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Removal of Zn (II) and Cu (II) From Aqueous Solution Using Dried Water Hyacinth as Adsorbent: Optimization of Process Parameters Using RSM and GAMS

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Abstract

Adsorption of Zn (II) and Cu (II) by dried water hyacinth was investigated in a batch system. The influence of contact time, adsorbent dose, pH, and initial metal ion concentration were studied. The study involves the use of statistical design to optimize process conditions for maximal adsorption of zinc and copper from aqueous solution. A Box-Behnken Design (BBD) involving Response Surface methodology (RSM) is used. In process systems engineering, it is challenging to design an optimized and effective process in a short period with minimum experimental trials, also the improvement of some variables of the process may deteriorate some other criteria due to conflicting regions of factor interests for optimal solution in multi-objective optimization processes (MOO). Optimization of the adsorption case study based on multi- objective RSM design is simplified with the application of the branch-and-reduce optimization navigator (BARON) solver based on (GAMS) General Algebraic Modelling System with identical factor variables, levels, and model equations. RSM suggested a number of different optimum settings, the validation of which is quite expensive, while GAMS suggested a single optimum setting which makes it more efficient. Optimum design variables of 90 mins. contact time, 2.337 g adsorbent dose, 7.135 pH and 10 mg/l initial metal ion concentration were identified for maximum percentage of removal of 98% and 87.537% for Cu and Zn respectively. These percentages of removal are higher compared to the RSM-based solution for each metal. The experimental validation of these values was carried out and the errors are found to be less than 5%. This render the GAMS based solution more reliable than RSM-based solution.

Keywords: GAMS, RSM, Optimization, Adsorption, Water Hyacinth

1. Introduction

Heavy metal pollution is increasing because of rapid human pollution and industrialization, this increase in pollution has consequently led to increase in the effluent discharge into the aquatic ecosystem. At least 20 heavy metals are classified as toxic and most of them are released into the environment in amounts that cause risks to human health (Kamsonlian and Bipin. 2013).

Copper is an example of these heavy metals and it has been used by man for years; however, it is regarded as a longstanding environmental contaminant. Several industries like mining, printing, painting, dyeing, battery manufacture and other industries discharge effluent containing Cu (II) to waterways. Copper smelting and mining are major industrial processes that lead to copper contamination of water and soil. Short periods of exposure can cause gastrointestinal disturbance, including nausea and vomiting. Use of water containing copper that exceeds the permissible level over many years could cause liver or kidney damage (Rana *et al., 2014)*. Copper is rarely found in source water, but copper mining and smelting operations and municipal incineration may be sources of contamination (Ye *et al*., 2012).

Zinc (Zn) as a heavy metal is an essential and beneficial element for human and plants. Complete exclusion of Zn is not possible due to its dual role, an essential microelement on one hand and a toxic environmental factor on the other. Zinc (II) is a well-known toxic metal ion and can threaten human life by bio accumulating in the food chain. Zn can cause nonfatal fume fever, pneumonitis, and is a potential hazard as an environmental pollutant (Zhang *et al*., 2017 and Zwain *et al*., 2014). Even though zinc is an essential requirement for a healthy body, excess zinc can be harmful, and cause zinc toxicity. Zn (II) is a common metal ion found in effluents of large number of industries (Kabeer *et al*., 2013).

Percentage of removal of heavy metal ions mainly depends on some parameters including contact time, adsorbent dose, pH and initial metal ion concentration. Accordingly, it is of great importance to investigate the influence of different parameters on the percentage of removal. The conventional method for investigating the influence of parameters is one factor at a time (OFAT) technique. Using OFAT, only one parameter is subjected to analysis while keeping all other parameters at a constant value. Recently using OFAT has been considered as a time consuming and expensive technique while statistical method, known as design of experiments (DOE), is considered as a powerful tool for the process optimization. Response surface methodology (RSM) is one of the methodologies in DOE which includes Box–Behnken design (BBD) (Yusup and Khan 2010), central composite design (CCD) (Cavalcante *et al*., 2010), Taguchi technique (Araujo and Brereton 1996), generic algorithm coupled with artificial neural network (ANN) and other combination of fractional factorial and Doehlert experimental designs (Baş and Boyacı 2007). The main advantages of using any of DOE methodologies are the possibility of studying the interaction effect between variables (not only the direct effect of variables as applied in OFAT) where better observations and understanding for the process, evaluating the optimum conditions for the process and to develop more efficient process.

The design of General Algebraic Modeling system (GAMS) has integrated ideas dragged from mathematical programming and relation data base theory and has attempted to combine these ideas to suit the needs of strategic modelers. Mathematical programming supply a way of characterizing a problem and a variety of methods for solving it. Relational database theory provides a structured frame work for developing general data organization and transformation capabilities. This has made GAMS a high-level modeling system for optimization and mathematical programming. It consists of a language composer and a stable of integrated high-performance solvers for formulating, solving, and/or analyzing an optimization problem. GAMS is suitable for complex, large scale modeling applications, and helps in building large maintainable models that can be adapted quickly to new situations. It is specifically designed for modeling linear, non-linear and mixed integer optimization problems, which is especially useful with large and complex problems (Amosa and Majozi 2016).

2. Methods

In this study, adsorption process carried out for the removal of zinc and copper from aqueous solution using water hyacinth as an adsorbent. All adsorption experiments for the heavy metal ions removal were designed according to RSM using BBD with the aid of a Design Expert® software and percentage of removal of zinc and percentage of removal of copper were selected as objective functions for optimization. Since it is often necessary to investigate several different effects on a response of interest, contact time, Adsorbent dose, pH and initial metal ion concentration were selected as process variables.

The regression equation for the optimization of medium constitutes: % removal of Copper (Y_1) is a function of contact time (X_1), adsorbent dose (X_2), pH (X_3) and initial metal ion concentration (X_4).

$$Y_1= 10.88214 + 0.080054X_1 + 109.68103 X_2 + 6.24092 X_3 -0.239127 X_4 +0.279195 X_1 X_2- 0.017897 X_1 X_3 +0.000247 X_1 X_4 -0.85333 X_2X_3 +0.075368 X_2 X_4 +0.000772 X_3 X_4 -0.002673 X_1^2-51.66933 X_2^2-0.341926 X_3^2+0.000186 X_4^2. \quad (1)$$

The regression equation for the optimization of medium constitutes: % removal of Zinc (Y_2) is a function of contact time (X_1), adsorbent dose (X_2), pH (X_3) and initial metal ion concentration (X_4).

$$Y_2= 23.29651-0.253351 X_1+37.89735 X_2-2.69092 X_3-0.171095X_4-0.016807X_1 X_2 +0.008824X_1X_3 +0.000377 X_1X_4- 0.089286X_2 X_3-0.033883 X_2 X_4+ 0.000321 X_3X_4+ 0.001176 X_1^2-5.5168 X_2^2 +0.183594 X_3^2+ 0.000306X_4^2 \quad (2)$$

3. Case study and results

Model results for the adsorption process are represented here. Models Eqs. (1), (2) characterize the important parameters of an adsorption process.

Analysis of variance (ANOVA) with respect to copper and zinc was carried out and it was observed that the models were highly significant (p-value<0.05), that means that the models provided good fit to the experimental data, the coefficient of determination (R^2), adjusted R^2 and predicted R^2. This state the close agreement between the model and experimental values. This explain the close agreement between the experimental and model values. The effect of amount of adsorbent and initial metal ion concentration had significant effect on the response of the adsorption process rather than the contact time and the pH.

Table 1 ANOVA for quadratic models.

Indices	Objectives/Response	
	Y_1	Y_2
R^2		0.9677
0.9494		
Adjusted R^2		0.9354
0.8988		
Predicted R^2		0.8140
0.7086		
Standard Deviation	5.90	5.79
Model p-value	<0.0001	
<0.0001		
X_1 p-value	0.1920	
0.3477		
X_2 p-value	<0.0001	
<0.0001		
X_3 p-value	0.1418	
0.7324		
X_4 p-value	<0.0001	
<0.0001		

3.1 Single objective optimization

The experimental results obtained were analyzed using response surface regression procedure of the statistical analysis system. For copper, the maximum percentage of removal attained was 85.5% at operating conditions of 75 min. contact time, 0.875 g adsorbent dose,6.25 pH and 20 mg/l initial metal ion concentration. 61% was achieved for zinc removal at 47.5 min. contact time, 3 g adsorbent dose, 6 pH and 10 mg/l initial metal ion concentration as the operating conditions.

Since the aim of this study is to evaluate, compare and then facilitate the RSM-optimization process with the assistance of GAMS, the second order polynomial models generated were performed directly in GAMS without any modification, to allow easy comparison of the optimization results.

Meantime, the models are in non-linear form, so they are handled as NLP models and solved by GAMS 24.3.3 (Generalized Algebraic modelling systems), using Branch-And-Reduce Optimization Navigator (BARON).

The four parameters were bounded as presented in Eq (3) for Cu and Eq (4) for Zn, and it serves as the constraint necessary for the solver in carrying out the search for optimal solutions.

$$0.5 \leq X_1 \leq 75$$
$$0.25 \leq X_2 \leq 1.5$$

$2.5 \leq X_3 \leq 10$
$20 \leq X_4 \leq 400$ (3)

$5 \leq X_1 \leq 90$
$0.2 \leq X_2 \leq 3$
$2 \leq X_3 \leq 10$
$10 \leq X_4 \leq 400$ (4)

The results were compared using the percentage error. Percent error, which is absolute value of the difference of two values divided by the theoretical value, was applied here because the experimental result was compared with a theoretical value (model).

3.1.1 Removal of Cu

A maximum percentage of removal of 85.5% was attained at control variables of 75 min. contact time, 0.875 g adsorbent dose, 6.25 pH and 20 mg/l initial metal ion concentration. When these control variables were fitted into the model in Eq (1), the resulting percentage of removal was 86.261%, which was a percentage error of 0.88%. Furthermore, GAMS application suggested 56.674 min. contact time, 1.178 g adsorbent dose, 6.196 pH and 20 mg/l initial metal ion concentration as the optimal solution with optimized percentage of removal of 93.449%. This represents a percentage of error of 7.4% when compared with the experimental results.

3.1.2 Removal of Zn

As for removal of zinc, its maximum percentage of removal given by the experimentation was 61% at optimal control variables of 47.5 min. contact time, 3 g adsorbent dose, 6 pH and 10 mg/l initial metal ion concentration. A percentage of error of 5.4% was discovered from its comparison with the model value presented in Eq. (2) which gave 64.48%. When the GAMS approach was implemented on the percentage of removal, an optimal solution of control variables attained was 5 min. contact time, 3 g adsorbent dose, 2 pH and 10 mg/l initial metal ion concentration with a maximum percentage of removal of 78.081%. This represent a percent error of 11.63% when compared with the experimental results.

The conflicting region of control variables that resulted from the single objective optimization approach is summarized in Table 2.

Table 2 Conflicting control variables for optimized single objective functions.

Objective functions	Optimized results and control variables across each platform		
	Experiment	RSM prediction	GAMS prediction
% Removal of Cu	85.5% at 75 min. 0.875g 6.25pH 20 mg/l	86.261% at 75 min. 0.875g 6.25 pH 20 mg/l	93.449% at 56.674 min. 1.178g 6.196pH 20 mg/l
% Removal of Zn	61% 47.5 min. 3g 6pH 10 mg/l	64.48% 47.5 min. 3g 6pH 10 mg/l	78.081% 5min. 3g 2pH 10 mg/l

3.2 Simultaneous optimization of the multi objective process

In the previous part, it was obvious that there was no single optimal solution that simultaneously optimized the two objective functions. It is much easier to obtain optimum conditions for single response optimization process than a multi response type. A multi objective optimization approach has to be performed to identify the single optimal solution. Numerical optimization method is usually employed in solving such conflicting multi objective problems in response surface methodology (RSM).

The multi response optimization technique has been incorporated into Design Expert software and it is able to simultaneously finding a maximum desirability from a range of zero to one for up to dozens of responses /objective functions (Amosa and Majozi 2016).The program combines individual desirability into a single number and then search for the highest global desirability.

In this study, simultaneous optimization of the two objective functions (% removal of Cu and % removal of Zn) was carried out numerically with the implementation of RSM approach.

Combination of the two objective functions (maximizing the percentage of removal of Cu and Zn) is demonstrated here for possible simultaneous optimization, application of the RSM-based numerical optimization technique brought hundred optimal sets of solutions for the multi objective optimization problem. Evidently, validation of all the hundred solutions set experimentally was obviously exhausting and waste a lot of time, hence, just the 10 solution sets with high percentage of removal for both Cu and Zn were validated for finding a representative optimum solution having the best agreement between the theoretical and experimental solution. The decision maker will only be able to look for the most preferred solution based on the connection between the experimental and theoretical solutions. This considered the significant disadvantage of this method as different decision makers could easily end up with different choice of optimum solutions.

Optimum settings for the percentage of removal of zinc and percentage of removal of copper were generated by the numerical optimization technique. The process was theoretically optimized for the response and control variables were predicted for each optimum setting. Optimal solution set according to the experimental validation result is: contact time 64.856 min., adsorbent dose 2.586 g, 8.014 pH and initial metal ion concentration 48.78 mg/l as the best as it has the highest percentage of removal for both zinc and copper.

Table 3 Validation of optimal solution

Platform	Objective function	Theoretical	Experimental	% Error
RSM-based	Y_1	95.628%	92.5%	3.3%
	Y_2	80.994%	77.4%	4.4%
GAMS-based	Y_1	98%	94.4%	3.6%
	Y_2	87.537%	84.4%	3.5%

Subsequently, in order to simultaneously optimize the removal of each heavy metal previously coded as process objective functions (POFs) Y_1 and Y_2, the objective functions were combined as a single multi-objective function (MOF) represented as Z for the optimization process as follows:

Max $Z= Y_1+Y_2$

The MOF is subjected to constraint: $0.5\leq X_1\leq 90$, $0.2\leq X_2\leq 3$, $2 \leq X_3\leq 10$, $10\leq X_4\leq 400$ and as GAMS approach was implemented in solving the multi-objective optimization problem, an optimal solution of 98% for copper and 87.537% with a set of control variables of 90 min. contact time, 2.337 g adsorbent dose, 7.135 pH and 10 ppm initial metal ion concentration.

Table 3 shows the experimental validation and agreement trends alongside the % errors between the theoretical and experiments results from the RSM and GAMS optimization platforms.

Comparing the control variables influencing the removal of the pollutants as presented by the RSM- and GAMS-based optimal solution in Table 3, it was observed that both approach suggested very close value for the amount of adsorbent and the pH with almost similar trend in percentage of removal of copper. Furthermore, the discrepancy between the theoretical contact time and initial concentration for the best removal was high, and this had a significant impact on percentage of removal of zinc in theoretical value. GAMS- and RSM based optimal solutions agreed with the experimental values as the % error we all less than 5%, but GAMS could make a combination of variables which gave highest percentage of removal for both zinc and copper theoretically and also when it applied experimentally the percentage of removal of both copper and zinc was higher than that was given by RSM.

Lastly, GAMS implementation in simultaneously solving the multi objective optimization (MOO) problem appeared more accurate, reliable and economically viable in that just a single set of control variables was suggested as the optimum. This was easier to validate experimentally even with the fact that the optimal was somewhat close to that obtained from RSN-based solution.

4. Conclusion

This work has target to reach the optimum conditions for the highest percentage of removal of copper and zinc by adsorption using water hyacinth with the implementation of GAMS to facilitate an RSM-based optimization of the process. It was observed that an increase in amount of adsorbent and decrease in initial metal ion concentration could led in increase in percentage of removal of both copper and zinc. Optimum condition for the multi-objective sorption process was searched using the numerical optimization that suggested a number of different optimum solutions; ten solutions with highest percentage of removal value were chosen to be applied experimentally. Operating conditions with 64.856 min. contact time, 2.586 g adsorbent dose, 8.014 pH and 48.780 mg/l initial metal ion concentration gave the highest percentage of removal for both zinc and copper and it was selected as optimal solution set. Consequently, the second order polynomial models were combined, subjected to fixed control variables and it was solved as a NLP optimization problem with the selection of BARON solver for GAMS implementation. An optimum and design variables of 90 min. contact time, 2.337 g adsorbent dose, 7.135 pH and 10 mg/l initial metal ion concentration was identified for maximum percentage of removal of 98% for Cu and 87.537% for Zn. These percentages of removal are higher compared to the RSM-based solution for each pollutant. The experimental validation of these values was carried out and the errors are less than 5%. This makes the GAMS based solution to be more reliable than RSM-based solution. In addition, the RSM approach gives more than one optimum setting, which make the validation quite expensive and tedious. While GAMS approach is simultaneously solving for the best operation conditions, which make it economic since only one operation condition setting, was suggested as the optimum.

5. References

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