

Enhanced Removal of Cr (VI) from Wastewater with Green and Low-Cost Nanomaterial Using Fuzzy Inference Systems (FIS) and Artificial Neural Networks (ANN) [†]

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[†] Presented at the 2nd International Electronic Conference on Processes: Process Engineering—Current State and Future Trends (ECP 2023), 17–31 May 2023; Available online: <https://ecp2023.sciforum.net/>.

Abstract: In this study, an artificial neural network (ANN) and an adaptive neuro-fuzzy inference system (ANFIS) were used to predict the adsorption potential of the adsorbent for the removal of chromium (VI) from an aqueous solution. Four operational variables were studied to assess their impact on the adsorption study in the ANFIS model, including initial Ni (II) concentration (mg/L), pH, contact duration (min), and adsorbent dose (mg/L). To build the ANN model, 70% of the data was used for training and 15% for testing and validation. The network was trained using feedforward propagation and the Levenberg-Marquardt algorithm. The regression coefficients (R^2) for the ANFIS and ANN models were 0.99 and 0.98, respectively. The results show a good match between model-predicted and experimental data, indicating that the models are appropriate and compatible. The RMSE between predicted and observed removal percentage values for the ANFIS model was 0.008, whereas the RMSE for the ANN model was 0.06. The AARE between predicted and experimental removal percentage values for the ANFIS and ANN models was determined to be 0.009 and 0.045, respectively. The MSE between predicted and experimental removal percentages for the ANFIS and ANN models was found to be 0.002 and 0.035, respectively. The optimum conditions were pH 6, an initial concentration of 275 mg/L, a contact time of 60 min, and a dosage of 12.5 mg/L; the absorption was 91.00%.

Keywords: artificial neural network; adaptive neuro-fuzzy inference system; wastewater; removal; Levenberg-Marquardt algorithm

Citation: Banza, M.; Seodigeng, T. Enhanced Removal of Cr (VI) from Wastewater with Green and Low-Cost Nanomaterial Using Fuzzy Inference Systems (FIS) and Artificial Neural Networks (ANN). *Eng. Proc.* **2023**, *37*, x.

<https://doi.org/10.3390/xxxxx>

Published: date



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1. Introduction

Heavy metals are primarily found in wastewater from various chemical industries, including steel production, chemical manufacturing, fertilizer, mining, pulp, and pesticides, as well as metallurgy, mining, coal power, leather industries, and the production of various polymers, such as polyvinyl chloride [1]. The rapid rise of industrialization has significantly contributed to releasing pollutants into the environment. Since heavy metals are not biodegradable, they accumulate in human beings. Toxic heavy metals such as arsenic, chromium, copper, cadmium, lead, nickel, zinc, and mercury are critical in industrial wastewater treatment [2]. Being the sixth most common transition metal, chromium is one of the metals with the highest abundance in the planet's crust. Crocoite, ferric chromite, and chrome ochre are mineral deposits, including metal chromium and other components. It is a well-known fact that this hazardous metal may be found in water [3]. Due to its necessity for human beings, Cr (III) is far less hazardous than Cr (VI). Nevertheless, Cr (VI) is extremely dangerous and may be present in different industrial effluents, leading to severe nausea, vomiting, lung congestion, and liver and kidney issues. Chromium

metal is used for chromate preparation, metal polishing, textile manufacturing, electroplating, and leather tanning [4].

To minimize the adverse effects of heavy metals on the public and the environment to an acceptable level, various techniques have been explored, including chemical oxidation/reduction, precipitation, ion exchange and adsorption, and membrane filtration [5]. Its drawbacks are its selectivity, saturation, temperature, pressure, expense, fouling, and specificity of the adsorption process. Adsorbents may also get contaminated and saturated, lowering their effectiveness and cost [6]. The procedure's efficiency also depends on the chemical composition of the compounds to be adsorbed and the adsorbent. Many researchers are now focusing on creating bioresource adsorbents as a result. Due to its renewability, biodegradability, and high stability, cellulose is a bioresource, and its derivatives have attracted the attention of several individuals. Due to their high affinity for different water pollutants among bio-based natural polymer nanocomposites, cellulose nanocrystals (CNCs) nanocomposites have previously been proven to be viable biosorbents for water purification [1].

Adaptive neuro-fuzzy inference systems (ANFIS) are a type of artificial intelligence (AI) that combines the learning skills of artificial neural networks (ANN) with the reasoning abilities of fuzzy systems. As a result, it incorporates the advantages of both strategies into a single method. Instead of using only one technology, integrating fuzzy systems with ANNs is often more effective in engineering applications [7]. ANFIS is a powerful tool for modelling, mapping, forecasting, problem-solving, and data mining, the interplay between input and output values to help explain non-linear behaviour in complex systems. The input and output of an ANFIS model are divided into two sections and connected by fuzzy rules into a network. It is commonly acknowledged as a technology because of its extensive ability to mimic non-linear variation, usage in predicting the effectiveness of various processes, and extrapolation based on historical data in various industries [8].

As modelling of Cr (VI)removal behaviour can be predicted using both models, that is the study's primary objective (ANN and ANFIS techniques). As a first step in the adsorption of Cr (VI) from an aqueous solution, cellulose nanocrystals are utilised as an adsorbent. The operational variables are the input data and include the initial concentrations, solution pH, contact time, and adsorbent dosage. Lastly, the predicted output data derived from the two models are compared to the experimental data output data.

2. Materials and Methods

The cellulose nanocrystals (CNCs) utilized in this study were extracted from waste papers via acid hydrolysis ($\geq 90\%$), cellulose nanocrystals were treated with succinic anhydride and EDTA (99%), and the pH of the solution was adjusted using NaOH (98%) and HCl (37%). The reactor containing CNCs was agitated at a speed of 180 rpm for 55 min while 0.02 M EDTA tetrasodium salt was added to allow the reaction to occur. The agitation period was then extended to 4 h, and 20 mL of hydrochloric acid was added. The modified product was centrifuged for 45 min at 450 rpm, washed to remove unreacted chemicals, and then centrifuged again until the pH was neutral. Further changes to the CNCs occurred after three hours of treatment with 0.02 M succinic anhydride at 25 °C. Batch investigations were conducted in 500 mL glass vials. Reactors with stoppered Erlenmeyer flasks carrying test solutions at room temperature (25 °C) with the appropriate Cr (VI) concentration, contact time, pH, and adsorbent dose levels. In each test, 50 mL of a solution with a particular concentration of Cr (VI) was added to the reactor. The pH of the solution was adjusted using diluted 0.01 M HCl or 0.01 M NaOH to maintain a constant pH throughout the experiment. Table 1 provides the range of process variables for the two models.

Table 1. The range of variables used for the models.

Input	Range	Output
1. pH	3–9	Removal percentage (%)
2. Concentration Ni (II)	50–500	
3. Time (min)	0–120	
4. dosage adsorbent (mg/L)	5–20	

3. Results and Discussion

The modular artificial neural networks and a Neuro-fuzzy were built with a NN toolbox using MATLAB 2019 mathematical software. All calculations to evaluate adsorption efficiency were performed with Origin 2019. The RMSE, AARE, and MSE of the training and prediction sets were also used to identify the two models and the parameter changes. To evaluate how well the model can predict results from experiments that have not yet been seen and were not used for training, we have 26 experimental runs that were randomly divided into training, validation, and test sets. (20-3-3). Averaging was done across all samples. R^2 is a standard statistical metric to assess how much experimental and model predictions vary. In Figure 1, a three-layer system is built with an input layer consisting of four neurons (Cr (VI) concentration, contact time, solution pH, and adsorbent dose), a hidden layer made up of nine different nodes, and an output layer made consisting of one neuron (4-6-1). The most widely used network, a back-propagation (BP-ANN), trains an algorithm for modelling experimental data using a first-order gradient descent method. It's a suitable method for minimizing mistakes throughout each cycle

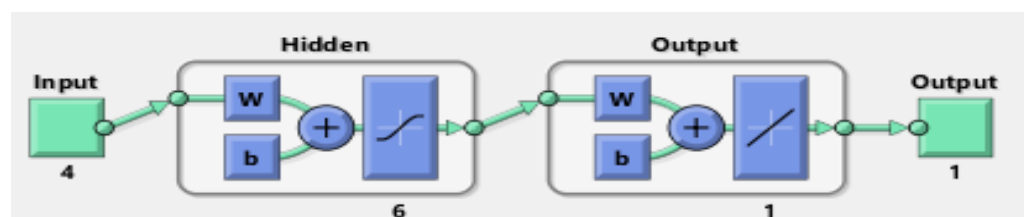
**Figure 1.** The architecture of the ANN model.

Figure 2 depicts how the network interacts with the training, testing, and validation data. The correlation coefficients for the training, testing, validation, and test data were found to be 0.999, 0.988, 0.972, and 0.988, respectively. The straight line also demonstrates the linear connection. The experimental (target) data and predicted (output) data from the model correlate. The results suggest high agreement between the actual data and the data predicted by the model.

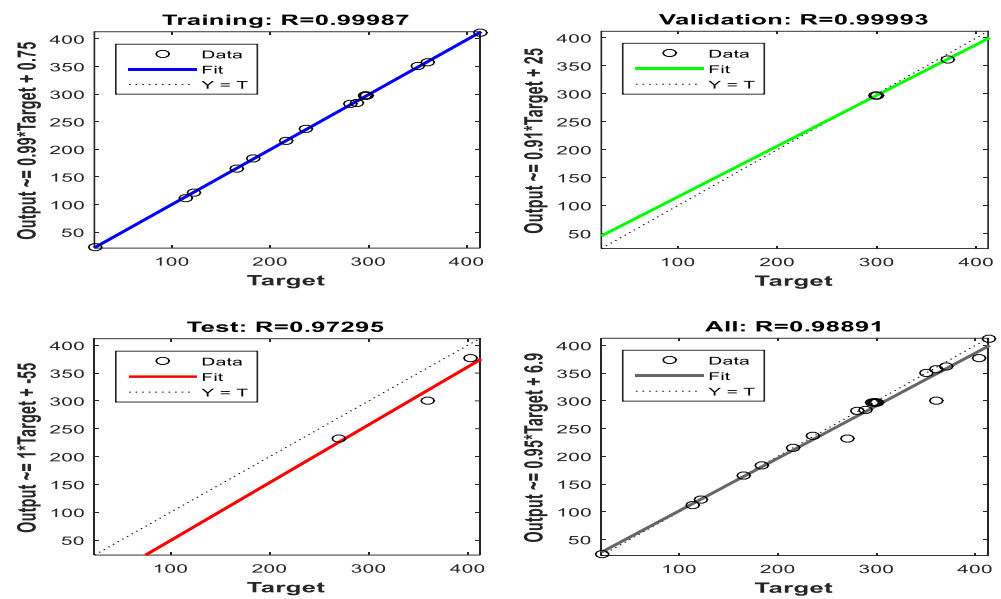


Figure 2. Training, validation, and testing for the Levenberg-Marquardt algorithm.

A fuzzy system’s membership parameters and rules are defined using a trial-and-error approach. A suitable model between observed inputs and precise target values has to be developed using the ANFIS system. The product layer, the normalized layer, the fuzzy layer, the defuzzy layer, and the final layer have all been identified as performing different tasks as part of this experiment (Figure 3).

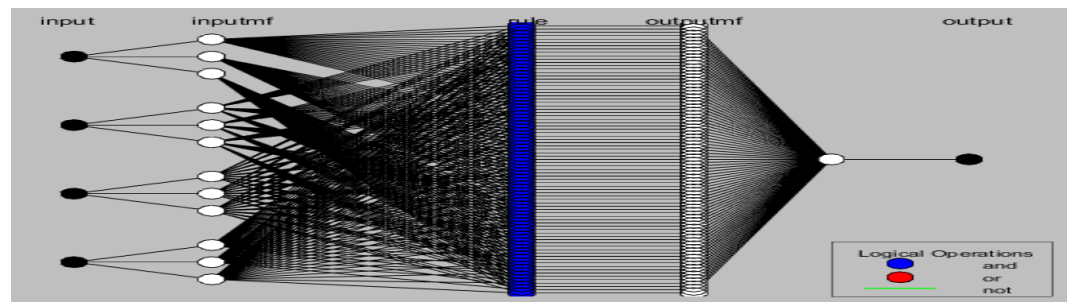


Figure 3. The architecture of the ANFIS model.

In response to four input parameters, which include three membership functions, the system creates 81 “and”-based rules. (inputmf). After that, they are converted into output by being sent through the same amount of (outputmf). Figure 4 illustrates the ANFIS model’s ability to predict data. (rule viewer). The optimum absorption condition was pH 6, starting concentration 275 mg/L, contact duration 60 min, and dose 12.5 mg/L is around 91.00%.

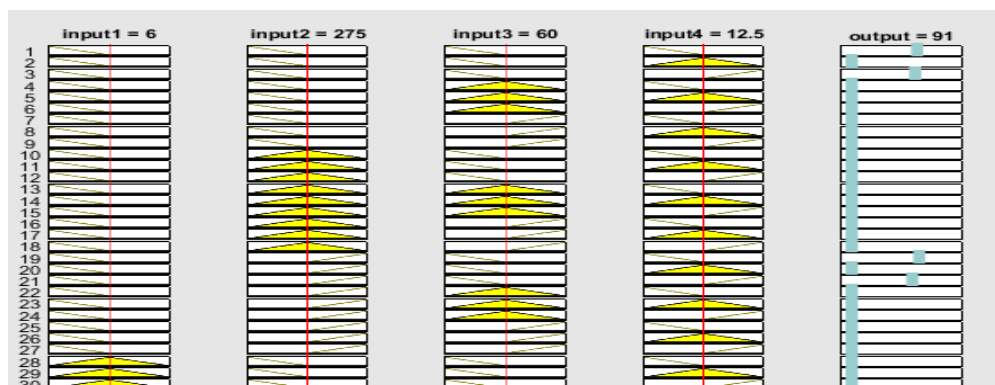


Figure 4. Rule viewer of the ANFIS model.

Table 2 compares the actual (experimental) data, and the model-predicted data for the percentage of Cr (VI) removed using the CNCs. The findings show that both models can accurately predict the adsorption’s features. Compared to the ANN model, the ANFIS model’s RMSE, AARE, MSE, and R² values were determined to be 0.008, 0.09, 0.002, and 0.99, respectively, and ANN was found to be 0.06, 0.045, 0.035, and 0.98.

Table 2. Comparison of ANN and ANFIS model for Cr (VI) removal.

pH	Conc (mg/L)	Time (min)	Dosage (mg/L)	Actual (%)	ANN (%)	ANFIS (%)
6	250	120	10	92.00	92.2	92.7
6	250	60	10	93.01	92.7	93.07
3	50	0	20	79.52	78.05	78.9
9	50	120	5	82.94	84.82	83.89
3	500	0	20	75.51	75.28	76.14
9	50	0	20	72.47	71.90	71.12
6	250	60	10	93.92	93.24	93.82
6	250	60	10	93.97	93.51	93.77
9	50	120	20	76.70	76.28	77.27
3	50	0	5	81.54	81.25	81.54
6	50	60	10	84.92	84.85	84.73
3	500	0	5	84.08	83.25	83.79
9	500	0	20	71.05	71.02	71.08
9	500	120	20	75.05	74.56	74.28
6	250	60	10	93.91	93.24	92.71
RMSE (Root means square errors)					0.06	0.008
AARE (Absolute average relative errors)					0.045	0.09
MSE (Mean square errors)					0.035	0.035
R ² (Regression coefficient)					0.98	0.99

4. Conclusions

The research not only achieved its primary goals but also created new areas for investigation. It could be possible to predict an adsorbent’s adsorption capability. When ANFIS and ANN, two recently created models, are compared to one another, it becomes clear which model is most suited for usage in the effectiveness of the research area. The regression coefficients (R²) for the ANFIS and ANN models were 0.99 and 0.98, respectively. The results demonstrate that the models are appropriate and compatible since there is an excellent fit between experimental data and data expected by the model. The ANFIS model had an RMSE of 0.008, whereas the ANN model had an RMSE of 0.06. The AARE

for the ANFIS and ANN models was determined to be 0.009 and 0.045, respectively. The MSE for the ANFIS and ANN models was found to be 0.002 and 0.035, respectively.

Author Contributions: M.B.: conceptualization, methodology, formal analysis, investigation, data curation, writing, writing—original draft. T.S.: methodology, validation, formal analysis, investigation, writing—reviewing and editing. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The author would like to thank the Vaal University of Technology's Department of Chemical & Metallurgical Engineering for providing continuous operating facilities.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Vincent, S.; Kandasubramanian, B. Cellulose nanocrystals from agricultural resources: Extraction and functionalisation. *Eur. Polym. J.* **2021**, *160*, 110789. <https://doi.org/10.1016/j.eurpolymj.2021.110789>.
2. Kabuba, J.; Banza, M. Modification of clinoptilolite with dialkylphosphinic acid for the selective removal of cobalt (II) and nickel (II) from hydrometallurgical effluent. *Can. J. Chem. Eng.* **2021**, *99*, S168–S178. <https://doi.org/10.1002/cjce.24005>.
3. Katha, P.S.; Ahmed, Z.; Alam, R.; Saha, B.; Acharjee, A.; Rahman, M.S. Efficiency analysis of eggshell and tea waste as Low cost adsorbents for Cr removal from wastewater sample. *South African J. Chem. Eng.* **2021**, *37*, 186–195. <https://doi.org/10.1016/j.sajce.2021.06.001>.
4. Banza, M.; Rutto, H. Selective removal of Cr (VI) from hydrometallurgical effluent using modified cellulose nanocrystals (CNCs) with succinic anhydride and ethylenediaminetetraacetic acid: Isotherm, kinetics, and thermodynamic studies. *Can. J. Chem. Eng.* **2023**, *101*, 896–908. <https://doi.org/10.1002/cjce.24384>.
5. Ahmadi, S.; Mesbah, M.; Igwegbe, C.A.; Ezeliora, C.D.; Osagie, C.; Khan, N.A.; Dotto, G.L.; Salari, M.; Dehghani, M.H. Sono electro-chemical synthesis of LaFeO₃ nanoparticles for the removal of fluoride: Optimization and modeling using RSM, ANN and GA tools. *J. Environ. Chem. Eng.* **2021**, *9*, 105320. <https://doi.org/10.1016/j.jece.2021.105320>.
6. Banza, M.; Rutto, H.; Seodigeng, T. Soil and Sediment Contamination: An International Application of Artificial Neural Network and Shrinking Core Model for Copper (Ii) and Lead (Ii) Leaching from Contaminated Soil Using Ethylenediaminetetraacetic Acid Application of Artificial Neural N. *Soil Sediment Contam. An Int. J.* **2023**. <https://doi.org/10.1080/15320383.2023.2178384>.
7. Husien, S.; El-taweel, R.M.; Salim, A.I.; Fahim, I.S.; Said, L.A.; Radwan, A.G. Review of activated carbon adsorbent material for textile dyes removal: Preparation, and modelling. *Curr. Res. Green Sustain. Chem.* **2022**, *5*, 100325. <https://doi.org/10.1016/j.crgsc.2022.100325>.
8. Kabuba, J.; Banza, M. Results in Engineering Ion-exchange process for the removal of Ni (II) and Co (II) from wastewater using modified clinoptilolite: Modeling by response surface methodology and artificial neural network. *Results Eng.* **2020**, *8*, 100189. <https://doi.org/10.1016/j.rineng.2020.100189>.

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