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Research paper

Predicting the Capability of Oxidized CNW Adsorbents for the Remediation of Copper Under Optimal Operating Conditions Using RSM and ANN Models

Hazren A. Hamid[1]*, H. Harun[2], N.M. Sunar[3], Faridah Hanim Ahmad[4], Latifah Jasmani[5], Norhidayah Suleiman[6]

[1, 2, 3 ,4] Department of Civil Engineering Technology, Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia
[5]Forest Research Institute Malaysia (FRIM), Malaysia
[6] Department of Food Technology, Faculty of Food Science and Technology, University Putra Malaysia
**Corresponding author E-mail:norhazren@uthm.edu.my*

Abstract

Metal pollutants such as copper released into the aqueous environment have been increasing as a result of anthropogenic activities. Adsorption-based treatment technologies offer opportunities to remediate metal pollutants from municipal and industrial wastewater effluent. The aim of this work was to evaluate the capability of modified cellulose nanowhisker (CNW) adsorbents for the remediation of copper from water matrices under realistic conditions using response surface methodology (RSM) and artificial neural network (ANN) models. Considerations for design and application to remediate Cu(II) from wastewater by developing a continuous flow experiment are described in this study. However, the physical structure of modified CNW adsorbents renders them unsuitable for use in column operation. Therefore, a more detailed study of the mechanical properties of CNW adsorbents would be necessary in order to improve the strength and stability of the adsorbents. This work has demonstrated that modified CNW are promising adsorbents to remediate copper from water matrices under realistic conditions including wastewater complexity and variability. The use of models to predict the test parameter system and account for matrix variability when evaluating CNW adsorbents for remediating Cu from a real-world wastewater matrix may also provide the foundation for assessing other treatment technologies in the future.

Keywords: *Adsorption; Copper; Cellulose; Optimization; Wastewater.*

1. Introduction

The complexity and variability of wastewater is difficult to model and simulate using traditional modelling procedures. Because of the interaction between a numbers of adsorption variables/factors, the resulting relationships are highly non-linear and require a large number of experiments. This has placed increasing demands on both research and process optimization, and has resulted in the increased use of RSM and ANN modelling tools. The statistical aspects of RSM and ANN enable the identification of factors that have a significant effect on the adsorption process and are able to provide a large amount of knowledge from a small number of experimental runs.

RSM is an efficient tool to predict the best performance conditions with a minimum number of experiments. It has also been effectively and widely applied in water and wastewater treatment optimization, such as of textile dye wastewater, tannery wastewater, industrial paint wastewater, landfill leachate, and palm oil mill effluent. Moreover, removal chemical oxygen demand (COD), biological oxygen demand (BOD), colour and nitrate were also optimized via both RSM and technological treatment. Bashir *et al.* (2016) found that ion exchange treatment with RSM application not only showed maximum removal of COD and colour, but also removed turbidity from landfill leachate.

ANN has been successfully employed in environmental engineering, due to its superior ability to learn and classify data and its reliable and robust characteristics in capturing the non-linear relationships of variables in a complex system such as an adsorption process. An ANN model was developed by Krishna and Sree (2013) to predict the removal efficiency of Cr(VI) from aqueous solution using coir powder as adsorbent. They found that the model and the test data showed a high R^2 value (0.992), and the ANN model successfully tracked the non-linear behaviour of percentage removal of Cr(VI) versus independent variables, with low relative percentage error. Ghosh *et al.,* (2013) applied RSM with CCD to investigate the removal of Cu(II) from aqueous solution using modified orange peel, and their study showed that pH, sorbent dosage and initial metal ion concentration influenced the adsorption process. Oguz and Ersoy (2010) studied the feasibility of sunflower shell for the removal of Cu(II) from aqueous solution in a fixed-bed adsorption column with an ANN approach. They noted that ANN effectively predicted the removal efficiency of Cu(II) using sunflower shell as adsorbent.

Moreover, ANN is also a reliable model for predicting the performance of wastewater treatment plants (WWTPs) and in forming a basis for controlling the operation of the process. It is used as a valuable performance assessment tool for plant operators and decision makers. A study by Nasr *et al*. (2012) signifies that an ANN can effectively predict plant performance and act as an efficient analysis and diagnostic tool to understand and stimulate the non-linear behaviour of the plant. Therefore, in this study, RSM and ANN were used to develop an approach for the remediation of spiked Cu(II) from wastewater effluent. As remediation processes from wastewater are often complicated due to the variation in wastewater compositions, results obtained from the benchmark experiments are included as one of the independent variables for ANN modelling, unlike in other optimization studies.

2. Related work

2.1. Traditional modelling procedure

Adsorption is a complex process dependent on various parameters and outputs, which requires a large number of experiments to investigate the relationship between those factors and the process performance output [6]. Traditionally, optimization of an adsorption process has been performed by applying one factor at a time to an experimental response, where the other factors remain constant [7]. This method is known as one variable at a time (OVAT). The disadvantages of this method are that it is time consuming and requires a large number of experiments, which lead to an increase in expense and in the utilisation of reagents and materials [8]. Moreover, OVAT does not take account of interactions between the selected factors and does not describe the complete effects of those factors on the response and process performance. Thus, to overcome this difficulty, factorial experimental design can be employed to optimize the conditions of adsorption of heavy metals from a water matrix. RSM and ANN modelling are methods that are applied extensively in industry for the optimization of process design parameters [9-11].
Although RSM and ANN are widely used in the study of adsorption processes, studies on Cu(II) removal from real wastewater samples tend to focus on one single parameter at a time [12, 13]. For example, the potential of amine-functionalised SBA-15 as an adsorbent to remove Cu(II) ions from river water, tap water and electroplating wastewater [14], and the potential of *Ulothrix Zonate* algae to remove Cu(II), Pb(II) and Cd(II) from industrial wastewater [15] have focused only on one single parameter at a time. However, the adsorption capacity and selectivity in both studies were investigated through batch kinetic experiments, and Langmuir and Freundlich models were used to describe the equilibria between metal ions and adsorbent. Therefore, the adsorption of copper from real wastewater samples was studied; where optimisation studies were carried out by studying the effect of three variables (temperature, initial Cu(II) concentration, sorbent dosage and pH)

2.2. Comparison of RSM and ANN models

Interestingly, most of the previous literature has focused its attention on adsorption studies by using either RSM or ANN, without comparing the performances of these two models. Furthermore, the testing of both RSM and ANN, using new sets of experiments not belonging to the training data set, has only been undertaken in a limited number of studies on biomass adsorption, and without consideration of how the additional experiments represent the system and give a more accurate indicator of performance [3, 16]. Therefore, model suitability for interpolated and extrapolated experimental parameters was tested. This is rare in the existing literature, but provides valuable insights into the applicability of the approaches tested in this work. The performance of the ANN and RSM models were statistically evaluated using a continuous error metric, such as the coefficient of determination (R^2), absolute average deviation (AAD), and root mean squared error (RMSE).

2.3. RSM and ANN advantages and limitations

Recently, response surface methodology (RSM) and artificial neural network (ANN) methods have been used together for both modelling and optimisation applications in wastewater treatment and environmental studies [17, 18]. Generally, by applying these models, the number of experimental trials is reduced, which requires the evaluation of multiple parameters and their interactions. Furthermore, it is less laborious and time consuming than the conventional ‘one variable at time’ (OVAT) approach [9]. Factorial experimental designs such as central composite design (CCD) and Box-Behnken design (BBD) provide more information per experiment than OVAT approaches. Design of experiment (DOE) allows the identification of interactions among experimental variables within the range studied, providing better knowledge of the process and hence reducing research time and costs [19].
ANNs are algorithms that can be used to perform nearly all types of nonlinear statistical modelling and provide a number of advantages, while RSM is suitable only for quadratic estimations [20]. ANN is a simple nonlinear model that is easy to use and to understand compared to other statistical methods. This model requires less formal statistical training, is able to implicitly detect complex nonlinear relationships between dependent and independent variables, to detect interactions between the variables, and to determine the availability of multiple training algorithms [21]. Moreover, ANN works well for large data sets and reduces drastically the processing time compared to other models.
However, ANN is also known as a ‘black box’, the development of which is mainly a trial and error process, and which is poor in interpreting the relationship between input and output, and in handling uncertainties [22]. Thus, the calculated model can only be used within the experimental range and cannot be used for extrapolation. Furthermore, it is believed that an ANN model requires a larger number of experiments for training to build an efficient model than does RSM [7]. There is also no exact method in order to determine the minimum number of experiments for ANN training [9]. Therefore, it is troublesome while designing the experiments. However, with scoping experiments and realistic conditions in real WWTPs, ANN can also work well with less data, if that data is well distributed in the design. Thus, the experimental data (20 CCD experiments) of RSM should be sufficient to build an effective ANN model.

3. Methodology

3.1. Batch adsorption studies using wastewater effluent

The procedure for adsorption experiments was performed using wastewater effluent spiked with Cu(II). Batch experiments were performed in 100 mL conical flasks in an incubator, with temperature control and agitation (150 rpm) using a mini table shaker. The contact time (30 min), and the initial pH (pH 6.0) were selected on the basis of the results obtained from the scoping experiments [23]. The required mass of sorbent was measured separately into the 100 mL conical flask, and then 20 mL of Cu(II) solution with known concentration were added into the flasks. The effluent was previously filtered through a standard 1.2 µm glass fibre filter. The effect of pH (5–8), sorbent dosage (0.5–10 g/L) and initial concentration of wastewater effluent spiked with Cu(II) (1–5 mg/L) were carried out using effluent while keeping the other conditions the same, as with the clean water matrix. Batch experiments were performed with pH adjustment using 1M H_2SO_4 and 1M NaOH to give a range from 5.0 to 8.0. In order to avoid any contamination, no efforts were made to maintain the pH throughout the adsorption process. The final pH was recorded. The initial and final solutions were separated by filtration using 0.2 µm surfactant-free cellulose acetate membrane syringe filter and Cu(II) concentration determined using AAS.
The percentage of the removal Cu (II) ions by the sorbent and the adsorption capacity (mg Cu(II)/g) were expressed by:

$$\%\text{removal} = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

$$q_e = \left(\frac{(C_o - C_e)V}{W} \right) \quad (2)$$

Where Co (mg/L) is the initial Cu(II) concentration and Ce (mg/L) is the equilibrium Cu (II) concentration in solution, V is the vol

volume of the solution (L), and W is the mass of adsorbent (g) [3].

3.2. Experimental set up for fixed bed adsorption

In order to study the practical relevance of oxidised CNWs as adsorbent in large-scale water treatment, column study by down-flow mode was studied. A continuous flow adsorption study was conducted in a solid phase extractions (SPE) vacuum manifold, with 20 positions. An empty cartridge made of polypropylene with 1.5 cm inner diameter and 7.4 cm height was packed with adsorbent and set up on the SPE vacuum manifold. A polyethylene frit

was placed at the bottom of the cartridge to prevent loss of the adsorbent. The experiment was performed at room temperature (20 ±1°C) by pumping a known concentration of wastewater effluent spiked with Cu(II) in a down-flow mode through the cartridge using pump. The wastewater effluent was placed in a polypropylene container and connected with a tube through which the effluent will pass through the cartridge. The treated effluent was collected in a polypropylene container through the exit valve at the base of the glass chamber. Fixed bed sorption studies were performed under optimum conditions (pH 8, sorbent dosage = 6.45 g/L, initial concentration of wastewater effluent spiked with Cu(II) = 4.72 mg/L), obtained from previous experiment performed in a batch system for removal of Cu(II) from the wastewater effluent. For each sorption test, the cartridge was flushed with 5 ml deionised water to ensure compact packing and that the closely packed arrangement of adsorbent had no voids and channels.

The treated effluent (C_t) was collected after every 10 ml and analysed for metal concentration with AAS. The breakthrough curves of C_t/C_o were plotted against volume. The experiments were continued until a constant concentration of Cu(II) was obtained. The adsorption capacity $q_{e,cont}$ (mg/g) can be determined by the equation as in batch studies, but with slight modifications:

$$q_{e,\,cont} = \left(\frac{(C_0 - C_b)}{W} x V_{ef} \right) \quad (3)$$

Where W is the mass of adsorbent (g), C_o is the initial concentration (mg/L), C_b is the breakthrough concentration (mg/L) and V_{ef} is the volume (L) of effluent that is required to reach the exhaustion of the column.

4. Process optimization and optimum parameters

Process optimization is a function of maximising the removal of Cu(II) from the wastewater matrix via a combination of different studied factors. There are two options for finding the optimal operating conditions for spiked Cu(II) removal from wastewater effluent: the graphical optimisation function and the desirability function.

Graphical representation of the model is the simplest approach for determining optimal operating conditions, particularly when the optimisation procedure involves two factors and one response. Vera Candioti *et al.* (2014) illustrated a suitable method for determining optimal operating conditions that involves one response via the graphical representation of the model, either by 3D space or contour graphs. In these graphs, the response is represented as a function of two factors. When more than two factors are studied, the other factors that are not plotted must be set at a constant value. Therefore, only a limited part of the experimental domain is shown, which leads to the difficult establishment of optimal operating conditions [24].

Desirability is an objective function that ranges from zero outside of the limits, to one at the goal. In 1980, Derringer and Suich (1980) developed the desirability function, which has been widely used in industry to find optimal operating conditions. The main aim of this function is not only to find a good set of operating conditions that meet all the relevant criteria, but also to give the best desirability value. Moreover, the desirability function has been successfully applied in several studies to determine the desired parameters for maximum heavy metals removal from the water matrix [26-29]. Therefore, the appropriate way to find the optimal operating conditions for this study is by applying the desirability function.

In this study, the optimal operating conditions for the spiked Cu(II) removal from the wastewater effluent were determined using the desirability functions available in MINITAB 16 statistical software. The optimum operating conditions suggested by the design of experiment (DoE) model for the three variables, i.e., pH, sorbent dosage and initial Cu(II) concentration studied in this experiment, were pH 8.0, 6.45 g/L and 4.72 mg/L, respectively. Benchmark experiments were performed to account for wastewater matrix variability and impact on adsorbent performance, prior to determining optimal operating conditions. As the value of desirability obtained for Cu(II) removal was 1, it has been proven that the estimated function may represent the experimental model and the desired conditions [29].

In order to confirm the model's adequacy, batch experiments were conducted in triplicate at optimum conditions to obtain maximum spiked Cu(II) removal experimentally. The predicted and experimental optimum conditions of the process variables for the maximum percentage spiked Cu(II) removal from the wastewater effluent is shown in Table 1. The removal percentages obtained were lower than predicted removal efficiency in optimal conditions. This was because the composition and concentration of substances in wastewater varies significantly over time [30].

4.1. Performance of continuous flow experiment under optimal operating conditions

Continuous flow experiments were carried out using oxidized adsorbent for the removal of spiked Cu(II) from wastewater effluent. For the continuous flow experiments, each experiment was conducted under optimal conditions, which was determined from the desirability functions. Continuous flow experiments were performed in a solid phase extraction (SPE) vacuum manifold, with the adsorbent continuously in contact with wastewater effluent spiked with Cu(II).

Continuous flow experiments were operated at two different pressures (P), 10 and 15 mmHg in a column filled with oxidized CNW adsorbents. The final Cu(II) concentration in the effluent was plotted against the volume of treated effluent, the profile for which is shown in Figure 1. As the pressure increased, the final concentration of Cu(II) in the effluent also increased, thereby decreasing removal efficiency (Table 2).

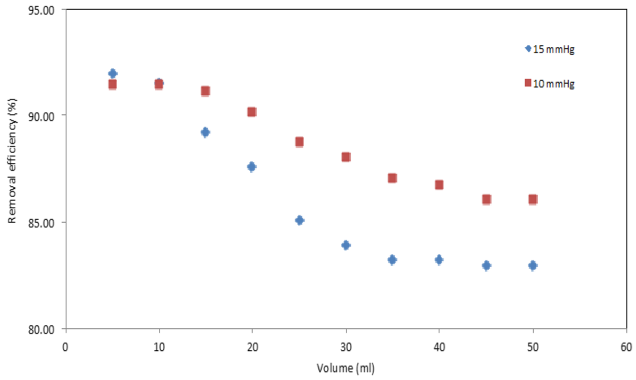

Fig. 1: Effect of pressure on Cu(II) removal from wastewater effluent

Table 1: Optimized operating conditions for spiked Cu(II) removal from wastewater effluent via adsorption process.

Run	Optimal operating conditions			Experimental operating conditions				Cu(II) removal (%)		% Error
	pH	Sorbent dosage (g/L)	Initial Cu(II) concentration (mg/L)	pH	Sorbent dosage (g/L)	Initial Cu(II) concentration (mg/L)	Benchmark experiments (%)	Actual	Predicted	
1	8.0	6.45	4.72	7.8	6.50	4.61	77.27	91.36	92.11	-0.75
2	8.0	6.45	4.72	7.9	6.50	4.61	80.11	91.36	92.11	-0.75
3	8.0	6.45	4.72	8.0	6.15	4.31	78.75	90.54	92.11	-1.57

The results suggest that at a high pressure, the adsorbent in the cartridge may compact as a result of the pressure, thereby reducing the availability of sorption sites for adsorption. This result corresponds well with those of Maheshwari and Gupta (2016), who suggested that with an increase in pressure, there is a decrease in contact time between metal ions and adsorbent, which may lead to a reduction in the overall percentage removal of heavy metals.

Table 2: Effect of pressure on spiked Cu(II) removal efficiency from wastewater effluent by oxidized CNW adsorbents.

Run	Volume (ml)	Final Cu(II) concentration (mg/L)		Removal efficiency (%)	
		10 mmHg	15 mmHg	10 mmHg	15 mmHg
1	0	C_i=4.98	C_i=4.98	0	0
2	5	0.43	0.40	91.48	91.99
3	10	0.43	0.42	91.48	91.53
4	15	0.44	0.54	91.16	89.21
5	20	0.49	0.62	90.14	87.59
6	25	0.56	0.75	88.75	85.05
7	30	0.60	0.80	88.06	83.89
8	35	0.65	0.84	87.04	83.20
9	40	0.66	0.84	86.76	83.20
10	45	0.69	0.85	86.02	82.97
11	50	0.70	0.85	86.02	82.97
C_i = Initial Cu(II) concentration (mg/L)					

As noted in literature, chemically modified adsorbents improve removal efficiency and adsorption capacity. Although oxidised CNW adsorbents are able to remove approximately 90% of spiked Cu(II) from wastewater effluent, without reinforcement and granulation, it is not a suitable structure for use in continuous flow column operations. This is because the physical structure of oxidised CNWs is extremely soft and in this study, easily caused column clogging when wet [32]. These observations are in agreement with those of Mason (2007), who stated that natural biomass, including cotton wool, is extremely soft and not suitable for column operation [33]. Therefore, the mechanical properties of adsorbents must be improved in order to provide a more stable structure, where the adsorbent can be used directly in a standard operation process.

5. Conclusion

Oxidized CNW adsorbents are capable of removing spiked Cu(II) ions from wastewater effluent. The RSM and ANN models were employed to optimize the system and to create a good predictive model. No work in the reviewed literature included matrix complexity and the variability of the wastewater as one of the independent variables in ANN modelling. Evidently this novel approach and the outcomes were employed in this study for the first time, as most studies do not consider matrix variability and its impact when evaluating the efficiency of an adsorbent. The optimum adsorption conditions were determined as an initial pH value of 8.0, a sorbent dosage of 6.45 g/L and initial Cu(II) concentration of 4.72 mg/L. At optimum adsorption conditions, the percentage removal of spiked Cu(II) from the wastewater effluent was found to be 92.11%. Although oxidized CNW adsorbents were able to remove approximately 90% of spiked Cu(II) from wastewater effluent, the physical structure of oxidized CNW adsorbents is not suitable for use in continuous flow column operations.

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