curves

Figure 11. Neural network comparison plot

The result in Table 5 shows that the three samples' prediction is consistent with each other as each sample produces satisfactory results with reasonable accuracy, as suggested by R's final value for all three samples. This information alone provides the indication, that the whole

Table 5. Results related to the prediction using LM algorithm

Sample number	Minimum cross-validation error	AARE	SD	MSE	R
S_1	0.002855	0.012310	0.034033	0.003310	0.999999
S_2	0.002720	0.001051	0.002449	0.001496	0.999999
S_3	0.001557	0.023013	0.078862	0.002832	0.999999

modelling, i.e., the training, the cross-validation along with the network's final prediction has been exceptionally accurate. The observation of the Figure 11 further emphasises this fact. Figure 11 presents a comparison concerning the experimental and it's corresponding neural network prediction when Rice husk is used as bio adsorbent to evaluate Cu(II) removal efficiency from aqueous solution.

Conclusions

Rice husk is used to treat Cu(II) ions in fixed-bed column mode without any modification or treatment. Physical characterization was made to identify rice husk's physical properties, and the experiment was done to check the suitability of rice husk to remove Cu(II) ions. The maximum adsorption capacity obtained from the Thomas model is 10.93 mg/g at influent concentration 30 mg/L, flow rate 10 ml/min, along with the bed height of 4 cm. Thomas and Bohart-Admas models are used for predicting the breakthrough curves. Thomas model predicts the breakthrough curve better than the other model. Experimental data was used to predict the Empirical/semi-empirical model. Artificial neural network prediction was performed with the experimental data to check the adsorption capacity (i.e., percentage removal) of rice husk and MLR. The ANN prediction was found to be better than the prediction using MLR.

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APPENDIX

Nomenclature

C_0 the influent metal ion conc. when t is equal to 0 (mg/L).

C_t the effluent metal ion conc. in mg/L when the time is t.

C_t/C_0 the relative conc.

N_0 Saturation conc. (mg/L).

q_0 Maximum value of metal uptake for each gram of adsorbent (mg/g).

t Contact time (min).

u_0 Superficial velocity (m/min).