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Original Article

Experimental studies and artificial neural network modeling of hydrogen sulfide removal from wastewater by calcium-modified coconut shell based activated carbon

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Abstract

In this study, activated carbon-based adsorbent was prepared from eggshells and coconut shells. The effects of contact time, initial H2S concentration, and the calcium impregnated coconut shell activated carbon (Ca-CSAC) adsorption dosage on the hydrogen sulphide (H2S) removal efficiency and adsorption capacity were investigated. The batch adsorption data obtained from the experimental runs were employed to fit an artificial neural network (ANN) model. An initial optimization was performed to obtain the most suitable number of hidden neurons for training and validation of the ANN. The optimization results show that 16 hidden neurons was the most appropriate choice. The trained ANN was adequately validated and tested with coefficients of determination (R2) of 0.99 and 0.95, respectively. The ANN was found to be a robust tool for modeling of H2S removal efficiency by and adsorption capacity on Ca-CSAC under different process conditions.

Keywords: artificial neural network, adsorbent, hydrogen sulfide, coconut shell, modelling

1. Introduction

The refining of crude oil to obtain different fractions of petroleum products is often accompanied with negative environmental impacts from the release of pollutants, such as hydrogen sulphide (H2S) usually present in the discharged process wastewater (Elmawgoud, Elshiekh, Khalil, Alsabagh, & Tawfik, 2015). The presence of H2S in process water is a potential health risk and often results in significant economic losses arising from the fouling of the resin bed and the corrosion of process equipment (Strahand, 2010). In order to mitigate these economic losses and negative environmental impacts, prior studies have sought to develop state-of-the-art techniques for the removal of this toxic gas pollutant (Guerrero et al., 2016).

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Physicochemical techniques such as air stripping (Al-Haddad, Azrag, & Mukhopadhyay, 2014), catalytic oxidation (Kastner, Das, Baqqui, & Melcar, 2003), the use of ferric/alum water treatment residuals (Wang & Pei, 2012) and adsorption (Xiao, Wang, Wu, & Yuan, 2008) have been employed for the removal of this toxic pollutant from process waters. In comparison to other methods, adsorption as the separation process has gained wide acceptance as a technique for purifying wastewater on an industrial scale by using porous media such as activated carbon (Seredyck & Bandosz, 2011). The discovery of using porous media by McBain (1932) for the adsorption of vapours in large quantities can be dated to 1932. However, its industrial applications to wastewater treatment span only a few decades due to some advances made. The use of activated carbons to remove toxic H2S is gaining wide acceptance due to several benefits, such as large savings in energy costs, low operating costs, and comparatively small equipment size (Mailler et al., 2016). Besides, activated carbons possess excellent physicochemical properties, such as large surface area, microporosity, and good surface chemistry, which have made them the most sought after medium for removing toxic pollutants from refinery effluents (Dias et al. 2007; Ioannidou & Zabaniotou 2007). However, commercially available activated carbon is not cost effective, motivating the quest for low-cost sources of activated carbons from locally available materials (Ioannidou & Zabaniotou 2007).

Several authors have investigated the use of activated carbon for the removal of toxic substances from water, by using coconut shell (Bagreev, Rahman, & Bandosz, 2000), palm kernel shell (Guo et al., 2007), wood, and lignite (Adib, Bagreev, & Bandosz, 1999). All the aforementioned studies focused on the adsorption capacity and kinetic modeling of the H2S removal from wastewater. To the best of the authors’ knowledge, there is no prior published study on predictive models for H2S removal from wastewater using calcium (Ca) modified coconut shell activated carbon. The main objective of this study was to investigate the effects of process parameters, such as adsorption contact time, initial H2S concentration and adsorbent dosage on the H2S removal efficiency and on the adsorption capacity of Ca-CSAC; as well as developing an artificial neural network model that can predict the H2S removal efficiency and the adsorption capacity of the Ca-modified coconut shell–based activated carbon. The application of ANN in predictive modelling of the adsorption process will facilitate dealing with the non-linear relationships between the input and the output variables. This will enhance setting the process variables for optimum performance.

2. Materials and Methods

2.1 Preparation of adsorbent

The coconut shell waste residue (CNS) used in this study was collected from a commercial farm located close to the Universiti Malaysia Pahang (UMP), Gambang, Pahang, Malaysia. The collected CNS was washed with distilled water to remove soil and other impurities. Thereafter, the CNS was dried in the sun and subsequently ground and sieved to particle sizes of 0.5-1 mm. In order to ensure that the ground CNS is free from moisture, it was further dried in an oven at 110 °C for 24 h. After drying, the CNS precursor was mixed with KOH at optimum KOH/precursor ratio of 4:1 as stipulated by Cazetta et al. (2011) and left in a mechanical shaker for proper mixing. After 24 h of mixing, the slurry was filtered and placed in a tubular horizontal reactor for treatment with N2. The reactor temperature was increased from room temperature to 750 °C in order to gradually heat the slurry for contact activation time of 120 min. The gas was thereafter switched to CO2 for an additional 2 h. The resulting activated carbon formed from the heat treatment was washed using boiled aqueous solution of HCl for 1 h in order to neutralize the KOH. This was followed by washing the activated carbon with distilled water until a neutral pH was attained. The final activated carbon products were dried at 110 °C for 24 h in order to remove any traces of moisture, and are here labeled as coconut shell activated carbon (CSAC).

The eggshells used as a source of calcium were obtained from poultry waste disposal Centre at Kajang-Malaysia. The eggshells were washed to remove dirt and other traces of impurities. After washing, the eggshells were dried, blended, and sieved using a sieve to a diameter range of 0.25-0.5 mm. The powdered eggshell was further dried at 105 °C for 8 h and thereafter soaked in acetic acid solution (25-75 vol. %) for 48 h in order to extract the calcium. The Ca solution to be impregnated into the adsorbent was prepared by mixing 0.2 g of the powdered eggshell per ml of acetic acid. The mixing was performed under constant stirring (150 rpm) at 30 °C for 2 h. Subsequently, the slurry obtained was evaporated at 66 °C and thereafter dried at 100 °C for 15 h. Finally, the Ca-impregnated carbon was further heat-treated and then washed with deionized water at 50 °C until neutral pH of adsorbent was obtained. The final Ca-impregnated adsorbent was finally dried at 100 °C for 24 h. The pyrolyzed Ca-CSAC was stored in a sealed flask and kept in a desiccator prior to the adsorption study.

2.2 Adsorbent characterization

Scanning electron microscopy (SEM) (HITACHI S-3400N system) was employed for investigating the textural morphologies of the Ca-CSAC. The textural properties of the activated carbon were measured by N2 adsorption-desorption isotherms at −196 using an ASAP 2010 apparatus (Micromeritics Co., USA). Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods were used to estimate the specific surface area (SBET, m² g⁻¹) and total pore volume (Vt, cm³ g⁻¹ at STP) of the adsorbent. The actual density (ρa) of the sample was measured using helium displacement method (AccuPyc 1330 pycnometer, Micromeritics Co., USA). The pH of the carbon surface was measured by the addition of 0.4 g of dry carbon powder to 20 mL of water, followed by stirring the suspension overnight for attaining equilibrium. Elemental composition of the activated carbon was analyzed using energy-dispersive X-ray spectroscopy (EDX).

2.3 Formulation of H2S-contaminated wastewater solution

In this study, synthetic wastewater was prepared according to the procedure reported by Asaoka et al. (2009a). First, a known amount of Na2S·9H2O was dissolved in a 500
mL solution of 0.01 M KCl purged with N₂. Second, the pH of the solution was adjusted to neutral using 0.2 M HCl (Asaoka, Yamamoto, Kondo, & Hayakawa, 2009a). H₂S can exist in solution in three forms: H₂S, bisulfide (HS⁻), and sulfide (S²⁻) (Silva, Ponte, Ponte, & Kaminari, 2011).

2.4 ANN data acquisition via batch equilibrium studies

The dataset employed in ANN modeling was obtained using batch mode experimental runs for the adsorption of H₂S. To measure the adsorption capacity and the H₂S removal efficiency, 0.1 g of the Ca-CSAC adsorbent was used in each run after degassing at 105 °C for 24 h in an oven. Batch adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 100 mL of H₂S solution at various initial concentrations (100, 200, 300, 400, and 500 mg L⁻¹). The flasks were agitated in a thermostatic orbital shaker at 150 rpm and 30 °C until the equilibrium was reached. The pH of the solution was controlled to neutral by using NaOH or HCl. The adsorption capacity of the pollutants was calculated by Equation (1). Subsequently, the initial and final concentrations were measured after the suspensions were filtered.

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  

(1)

where V is volume (L), m is amount of adsorbent (g), C₀ and Cₑ are the initial and final concentrations of H₂S, respectively, and (qₑ) is adsorption capacity (mg g⁻¹). The experiment was performed in a fume hood as H₂S is a very poisonous gas. Equation (2) was employed for calculating the H₂S removal efficiency.

\[ \text{Removal efficiency} = \frac{q_0 - q_e}{q_0} \times 100 \]  

(2)

2.5 Artificial neural network modeling

The ANN was employed to fit a non-linear model consisting of input, hidden with weight and bias, and output layers, using the neural networks toolbox in MATLAB software environment (Joo, Yoon, Kim, Lee, & Yoon, 2015). The input parameters of the ANN are the initial H₂S concentration (100-500 mg/l), adsorption contact time (360-720min) and adsorbent dosage (0.1-1 g), while the outputs are the adsorption capacity and the H₂S removal efficiency, as shown in Figure 1. The hidden neurons between the input and output layers are scaled within the range from -1 to 1 by using hyperbolic tangent activation functions, see Equation (3). The ways the neurons are linked to each other significantly influence the performance of ANN. In the present study, the input parameters subjected to summing mechanism of the next neuron, with a view to choosing the highest probability for the output (Agatonovic-Kustrin & Beresford, 2000). Each input exemplar (data record for one experiment) is assigned a weight, which is iteratively adjusted to minimize the training error. The ANN model was of feed-forward type, which has been widely applied in industrial processes (Scott, Coveney, Kilner, Rossiny, & Alford, 2007). In addition, the feed-forward configuration is easy to implement in a variety of chemical processes. The feedforward ANN was trained using the Levenberg-Marquardt optimization algorithm (Equation (4)). The training was performed by inputting a “training data set to the ANN network” (Scott et al., 2007). During the training, the ANN matches the input and output values by minimizing the difference between the predicted and the targeted values (Agatonovic-Kustrin & Beresford, 2000) by adjusting the network’s interconnection weights to reduce the prediction errors iteratively. The difference between the target and the model output was quantified using the MSE defined in Equation (5) (Zamaniyan, Joda, Betroozazarand, & Ebrahimi, 2013). The ANN training and modeling were performed using the neural network toolbox in MATLAB computing environment (The Mathworks, Inc. ver.2010 a).

\[ F(\lambda) = \frac{2}{1 + e^{-2n}} - 1 \]  

(3)

where n is the number of neurons.

\[ \lambda(\bar{J} + \lambda I) \delta = \bar{J} \in \]  

(4)

where \( \frac{\delta}{\delta} \) is the Jacobian matrix for the process, \( \lambda \) is the Levenberg’s damping factor, \( \delta \) is the weight update vector and E is the output vector.

\[ \text{MSE} = \frac{1}{N} \sum_{i=1}^{N} (X_i - Y_i)^2 \]  

(5)

where N, X, and Y are the number of data records in network training, the targeted output and the model output, respectively.

Figure 1. ANN architecture for the modeling of H₂S removal and adsorption capacity.
3. Results and Discussion

3.1 Characterization of the Ca-modified coconut shell adsorbent

The SEM is a useful technique for assessing the morphology of an adsorbent such as activated carbon. Figures 2 (a) and (b) respectively show the SEM images of the fresh coconut-based activated carbon impregnated with calcium (Ca-CSAC) (before the adsorption process) and a spent one. From Figure 2 (a), the activation with KOH helps in the formation of well-distributed pores in the activated carbon, which invariably facilitates the adsorption of sulfur compounds. In comparison with the used Ca-CSAC, the SEM image in Figure 2 (b) shows the possibility of the blockages of the pores in Ca-CSAC due to the adsorption of sulfur compounds. The adsorption of sulfur compounds can further be corroborated by the presence of a white-appearing particles on the surface of the adsorbent, seen in Figure 2 (b).

EDX micrographs showing the elemental compositions of the fresh and the used Ca-CSAC are shown in Figure 2 a and b, respectively. It can be seen from the EDX micrograph that the fresh Ca-CSAC had mainly C, Ca, K, and O. The presence of a metal such as calcium has been found to enhance the adsorption capacity of the adsorbent (Wang et al., 2016). This elemental make-up of the Ca-CSAC is consistent with that reported by Cazetta et al. (2011). On the other hand, the used Ca-CNSAC has S in addition to C, Ca K and O which implies the removal of sulfur from the simulated wastewater. The compositional analyses of fresh and used Ca-CSAC are presented in Table 1. The EDX also shows a slight decrease in the amounts of C, Ca, K and O, possibly due to the partial blockage of the pores by the adsorbed sulfur compound.

Table 1. Elemental compositions of the fresh and the used coconut shell-based adsorbent obtained from EDX analysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>Component of fresh adsorbent (Weight %)</th>
<th>Component of spent adsorbent (Weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (C)</td>
<td>88.639</td>
<td>83.16</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>9.156</td>
<td>13.02</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>0.916</td>
<td>0.029</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>1.289</td>
<td>0.543</td>
</tr>
<tr>
<td>Sulfur (S)</td>
<td>0.000</td>
<td>3.241</td>
</tr>
</tbody>
</table>

The BET specific surface of the fresh Ca-CSAC adsorbent was estimated as 582 m²/g with a corresponding pore volume and average pore diameter of 0.33 cm³/g and 3.547 nm, respectively. These values are typical of a mesoporous material as indicated by Gupta et al. (2011). The BET surface area of 582 m²/g obtained for the fresh Ca-CSAC is smaller than the 783 m²/g reported by Cazetta et al. (2011) for NaOH-modified coconut shell-based activated carbon. The difference in the BET surface areas of the two coconut shell-based adsorbents could be from effects of modification with Ca and NaOH. Nevertheless, the large surface area obtained for the fresh Ca-CNSAC is beneficial for the removal of sulphur compounds from wastewater.

Figure 2. (a) SEM image of the fresh Ca-CSAC adsorbent, (b) SEM image of the used Ca-CSAC, (c) EDX micrograph of the fresh Ca-CSAC adsorbent, and (d) EDX micrograph of the used Ca-CSAC adsorbent
The XRD pattern showing the crystallinity of the Ca-CNSAC adsorbent is seen in Figure 3. Interestingly, various diffraction peaks signifying components of the as-prepared Ca-CNSAC can be identified. The diffraction peaks at $2\theta = 29.84^\circ$, $36.97^\circ$, $39.89^\circ$, $47.59^\circ$, $57.79^\circ$, $61.11^\circ$, $61.77^\circ$, $65.98^\circ$, $69.62^\circ$, $70.52^\circ$, $73.26^\circ$, $76.65^\circ$ and $77.5^\circ$ can be attributed to cubic CS$_2$, as evidence of the adsorption of sulfide onto the surface of the Ca-CSAC adsorbent. In addition, the diffraction peaks at $2\theta = 23.53^\circ$, $26.93^\circ$, $31.87^\circ$, $36.44^\circ$, and $77.55^\circ$ could be due to cubic Ca, which confirms the presence of Ca in the adsorbent. The unused active sites of the coconut-based activated carbon are confirmed by the diffraction peak at $2\theta = 43.63^\circ$.

3.2 Effects of process parameters on the adsorption capacity of and removal efficiency by Ca-CSAC

Prior to the neural network modeling, the effects of initial H$_2$S concentration, adsorption contact time and adsorbent dosage on the adsorption capacity and removal efficiency of the Ca-CSAC were investigated. Figure 4 shows 3-D plots of the effects of the various parameters on the adsorption capacity and H$_2$S removal efficiency of the Ca-CSAC adsorbent. From Figures 4 (a) and (b), it can be seen that the initial H$_2$S concentration, the adsorption contact time and the adsorbent dosage have varying effects on the adsorption capacity of the Ca-CSAC adsorbent. In Figure 4 (a), increasing adsorption contact time from 100 to 500 min resulted in a corresponding increase in the adsorption capacity from 60 to 320 mg/g. A similar trend is also observed when increasing the initial ion concentration. However, varying the adsorbent dosage does not significantly impact the adsorption capacity. In Figures 4 (c) and (d), the H$_2$S removal efficiency was found to increase with adsorption contact time, initial H$_2$S concentration, and adsorbent dosage. The interactions between ad-
Sorption contact time, initial H$_2$S concentration, and adsorbent dosage gave the maximum H$_2$S removal efficiency of 95%. It can be seen that the various parameters have synergistic effects on the adsorption capacity and the H$_2$S removal efficiency rather than mutually independent effects.

3.3 Artificial neural network modeling

Prior to the neural network modeling, the hidden layer of the neural network was optimized in order to obtain the least mean standard error (MSE). Based on the optimization (Figure 5), it was noted that too few hidden neurons gave a large MSE. However, when the higher hidden layer was chosen appropriately, lower values of MSE were obtained. Hence, 14 hidden neurons were selected for the neural network modeling, which is consistent with that reported by Khataee, & Khani (2009).

Subsequently, the data from batch runs were employed to train and validate the neural network using 16 hidden neurons. The training of the neural network was done using 70% of the data as prescribed by Ayodele et al. (2016) and Hossain et al. (2016), while 30% was used for validation. The plots showing the ANN outputs obtained from training and validation are seen in Figure 6. The ANN model very accurately reproduced adsorption capacity and H$_2$S removal efficiency. A perfect coefficient of determination (R$^2$) was obtained from the training process. Similarly, the ANN was adequately validated and tested with R$^2$ values of 0.99 and 0.95, respectively.

The tested and validated ANN model was subsequently employed to predict the adsorption capacity and the H$_2$S removal efficiency of the Ca-CSAC. The parity plots comparing ANN predicted values of H$_2$S removal efficiency and adsorption capacity to actual values, from training and validation, are shown in Figure 7. Statistical parameters such as R$^2$, adjusted R$^2$ and standard error of estimate were employed to test the validity of the ANN predictions. The ANN predicted values of H$_2$S removal efficiency are in close agreement with the experimental values for both training and validation data, as seen from the statistical parameters summarized in Table 2. The R$^2$ value of 1 obtained for the ANN model in both training and validation implies that the H$_2$S removal efficiency was well fit by this type of model. In other words, the ANN predicted values are statistically reliable. The adjusted R$^2$ value of 1 signifies that 100% of the data can be explained by the linear model. In both training and validation, the standard error estimate was very low, an indication that the ANN predictive model is reliable with minimal estimation errors. The significance of the ANN predictive model is validated by the p-values below 0.0001 for both training and validation. This further reiterates the robustness of the ANN model to adequately predict the H$_2$S removal from wastewater.
Adsorption capacity was also fit with an ANN model subjected to testing and validation. The parity plots comparing ANN predicted values of the Ca-CNSAC adsorption to actual values, for training and validation, are shown in Figure 8. In order to assess the robustness of the predicted ANN values, the statistical parameters $R^2$, adjusted $R^2$ and standard error of estimate were employed, as shown in Table 3. Interestingly, the ANN predicted values of adsorption capacity matched experimental values similarly in both training and validation, as seen in the statistical parameters summarized in Table 2. The $R^2$ values of 1 obtained for the ANN both in training and validation indicate very good model fit by ANN to the experimental adsorption capacity. This is an indication that the ANN predicted values are statistically reliable. The adjusted $R^2$ value 1 signifies that 100% of the data can be explained by the model. In both training and validation, the standard error of estimate was very low, an indication that the ANN predictive model is reliable with minimal errors. The significance of the ANN predictive model is validated by $p$-values below 0.0001 in both training and validation, which further buttress the adequacy of the ANN model to adequately predict the adsorption capacity of the Ca-CSAC. The accuracy of the ANN model fit for H$_2$S removal from waste is consistent with the work of Aghav et al. (2011), who utilized an ANN for the predictive modelling of competitive adsorption of phenol and resorcinol by wood and rice husk-based activated carbon. The study showed that the ANN perfectly fit the removal efficiency of Phenol and Resorcinol with $R^2$ values of 0.965 and 0.968, respectively. This predictive performance of the ANN used in this study has demonstrated the capability of ANN models to represent non-linear complex relationships between the input variables and the target variables. In the eventuality of scale-up of the refinery wastewater treatment process using the Ca-CSAC adsorbent, there may exist a non-linear complex relationship between the input and the output variables which needs to be learned from data in order to improve the performance of the process and also to enable predictive control and process optimization.
4. Conclusions

This study confirms the suitability of Ca-coated CSAC as a suitable adsorbent for the removal of H$_2$S from wastewater. Process parameters such as adsorption contact time, initial H$_2$S concentration and the Ca-CSAC dosage were found to significantly affect the H$_2$S removal efficiency and the adsorption capacity of Ca-CSAC. The interactions between adsorption contact time, initial H$_2$S concentration and Ca-CSAC dosage enabled highest H$_2$S removal efficiency of 95%. The modeling results showed that ANN is a reliable tool for the prediction of H$_2$S removal efficiency and adsorption capacity over a range of process conditions. Both training and validation of the predictive models show perfect correlations of model predicted values and actual experimental responses (H$_2$S removal efficiency and adsorption capacity).

The reliability of the ANN as a predictive modeling tool was further assessed through the statistical parameters R$^2$, adjusted R$^2$, standard error of estimate, and p-values. The values of 1 obtained for both R$^2$ and adjusted R$^2$ confirm that both the predicted ANN values and the experimental values were perfectly correlated. The p-values < 0.0001 and low standard error of estimate obtained for the ANN model show that the ANN has a high degree of reliability for predicting the H$_2$S removal efficiency and the adsorption capacity. Therefore, with the aid of the predictive ANN model, it will be possible to anticipate and put necessary measures in place that can facilitate the removal of H$_2$S from wastewater.

References


