Nano-magnetic walnut shell-rice husk for Cd(II) sorption: design and optimization using artificial intelligence and design expert

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ABSTRACT

This study attempted to investigate the use of nanomagnetic activated carbon prepared from walnut shell and rice husk wastes for removal of Cd(II) from aqueous solution via application of ANN and design expert as adsorbent preparation design and optimization tools. The novel adsorbent was characterized using SEM, FTIR, EDS and BET. The result from 2-level factorial design expert revealed 78.58% Cd(II) sorption efficiency could be achieved for adsorbent prepared at optimum calcination temperature, calcination time, SS-RH mixing ratio and magnetite loading of 859.20 °C, 2.32 h, 2.54 and 5.56 wt% respectively. Sensitivity analysis by both proposed methodologies revealed calcination temperature as most influential factor in adsorbent preparation. Average relative errors and R² values of 1.2931% and 4.806%; and 0.9967 and 0.9055 obtained respectively for developed ANN model with 4-9-1 architecture and 2-level factorial design expert revealed ANN model as better prediction and optimization tool for Cd(II) sorption using NM-WS-RH-AC. Laboratory analysis revealed presence of –OH, –NH and COO” groups on adsorbent surface; presence of Cd(II) after adsorption; change in adsorbent textural and morphological structure after Cd(II) adsorption; and increase in its surface area and average pore diameter due to magnetization. Average relatively stable desorption strength of 62.74% towards Cd(II) was exhibited by adsorbent for four consecutive cycles using 0.1M HNO₃. Prepared adsorbent is effective in removing Cd(II) from solution than commercial activated carbon with economically viable regeneration attribute.

1. Introduction

It is well-known that the presence of heavy metals in waste water bodies due to natural and anthropogenic activities is extremely dangerous to the lives of humans and aquatic habitants as they interfere with body systems to cause diseases such as liver damage, chronic asthma, diarrhea, kidney congestion, headaches, nausea, vomiting, dermatitis and so on (Ernhart, 1992; Khlifi and Hamza-Chaffai, 2010; Sublet et al., 2003). In the past, findings have shown adsorption as the most prominent and efficient unit operation for the removal of hazardous heavy metals from aqueous solution (Oxcan et al., 2006; Yazdani et al., 2014; Wan Ngah et al., 2011; Popuri et al., 2009; Sahu et al., 2009) as a result of its design and operation simplicity (Bhatnagar and Sillanpaa, 2010); toxic pollutants insensitivity (Bailey et al., 1999); cost effectiveness (Panneerselvam et al., 2011); high heavy metals sorption efficiency (Yao et al., 2014); negligible sludge formation (Lasheen et al., 2017) and many more. The use of different eco-friendly and low-cost adsorbents from readily available agro-allied waste materials such as Eucalyptus camaldulensis Dehn bark (Chatterjee et al., 2011), timber industry waste (Garg, 2005), hen feathers (Mittal, 2006), coconut husk (Tan et al., 2008), Brazilian pine-fruit-shell (Calvete et al., 2009), cotton plant wastes (Tunc et al., 2009), orange peels (AbdurRahman et al., 2013), Solanum tuberosum peels (Rehman et al., 2015), grape stalk wastes (Miralles et al., 2010), rice husk-sstalk shell composite (Popoola et al., 2018), dead Sargassum sp. biomass (Ho, 2004), mesoporous fertilizer plant waste (Mall et al., 2002), corncob and barley husk (Robinson, 2002), tamarind wood (Sahu et al., 2009), peanut hull (Tanyildizi, 2011), custard apple peel (Krishnaa and Padma Sree, 2011), Araucaria angustifolia wastes (Lima et al., 2007), maize bran (Singh et al., 2006), mangosteen shell (Chen et al., 2011), succinylated sugarcane bagasse (Guimarães Gusmão et al., 2012), wheat shell (Bulut and Aydin, 2006), Ceiba pentandra hulls (Rao et al., 2006) as adsorbents for heavy metals sorption from aqueous solution to replace expensive and low sorption efficient commercial activated carbon (Gupta et al., 2016) is becoming obsolete in the research world on daily basis. After adsorption process, many of the adsorbents produced from these sources are highly dispersed in the solution which posed great difficulties for their removal. Nevertheless, some of them are difficult to
be recycled for continuous usage.

An ideal adsorbent for heavy metals removal from aqueous solution should exhibit easy removal of adsorbed pollutants from its surface and ability to be recycled over periods before depletion (Sharma et al., 2009; Ali, 2012). The enhanced flexibility function of magnetic particles in removing material from other compounds via attractive magnetic field has called for adsorbent modification with magnetic particles for sorption of heavy metal ions. Synthesized nanomagnetic adsorbents via impregnation and co-precipitation methods (Zainol et al., 2017; Makarchuk et al., 2016) have special features of non-toxicity, chelate complexes formation with ions of heavy metals by ion exchange process or electrostatic interaction, presence of surface functional groups with large active sites, short contact time, recyclability and reusability after separation under magnetic field. In recent times, nanomagnetic activated carbon particles prepared from oil palm (Zainol et al., 2017), chitosan (Ma et al., 2007), tea waste (Panneerselvam et al., 2011), orange peel (Gupta and Nayak, 2012), sugarcane bagasse (Wannahari et al., 2018), modified α-ketoglutaric acid chitosan (Zhou et al., 2009), titanate nanoflowers (Huang et al., 2012), fruit extract of Momordica cymbalaria (Swamy et al., 2015) and leaf extract of Cassia didymobotrya (Akhtar et al., 2015) had revealed high sorption efficiency for heavy metals from aqueous solution.

There had been world records of health effects and significance of human exposure to hazardous cadmium in developed countries (Moreno-Castilla et al., 2004; Henretig, 2006). Also, there had been enormous waste generated from walnut shell and rice husk in major cities of Nigeria. In this study, nanomagnetic adsorbent was synthesized for sorption of cadmium ion from solution by impregnation of magnetic particles on calcined particles of walnut shell-rice husk. Both artificial intelligence and design expert were used to design and optimize adsorbent preparation. Four inputs (calcination temperature, calcination time, walnut shell-rice husk mixing ratio, calcination time and magnetite loading) were varied with WS-RH-AC based on the coded levels of the adsorbent preparation conditions (calcination temperature, walnut shell-rice husk mixing ratio, calcination time and magnetite loading) obtained from 2² factorial experimental design of Design Expert 7.0.0 software presented in Table 1. To obtain homogenized and thoroughly mixed NM-WS-RH-AC, the mixture was mechanically stirred for 45 min and then separated with aid of magnetic filter using magnetic induction of 58 mT external magnetic field. The obtained residue was then dried at a temperature of 140 °C in an oven for 1 h.

2.4. Batch adsorption process

A temperature-controlled magnetic heat stirrer (Stuart heat-stirrer SB162) was used to study the batch adsorption process while concentration of Cd²⁺ was measured via atomic absorption spectrometer (AAS Buck Scientific 210 VGP). 0.5 g of NM-WS-RH-AC was mixed with 50 mL of Cd (II) salt in a 100-mL flask. Each batch adsorption process was conducted at 30 °C and 120 revolutions per minute at a contact time of 45 min to study the equilibrium attainment. NM-WS-RH-AC was separated from Cd (II) salt solution after adsorption using 10mm filter paper. Concentrations were measured in quadruplets at dilution factor of 50 such that the average values were recorded for the final concentration. The adsorption capacity of NM-WS-RH-AC, qe (mg/g) and Cd²⁺ sorption efficiency at equilibrium were measured using Eqs. (1) and (2) respectively.

\[
q_e = \frac{(C_0 - C_e)}{W} \times 100 \% 
\]

\[
\% \text{Cd}^{2+} \text{ Sorption} = \frac{(C_0 - C_e)}{C_0} \times 100 \% 
\]

where \(C_0\) and \(C_e\) are initial and final concentrations of Pb²⁺ and Cd²⁺ (mg/L), \(V\) is the volume of solution (L) and \(W\) is the weight of adsorbent (g).

2.5. Design of experiments for adsorbent preparation and optimization

The optimization goals include (1) experimental design and (2) maximization of NM-WS-RH-AC adsorbent preparation conditions that give optimum sorption of Cd²⁺ from aqueous solution using both artificial intelligence neural network and 2-level factorial design of Design Expert 7.0.0 to predict the outputs.

2.5.1. 2-Level factorial design

In this, the number of experiments required to determine optimum

| Independent Variables | Factor | Unit | Low Level (-1) | High level (+1) |
|-----------------------|--------|------|----------------|-----------------|
| Calcination Temperature | \(X_1\) | (°C) | 600 | 1000 |
| Calcination Time | \(X_2\) | (hr) | 1 | 5 |
| Walnut Shell-Rice Husk Mixing Ratio | \(X_3\) | - | 1 | 5 |
| Magnetite Loading | \(X_4\) | (wt %) | 2 | 10 |
process variables is varied over two levels (low and high) unlike central composite design where experimental values are varied over five levels (axial points, factorial points and center point). Thus, minimising the number of experiments to be conducted for optimum process variables determination to study variables interaction with one another. For this study, calcination temperature, calcination time, walnut shell-rice husk mixing ratio and magnetite loading were the process independent variables investigated with percent of Cd\(^{2+}\) sorption being the desired outputs to maximize NM-WS-RH-AC adsorbent preparation conditions. Table 1 presents NM-WS-RH-AC preparation factor coding and variable ranges. Sum total of 16 experimental runs were conducted for NM-WS-RH-AC preparation conditions optimization to predict Cd\(^{2+}\) removal efficiency. ANN configuration for optimization of NM-WS-RH-AC preparation conditions comprises of input layer with four experimental factors (calcination temperature, calcination time, walnut shell-rice husk mixing ratio and magnetite loading), hidden layer with 9 neurons (to avoid network overfitting) and output layer for the response (Cd\(^{2+}\) sorption efficiency). The networks’ weights and biases were adjusted iteratively for mean squared error (MSE) minimization such that 60%, 30% and 10% of the input and target vectors were respectively used for training, validation and testing. The weight and bias values were updated during training using the generalized form multilayer perceptron back-propagation algorithm stated as Eq. (3) while hyperbolic tangent sigmoid “tansig” function stated as Eq. (4) was used as hidden layer transfer function which limits the outputs between -1 and +1. The output signal \(y_k\) generated by neuron \(k\) of the ANN is given as Eq. (5). For function fitting in the output layer, “purlin” transfer function presented in Eq. (6) was used such that output was generated in the range of \(-\infty\) to \(+\infty\).

\[
w^{k+1}_j = w^k_j + \eta \delta_k^j f'(s) \\
\phi(s) = 2(1 + \exp(-2s))^{-1} - 1 \quad -1 \leq \phi(s) \leq 1 \\
y_k = \phi\left(\sum_{j=1}^{m} W_{kj} x_j + b_k\right) \\
\phi(s) = x \quad -\infty < \phi(s) < +\infty
\]

where \(W_{ij}\) = connection weights from unit \(i\) in layer \(k\) to unit \(j\) in layer \(k+1\), \(\eta\) = learning rate, \(\delta_k^j\) = signal error, \(I_i\) = input vector to the networks, \(f(s)\) = networks transfer function derivative, \(s\) = sum of all the weights, \(y_k\) = output signal, \(\phi =\) activation function, \(m\) = total number of inputs to the neuron, \(j =\) input, \(W_{kj}\) = synaptic weight of input \(j\) for neuron \(k\), \(x_j\) = input signal, \(b_k\) = bias value of neuron \(k\).

2.5.2. Artificial neural network (ANN)

An ANN is capable of learning relationships between given sets of input and output data via changing the weights called training using back propagation training algorithm (Popoola, 2016). Superiority advantages of ANN over other predictive tools have been presented elsewhere (Singh et al., 2017). In this study, neural network architecture with configuration 4-9-1 (Nasr et al., 2012) was used to optimize NM-WS-RH-AC preparation conditions as shown in Fig. 1 via prediction of Cd\(^{2+}\) removal efficiency. ANN configuration for optimization of NM-WS-RH-AC preparation conditions comprises of input layer with four experimental factors (calcination temperature, calcination time, walnut shell-rice husk mixing ratio and magnetite loading), hidden layer with 9 neurons to avoid network overfitting and output layer for the response (Cd\(^{2+}\) sorption efficiency). The networks’ weights and biases were adjusted iteratively for mean squared error (MSE) minimization such that 60%, 30% and 10% of the input and target vectors were respectively used for training, validation and testing. The weight and bias values were updated during training using the generalized form multilayer perceptron back-propagation algorithm stated as Eq. (3) while hyperbolic tangent sigmoid “tansig” function stated as Eq. (4) was used as hidden layer transfer function which limits the outputs between -1 and +1. The output signal \(y_k\) generated by neuron \(k\) of the ANN is given as Eq. (5). For function fitting in the output layer, “purlin” transfer function presented in Eq. (6) was used such that output was generated in the range of \(-\infty\) to \(+\infty\).

\[
w^{k+1}_j = w^k_j + \eta \delta_k^j f'(s) \\
\phi(s) = 2(1 + \exp(-2s))^{-1} - 1 \quad -1 \leq \phi(s) \leq 1 \\
y_k = \phi\left(\sum_{j=1}^{m} W_{kj} x_j + b_k\right) \\
\phi(s) = x \quad -\infty < \phi(s) < +\infty
\]

where \(W_{ij}\) = connection weights from unit \(i\) in layer \(k\) to unit \(j\) in layer \(k+1\), \(\eta\) = learning rate, \(\delta_k^j\) = signal error, \(I_i\) = input vector to the networks, \(f(s)\) = networks transfer function derivative, \(s\) = sum of all the weights, \(y_k\) = output signal, \(\phi =\) activation function, \(m\) = total number of inputs to the neuron, \(j =\) input, \(W_{kj}\) = synaptic weight of input \(j\) for neuron \(k\), \(x_j\) = input signal, \(b_k\) = bias value of neuron \(k\).

2.6. NM-WS-RH-AC adsorbent characterization

The NM-WS-RH-AC adsorbent that gives optimum removal efficiency of Cd\(^{2+}\) from aqueous solution was characterized before and after adsorption process. The existing chemical bonding and functional groups of NM-WS-RH-AC was observed over the wavelength range of 300–4000 cm\(^{-1}\) using FTIR spectrometer (Nicolet iS10 FT-IR Spectrometer) and
obtained spectra were analyzed further. The adsorbent's elemental analysis and structural morphology was investigated using scanning electron microscope (SEM/EDX-JEOL-JSM 7600F) at 5000×, 15 kV under high-vacuum evaporation of sample deposition methodology. In order to examine the effect of calcination and magnetization on surface area, pore volume and pore diameter of mixed walnut shell-rice husk, Brunauer-Emmett-Teller method was executed by using a Quantachrome Autosorb instrument (Nova 11.03A, USA version). This was achieved based on physical nitrogen adsorption principle at 77 K.

2.7. NM-WS-RH-AC regeneration and reusability

The sorption strength of prepared NM-WS-RH-AC for Cd\(^{2+}\) from aqueous solution was thoroughly investigated using 0.1M HNO\(_3\). After the first sorption process, distilled water at 7.0 pH was used to thoroughly wash the NM-WS-RH-AC adsorbent after which it was dried at 80°C for 6 h and reused for four consecutive times in order to affirm its reusability capacity for Cd\(^{2+}\) sorption from aqueous solution. The method of calculating desorption efficiency of prepared adsorbent presented by Giri et al. (2011) was adopted.

3. Results and discussion

3.1. 2-Level factorial design expert for NM-WS-RH-AC preparation conditions

The 2\(^k\) factorial level of design expert was instrumental in developing mathematical model to predict Cd(II) sorption, statistical analysis of data, studying of model factors contributory effects and optimum numerical point prediction of process variables for NM-WS-RH-AC preparation required for optimum Cd(II) sorption from aqueous solution.

Table 2

| Adsorbent Code | Calcination Temp. (°C) X1 | Calcination Time (hr) X2 | SS-RH Mixing ratio X3 | Magnetite loading (wt%) X4 | Adsorbent Capacity (mg/g) | Cd\(^{2+}\) Sorption efficiency (%) |
|----------------|--------------------------|--------------------------|-----------------------|---------------------------|--------------------------|-------------------------------------|
| NM-WS-RH-AC1   | 600.00                   | 1.00                     | 1.00                  | 10.00                     | 126.738                  | 55.3172 58.75089 6.207             |
| NM-WS-RH-AC2   | 1000.00                  | 5.00                     | 5.00                  | 2.00                      | 168.236                  | 79.4007 73.21679 7.788             |
| NM-WS-RH-AC3   | 1000.00                  | 5.00                     | 1.00                  | 2.00                      | 129.104                  | 58.2315 61.37179 5.393             |
| NM-WS-RH-AC4   | 600.00                   | 1.00                     | 5.00                  | 10.00                     | 103.305                  | 72.5418 68.74394 5.235             |
| NM-WS-RH-AC5   | 600.00                   | 5.00                     | 1.00                  | 2.00                      | 151.004                  | 77.7723 84.08097 8.112             |
| NM-WS-RH-AC6   | 1000.00                  | 5.00                     | 5.00                  | 10.00                     | 177.238                  | 83.4069 81.12487 2.736             |
| NM-WS-RH-AC7   | 1000.00                  | 1.00                     | 5.00                  | 10.00                     | 165.413                  | 81.2532 78.91269 2.881             |
| NM-WS-RH-AC8   | 1000.00                  | 1.00                     | 1.00                  | 2.00                      | 132.541                  | 66.8251 78.79934 17.919            |
| NM-WS-RH-AC9   | 1000.00                  | 1.00                     | 1.00                  | 2.00                      | 168.739                  | 84.6324 82.10544 2.986             |
| NM-WS-RH-AC10  | 600.00                   | 5.00                     | 1.00                  | 10.00                     | 137.335                  | 59.6318 57.03472 4.355             |
| NM-WS-RH-AC11  | 600.00                   | 5.00                     | 5.00                  | 2.00                      | 141.992                  | 68.4517 69.12837 0.989             |
| NM-WS-RH-AC12  | 1000.00                  | 1.00                     | 5.00                  | 2.00                      | 172.387                  | 87.2381 85.70969 1.752             |
| NM-WS-RH-AC13  | 1000.00                  | 1.00                     | 1.00                  | 10.00                     | 178.441                  | 91.3452 93.85459 2.747             |
| NM-WS-RH-AC14  | 1000.00                  | 5.00                     | 1.00                  | 10.00                     | 184.164                  | 96.9938 97.54227 0.565             |
| NM-WS-RH-AC15  | 600.00                   | 1.00                     | 5.00                  | 2.00                      | 127.527                  | 43.7617 46.37007 5.960             |
| NM-WS-RH-AC16  | 600.00                   | 5.00                     | 5.00                  | 10.00                     | 141.518                  | 73.9835 73.04044 1.275             |
| Average Absolute Error |                      |                          |                       |                           |                           | 4.806                                  |
3.1.2. Contributory effects of model factors

The order of percent contributory effect of main factors to Cd(II) sorption efficiency to level design expert to the Cd(II) sorption efficiency of model factors as obtained from the effect tools box of 2k factorial conditions.

Fig. 2(a) represents the plot of experimental and predicted value of 4.4182 and confidence level of 95% suggest developed model exactness. Fig. 2(a) depicts increase in Cd(II) uptake from aqueous solution as calcination temperature ($X_3$) and calcination time ($X_4$) increases from 1-5 h and 600–1000 °C respectively while SS-RH mixing ratio and magnetite loading were kept at centre point with respective values of 3.00 and 6.00. In conclusion, contributory order of factors effect is evident in NM–WS-RH–AC (shown in Table 2) prepared at 1000 °C calcination temperature, 5 h calcination time, 1 SS-RH mixing ratio and 10 wt% magnetite loading which gave the highest experimental Cd(II) adsorption efficiency with lowest SS-RH mixing ratio.

3.1.3. Numerical optimization point prediction of NM–WS-RH–AC process variables

Table 4 presents the optimum point predicted by the 2k factorial level design expert with the objective of maximizing Cd(II) sorption efficiency from aqueous solution subject to minimising process variables (preparation conditions) of NM–WS-RH–AC. At these points, an experimental run was conducted to check the efficiency of predicted model (Equation 7). The percentage of Cd(II) from aqueous solution using NM–WS-RH–AC prepared at calcination temperature, calcination time, SS-RH mixing ratio and magnetite loading of 859.20 °C, 2.32 h, 2.54 and 5.56 wt% respectively was 78.58%. This shows good agreement between experimental and predicted results at optimum points with an approximate relative error of 2.91%. This indicates maximum Cd(II) sorption could be attained at NM–WS-RH–AC optimum preparation conditions.

3.2. Artificial neural network

3.2.1. Network weights and biases adjustment

In order to improve the performance of the network, adaption of its adjustable parameters (weights and biases) during ANN model training is required for its output to match with the target value. The magnitude of performance gradient being lower than 1e−5 implies completion of training step (Popoola and Sunu, 2014). In this study, the network architecture has four, nine and one neurons in input, hidden and output layers respectively such that each element present in the 4-length input vector ($P_{1:4}$) was connected to each neuron present in the 9-length hidden layer via a 9×4 weight matrix ($W_{9 \times 4}$). This makes the sum of the weighted inputs to be $\sum W_{9 \times 4}P_{4:1}$ such that the

![Graph](image)

Fig. 2. (a) Percent values of experimental against predicted Cd(II) sorption (b) Standard error contour of 2k factorial design for Cd(II) sorption using NM–WS-RH–AC.
addition of a 9-length bias \( (b_{9,1}) \) gives \( u_{9,1} = \sum W_{9,4} P_{4,1} + b_{9,1} \). The summed net input was then transformed via “tansig” transfer function to the hidden layer to have \( f(u) = \tanh(\sum W_{9,4} P_{4,1} + b_{9,1}) \). In between the hidden layer and output layer, each neuron present in the vector of 9-length hidden layer \( (P_{9,1}) \) was connected to the one-neuron output layer via a \( 1 \times 9 \) weight matrix \( (W_{1,9}) \). The input weighted sum gives \( \sum W_{1,9} P_{9,1} + b_{1,1} \). The summed net input was then transformed via “purlin” transfer function to the output layer to give \( f(u) = \text{purlin}(u_{1,1} = \sum W_{1,9} P_{9,1} + b_{1,1}) \).

3.2.2. Performances of training and validation steps

The network training process was terminated after the validation check number and performance gradient magnitude of 7 and 0.2618 were respectively attained. The gradient magnitude greater than \( 1e^{-5} \) least error level is an implication of best validation performance. Table 5 presents values of weights connection \( (W_{9,4} \) and \( W_{1,9} \)) and threshold levels \( (b_{9,1} \) and \( b_{1,1} \)) at these conditions where minimum square error was achieved on the validation set. These neural network biases and weights were then used to develop best-fit outputs for training data.

### Table 4

The contributory effect (sensitivity analysis) of each of the process variables (calcination temperature, calcination time, walnut shell-rice husk mixing ratio and magnetite loading) on the sorption efficiency of prepared NM-WS-RH-AC towards Cd(II) was investigated using the proposed optimal ANN model weights presented in Table 5. To achieve this, Eq. (8) which employs network’s connection weights partitioning methodology (Garson, 1991) was used while date arrangement and sensitivity analysis computation has been presented elsewhere (Ranasinghe et al., 2017).

\[
S_j = \left( \sum_{i=1}^{N_h} \frac{\left| w_{ij} \right|}{\sum_{i=1}^{N_h} \left| w_{ij} \right|} \right) \times \left| \frac{W_{ij}}{W_{ij}} \right|
\]

where \( S_j \) is the \( j \)th input variable relative sensitivity on output variable, \( W \) stands for connection weight, \( N_h \) is the numbers of hidden neurons and \( N_i \) represents number of input neurons. The subscripts ‘x’, ‘y’ and ‘z’ represent number of input neurons.

### Table 5

Proposed ANN model weights and threshold levels.

| Hidden layer node | Input layer weight from node i to node j in hidden layer for \( W_{9,4} \) matrix | Hidden threshold \( (b_{9,1}) \) | Output layer node | Hidden layer weight from node j to node k in output layer for \( W_{1,9} \) matrix | Output layer threshold \( (b_{1,1}) \) |
|-------------------|-----------------------------------------------|-------------------------------|--------------------|-----------------------------------------------|-------------------------------|
|                   | \( x = 1 \) | \( x = 2 \) | \( x = 3 \) | \( x = 4 \) | \( y = 5 \) | \( y = 6 \) | \( y = 7 \) | \( y = 8 \) | \( y = 9 \) | \( y = 10 \) | \( y = 11 \) | \( y = 12 \) | \( y = 13 \) |
| \( y = 5 \)       | \( -0.0774 \) | \( -0.3392 \) | \( -2.7002 \) | \( -1.6619 \) | \( 3.7965 \) | \( -0.9898 \) | \( -0.2925 \) | \( 0.9889 \) | \( -2.7329 \) | \( 0.0150 \) | \( -0.2246 \) | \( -0.2252 \) | \( -0.8686 \) |
| \( y = 6 \)       | \( 1.2317 \) | \( -4.6182 \) | \( -0.8631 \) | \( -0.4106 \) | \( -0.1927 \) | \( 0.3391 \) | \( 0.1868 \) | \( -0.2291 \) | \( 0.9889 \) | \( -2.7329 \) | \( 0.0150 \) | \( -0.2246 \) | \( -0.2252 \) | \( -0.8686 \) |
| \( y = 7 \)       | \( -4.6302 \) | \( 0.6910 \) | \( -4.4379 \) | \( 2.7285 \) | \( 2.416 \) | \( 1.3432 \) | \( 5.5303 \) | \( -0.9224 \) | \( 0.3391 \) | \( 0.1868 \) | \( -0.2291 \) | \( 0.9889 \) | \( -2.7329 \) | \( 0.0150 \) | \( -0.2246 \) | \( -0.2252 \) | \( -0.8686 \) |
| \( y = 8 \)       | \( 9.5182 \) | \( 3.2164 \) | \( 1.4178 \) | \( -3.4201 \) | \( -1.5204 \) | \( 3.5480 \) | \( 3.5480 \) | \( 3.5480 \) | \( 3.5480 \) | \( 3.5480 \) | \( 3.5480 \) | \( 3.5480 \) | \( 3.5480 \) | \( 3.5480 \) | \( 3.5480 \) | \( 3.5480 \) | \( 3.5480 \) |
| \( y = 9 \)       | \( -0.5378 \) | \( -0.7231 \) | \( -0.0498 \) | \( 1.3432 \) | \( 5.5303 \) | \( -0.9224 \) | \( 0.3391 \) | \( 0.1868 \) | \( -0.2291 \) | \( 0.9889 \) | \( -2.7329 \) | \( 0.0150 \) | \( -0.2246 \) | \( -0.2252 \) | \( -0.8686 \) |
| \( y = 10 \)      | \( -0.6182 \) | \( 1.2871 \) | \( 2.7975 \) | \( -0.7554 \) | \( -0.9224 \) | \( 1.3432 \) | \( 5.5303 \) | \( -0.9224 \) | \( 0.3391 \) | \( 0.1868 \) | \( -0.2291 \) | \( 0.9889 \) | \( -2.7329 \) | \( 0.0150 \) | \( -0.2246 \) | \( -0.2252 \) | \( -0.8686 \) |
| \( y = 11 \)      | \( 3.7192 \) | \( -1.4198 \) | \( 1.8248 \) | \( 3.5480 \) | \( 2.5443 \) | \( 1.3432 \) | \( 5.5303 \) | \( -0.9224 \) | \( 0.3391 \) | \( 0.1868 \) | \( -0.2291 \) | \( 0.9889 \) | \( -2.7329 \) | \( 0.0150 \) | \( -0.2246 \) | \( -0.2252 \) | \( -0.8686 \) |
| \( y = 12 \)      | \( 1.3291 \) | \( 7.1828 \) | \( -1.7103 \) | \( -1.0934 \) | \( 2.9476 \) | \( 1.3432 \) | \( 5.5303 \) | \( -0.9224 \) | \( 0.3391 \) | \( 0.1868 \) | \( -0.2291 \) | \( 0.9889 \) | \( -2.7329 \) | \( 0.0150 \) | \( -0.2246 \) | \( -0.2252 \) | \( -0.8686 \) |
| \( y = 13 \)      | \( -1.7834 \) | \( -0.2937 \) | \( 3.6041 \) | \( 5.6183 \) | \( 6.2630 \) | \( 1.3432 \) | \( 5.5303 \) | \( -0.9224 \) | \( 0.3391 \) | \( 0.1868 \) | \( -0.2291 \) | \( 0.9889 \) | \( -2.7329 \) | \( 0.0150 \) | \( -0.2246 \) | \( -0.2252 \) | \( -0.8686 \) |

Note: \( x \) = input layer node, \( y \) = hidden layer node, \( z \) = output layer node.

Fig. 3. (a) Pareto chart of model factors contribution percent (b) 3D surface plot depicting calcination temperature and time effects on Cd(II) adsorption onto NM-WS-RH-AC.
represent input, hidden and output neurons respectively while superscripts ‘i’, ‘h’ and ‘o’ are input, hidden and output layers respectively. Fig. 4 presents the percent relative significance of the input variables for NM-WS-RH-AC preparation which enhanced its adsorptive efficiency for Cd(II) removal from aqueous solution. The order of significance was calcination temperature, magnetite loading, calcination time and SS-RH mixing ratio with respective percent contributory effect of 44.82%, 28.14%, 21.37% and 5.67%. From these, the calcination temperature was the most significant factor among the examined process variables exhibiting 44.82% adsorption contributory effect. Previous studies have also revealed the importance of temperature in adsorbent preparation (Panneerselvam et al., 2011; Tanyildizi, 2011). Also, similar order of variables significance was obtained for variables contributory effect studied using 2-level factorial design expert. This results revealed that none of the variables examined could be neglected from this study and proposed ANN model is a good representation of Cd(II) sorption from aqueous solution using NM-WS-RH-AC prepared within specified process variables ranges.

3.2.4. Developed ANN model testing, regression and optimization

Table 6 presents the results of the testing step of developed ANN model in order to check for its efficacy in predicting minimum NM-WS-RH-AC preparation conditions that give optimum Cd(II) sorption from aqueous solution. For comparative purpose, random input vectors from 2-level factorial were used as input variables for the ANN model. The average absolute error obtained was 1.2931% for Cd(II) sorption efficiency as compared to 4.806% obtained when 2-level factorial experimental design was used as the design and optimization tool. This reveals ANN model as better prediction tool than 2-level factorial design expert for Cd(II) sorption using NM-WS-RH-AC. A lower average absolute error implies better accuracy which is an indication of better prediction. Though this research work is first of its kind as none had used artificial intelligence and design expert as comparative tools for Cd(II) sorption from aqueous solution using activated carbon prepared from non-magnetised walnut shell-rice husk, previous studies have proved ANN as better design and optimization tool (Popoola, 2016; Khataee and Kasiri, 2011). The regression plot (testing result) of target (experimental) against predicted (ANN) output for the Cd(II) sorption efficiency by NM-WS-RH-AC using ANN architecture of 4-9-1 (shown in Fig. 5) revealed R² value of 0.9967. This shows only 0.33% of the response total variability could not be explained by the ANN model indicating excellent performance efficiency of developed ANN to be 99.67%. All these are evident enough to prove that the developed ANN was a better response prediction tool.

3.3. NM-WS-RH-AC characterization

3.3.1. SEM

The scanning electron micrographs of NM-WS-RH-AC prepared at optimum conditions (calcination temperature = 859.20 °C, calcination time = 2.32 h, WS-RH mixing ratio = 2.54 and magnetite loading = 5.56 wt%) predicted by two-level factorial design expert before and after Cd(II) sorption are presented in Fig. 6. The SEM image (Fig. 6a) revealed formation of pores having unevenly-distributed particle size and shape with high deposition of magnetite on the adsorbent surface before Cd(II) adsorption. These are special features that would enhance easy solutes adsorption and percolation onto active pores on adsorbent surface (Krishna Mohan et al., 2017). Similar studies have also obtained similar SEM image of nano-magnetic adsorbent before adsorption (Giri et al., 2011; Wannahari et al., 2018). However, a change in the textural and morphological structure of the used NM-WS-RH-AC was observed after Cd(II) sorption from aqueous solution as presented in Fig. 6b showing blockage of pores with reduction in their number, spaces and surface area. These changes revealed adsorption of Cd(II) onto NM-WS-RH-AC surface and pores.

3.3.2. FTIR

Fig. 7 presents the Fourier-Transform-Infrared spectra of NM-WS-RH-AC adsorbent before and after Cd(II) sorption studied over wavelength range of 300–4300nm. This was executed in order to know (i) active functional groups on adsorbent’s surface that have enhanced Cd(II) sorption from aqueous solution (ii) bonding structures present in adsorbent and (iii) adsorption mechanism between adsorbent and Cd(II) solution. Shift of broad peaks from 3428, 1814 and 1446 cm⁻¹ before adsorption to 3462, 1758 and 1428 cm⁻¹ after adsorption indicates bending vibration of –OH (Cao et al., 2014), stretching vibration of –NH and carbonyl stretching of COO⁻ (Panneerselvam et al., 2011) functional groups respectively. These indicate adsorption of Cd(II) onto NM-WS-RH-AC surface by formation of hydrogen bond involving –OH, –NH and COO⁻. The most affirmative proof of Cd(II) sorption onto NM-WS-RH-AC surface was the appearance of sharp broad peaks present at 2048, 3284 and 3764 cm⁻¹ on the IR spectrum after adsorption pertaining to cadmium presence which are missing on IR spectrum before adsorption.

3.3.3. EDS

The result of energy dispersive spectroscopy analysis showing elemental weight percent of adsorbent before and after Cd(II) adsorption from aqueous is presented in Table 7. The larger weight percent of calcium (13.21%) and silicon (21.20%) could be traced to walnut shell and rice husk respectively (Korotkova et al., 2016) while presence of iron (38.85%) is a strong evidence of their magnetization before Cd(II) adsorption. The following observations are strong evidence of Cd(II) sorption onto NM-WS-RH-AC (1) changes in the weight percent of adsorbent elemental composition (Popoola, 2019) (2) reduction in oxygen and hydrogen content implies H⁺ and OH⁻ reaction has occurred on adsorbent surface and (3) presence of cadmium in the adsorbent (found missing before adsorption) after adsorption.

3.3.4. BET

A comparison of pore volume, surface area and pore diameter of raw walnut shell-rice husk (RWS-RH), calcinated walnut shell-rice husk (CWS-RH) and nanomagnetic walnut shell-rice husk activated carbon (NM-WS-RH-AC) executed using Brunauer-Emmett-Teller analysis with commercial activated carbon (CAC) is presented in Table 8. The CWS-RH and NM-WS-RH-AC were prepared at predicted optimum operating conditions (X₁ = 859.20 °C, X₂ = 2.32 h, X₃ = 2.54 and X₄ = 5.56 wt%) suggested by 2⁴ factorial level design expert. The CWS-RH was prepared without magnetite loading. The contributory effects of calcination temperature and calcination time were manifested as surface area, total pore volume and average pore diameter increased from 38.08 m²g⁻¹, 0.0073 cm³g⁻¹ and 2.77 Å for RWS-RH to 94.54 m²g⁻¹, 0.0932 cm³g⁻¹ and 3.31 Å for CWS-RH respectively (Popoola, 2019). Magnetization of CWS-RH influenced increase in its surface area and average pore diameter from 94.54 m²g⁻¹ and 3.31 Å to 126.72 m²g⁻¹ and 4.18 Å for NM-WS-RH-AC.
respectively. This could be attributed to magnetic particles dispersion at high level on CWS-RH surface having a specific surface area (Park et al., 2011). Similar studies have also revealed increase in surface area of parent materials after magnetic particles impregnation (Hu et al., 2011; Panneerselvam et al., 2011; Zainol et al., 2014). However, a slight reduction in total pore volume from 0.0932 cm²/g for CWS-RH to 0.0811 cm²/g for NM-WS-RH-AC was observed which could result from smoother texture of NM-WS-RH-AC surface after impregnation of magnetite (Idan et al., 2018). Conclusively, the prepared NM-WS-RH-AC revealed better textural properties and porous structure than CAC. Table 9 presents textural properties of previous nanomagnetic activated carbons of parent materials used as adsorbent as compared with present study.

### 3.4. NM-WS-RH-AC regeneration and reuse

The adsorption-desorption cycles of NM-WS-RH-AC prepared at $2^k$ factorial level design expert predicted optimum operating conditions ($X_1 = 859.20$ °C, $X_2 = 2.32$ h, $X_3 = 2.54$ and $X_4 = 5.56$ wt%) was examined for its reusability efficiency for Cd(II) sorption from aqueous solution. As presented in Table 10, the adsorption and desorption efficiencies of regenerated NM-WS-RH-AC for Cd(II) sorption were maintained between 77.14 - 78.58% and 61.18 – 62.74% respectively for consecutive four cycles. This result reveals a relatively equal adsorption-desorption efficiencies which shows excellent reusability of adsorbent with good stability. This could be attributed to the presence of magnetite binding the walnut shell and rice husk particles together to enhance adsorbent’s stability nature towards Cd(II) removal from aqueous solution. This attribute makes NM-WS-RH-AC to be economically viable and proves its suitability as adsorbent for treatment of waste water.

### 3.5. Proposed adsorption mechanisms

For proper understanding of how Cd$^{2+}$ was being removed from aqueous solution using NM-WS-RH-AC, it is necessary to propose the

![Fig. 6. SEM image of NM-WS-RH-AC (a) before and (b) after Cd(II) sorption.](image-url)
reaction mechanism between the positively charged $\text{Cd}^{2+}$ and existing negatively charged ions on NM-WS-RH-AC surface by binding electrostatic forces. The executed FTIR analysis has revealed presence of $-\text{OH}$, $-\text{NH}$ and $\text{COO}^-$ on adsorbent surface whose ionisation is a function of the $\text{Cd}^{2+}$ solution pH by either gaining or losing a proton. The NM-WS-RH-AC surface becomes positively charged at low solution pH by gaining a proton. Thus, Eqs. (9), (10), and (11) exist.

\begin{align*}
\text{NM-WS-RH-AC} - \text{OH} + \text{H}^+ & \rightarrow \text{NM-WS-RH-AC} - \text{OH}_2^+ \quad (9) \\
\text{NM-WS-RH-AC} - \text{NH} + \text{H}^+ & \rightarrow \text{NM-WS-RH-AC} - \text{NH}_2^+ \quad (10) \\
\text{NM-WS-RH-AC} - \text{COOH} + \text{H}^+ & \rightarrow \text{NM-WS-RH-AC} - \text{COOH}_2^+ \quad (11)
\end{align*}

When the solution pH is very high, NM-WS-RH-AC surface becomes negatively charged by losing a proton as presented in Eqs. (12), (13), and (14).

\begin{align*}
\text{NM-WS-RH-AC} - \text{OH} + \text{OH}^- & \rightarrow \text{NM-WS-RH-AC} - \text{O}^- + \text{H}_2\text{O} \quad (12) \\
\text{NM-WS-RH-AC} - \text{NH} + \text{OH}^- & \rightarrow \text{NM-WS-RH-AC} - \text{N}^- + \text{H}_2\text{O} \quad (13) \\
\text{NM-WS-RH-AC} - \text{COOH} + \text{OH}^- & \rightarrow \text{NM-WS-RH-AC} - \text{COO}^- + \text{H}_2\text{O} \quad (14)
\end{align*}

Thus, electrostatic attractive forces favoured sorption of $\text{Cd}^{2+}$ onto NM-WS-RH-AC surface when solution pH was high such that the proposed adsorption mechanisms could be presented as Eqs. (15), (16), and (17).

\begin{align*}
\text{NM-WS-RH-AC} - \text{O}^- + \text{Cd}^{2+} & \rightarrow \text{NM-WS-RH-AC} - \text{O}^- \cdot \text{Cd} \quad (15) \\
\text{NM-WS-RH-AC} - \text{N}^- + \text{Cd}^{2+} & \rightarrow \text{NM-WS-RH-AC} - \text{N}^- \cdot \text{Cd} \quad (16) \\
\text{NM-WS-RH-AC} - \text{COO}^- + \text{Cd}^{2+} & \rightarrow \text{NM-WS-RH-AC} - \text{COO}^- \cdot \text{Cd} \quad (17)
\end{align*}

4. Conclusion

In this study, an eco-friendly low-cost activated carbon adsorbent was prepared from walnut shell and rice-husk wastes via calcination and magnetization processes with the objective of using it to remove hazardous Cd(II) from aqueous solution. An efficiency of 78.58% at 2-level factorial design expert was revealed while optimum preparation conditions of 859.20°C, 2.32 h, 2.54 and 5.56 wt% for calcination temperature, calcination time, SS-RH mixing ratio and magnetite loading were predicted respectively. Executed sensitivity analysis of model factors by both 2k factorial design and ANN revealed calcination temperature as the most contributory factor enhancing NM-WS-RH-AC efficiency for Cd(II) sorption with significance of 44.87% and 44.82% respectively. However, average relative errors and $R^2$ values of 1.2931% and 4.806%; and 0.9967 and 0.9055 obtained respectively for developed ANN model with 4-9-1 architecture and 2-level factorial design expert revealed ANN.

![FTIR spectra of NM-WS-RH-AC before and after Cd(II) adsorption.](image-url)
model as better prediction and optimization tool for Cd(II) sorption using NM-WS-RH-AC. SEM image revealed change in adsorbent textural and morphological structure after Cd(II) adsorption. FTIR revealed presence of –OH, –NH and COO− groups on adsorbent surface. EDS showed Cd(II) was present in the adsorbent after adsorption. BET revealed increase in NM-WS-RH-AC surface area and average pore diameter due to magnetization. In conclusion, the prepared adsorbent is effective in removing Cd(II) from solution than commercial activated carbon with economically viable regeneration attribute.

Declarations

Author contribution statement

Lekan Popoola: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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The authors declare no conflict of interest.

Additional information

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