CENTRAL COMPOSITE DESIGN OF ZINC REMOVAL FROM MODEL WATER USING CHITOSAN BIOPOLYMER

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Abstract
This research project intended to study the performance of *chitosan* as flocculating agent for removal heavy metal (zinc) from artificial water. *Chitosan* was used due to its special characteristics such as non-toxic, hydrophilic, biodegradable, biocompatible, and anti-bacterial, biopolymer and very good adsorption of heavy metal which has led to a very diverse range of its applications. The presence of a large number of amine groups on the *chitosan* chain increases it adsorption capacity. The effect of contact time, dosage of *chitosan*, agitation speed and pH were observed for optimal absorption of the zinc in synthetic water. Thus, the application of conventional jar test method used for removal of zinc from synthetic water. Thus, the results of this project which is 52.40% of percentage removal of zinc with optimum conditions; pH7, 30mg dosage, 12 minutes of contact time, and 190 rpm agitation speed approved that *chitosan* competent to be the alternative adsorbent.

Keywords: Experimental Design, Central Composite Design, Agitation Speed, Chitosan Biopolymer, Heavy metals, Environmentally Friendly.

24. Introduction

Heavy metals commonly found in local wastewaters consist mainly of chromium, cadmium, lead, zinc, arsenic, nickel and silver. Zinc (II), among others, although provides essential elements for human and plants, is comparatively toxic in high concentrations which can lead to various health diseases such as nausea, anemia, pancreas damage and decreased levels of high density lipoprotein (HDL) (USDH, 2005, Qudsieh et al. 2012). Chemical precipitation treatment and some other methods such as ion exchange and reverse osmosis processes are often required to treat leachate, which is costly and usually not an environment friendly solution. Removal of cadmium and cyanide from effluents through electro dialysis, removal of zinc by Water Hyacinth (*Eichhornia crassipes)* are few of the effective methods of heavy metals removal for the industrial applications. The costs for these types of operations were relatively high compared to the current requirements of treatments needed in this country. For example, treatment by Water Hyacinth will consume a vast amount of land spaces due to the large water surface area needed to grow the plants (Lu.X et al., 2004).

A variety of biological coagulants can be found throughout the globe as well. Moringa oleifera seeds can be used as a natural coagulant (primary coagulant) in household water treatment as well as in the community water treatment systems. Use of *Moringa Oleifera* seeds as a coagulant began in the Sudan but has spread significantly over the past several years (Dishna Schwarz,2000). However, there are still some disadvantages of using Moringa oleifera as coagulant such as the purified water might still carry some pathogenic microorganism although the treatment makes the water clear and drinkable. Moreover, there is a possible of bacteria increase after the coagulation of water and the coagulation is not available in pure form (Dishna Schwarz, 2000). In contrast, the used of *chitosan*, which is widely used because of its biodegradability and its structural properties (Dodane and Vilivalam, 1998), for removing the heavy metal had been approved where this biopolymer can collect the completely the ionic form of zinc, copper and cadmium (R. A. A. Muzzarelli and Laszlo Sipos, 1971). A process for removing heavy metals from waste-water is being developed using *chitosan* beads, a selective, high-capacity adsorbent. The process minimizes fouling and generates a concentrated heavy-metal stream that can be processed to recover the heavy metals. Nowadays, there is a growing interest in the production and use of new materials from renewable sources. Natural polymers are replacing synthetic polymers in different applications partly because the waste from natural polymers is normally biodegradable (Majeti and Kumar, 2000; Wood, 2001). In this study, the performance of *chitosan* used in removal of zinc from model water was investigated, the operating conditions were optimized by using Design Expert software and the results were validated to develop and design of a water treatment system.

25. Materials and Methods

2.1 *Removal of zinc from water by using chitosan*

Zinc was removed from model water (stock solution) through coagulation process. The experiment carried out by Jar test method. In this method, the amount of zinc before and after the reaction was determined and four varied parameters were considered; dosage of *chitosan*, agitation speed, contact time and pH. The effect of zinc removal was studied and optimization was done before the experiment started.

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2.2 Experimental materials

2.2.1 *Starting materials*

Chitosan powder (degree of deacetylation 88%) was used for the removal of heavy metals (Zinc) from water was provided by Department of Chemistry, University of Putra Malaysia.

2.3 Methods

2.3.1 Experimental Method

2.3.1.1 Preparation of standard solution

A standard solution containing 10 mg Zinc as zinc sulfide heptahydrate solution in water. A 4.4 g of zinc sulfide heptahydrate ($ZnSO_4.7H_2O$) was weighed and dried at 105 °C for an hour. Then, the dried $ZnSO_4.7H_2O$ was dissolved in 1L water in a volumetric flask. The solution was stored at below temperature 4°C. Then the 3.0 mg/L stock solution of zinc was prepared.

2.3.1.2 Methods for removal of zinc from the model water

Certain amount of *Chitosan* powder was added to the stock solution (50ml of the stock solution with the desired pH that had been prepared according to the design, was transferred into 100mL beaker) and at the same time, the agitation speed of the jar test impeller was adjusted according to the desired value, the experiment was started according to the design of experiment parameters by using jar test apparatus. Then, the experiment was repeated for different parameters with different factors. The amount of zinc present in the model water was tested by using the calibrated Atomic Absorption Spectrometer (AAS). As well as a blank solution of distilled water and standard solution with varied concentration of zinc were prepared.

2.4 Design of experiment and statistical analysis

A design experiment is a test which some changes are made into the input variables of a process or a system so as to observe and identify the reasons for changes in the output response. Design of experiments is the application of geometric principles to statistical sampling to obtain desired results such as minimizing the number of experiments necessary to obtain the answer to a problem. Cost and quality are the basis elements of value (Jayan, 2000). A well planned set of experiments, in which all parameters of interest are varied over a specified range, is a much better approach to obtain systematic data. Such a complete set of experiments will give desired results (Jayan, 2000). The optimization was done by using Design Expert software where the parameters involved got from the literature review were prompted together with their values. This step was done to reduce the number of runs due to the limitation in time and resources. Four factors with three levels (low "-1", moderate "0" and high "+1") were applied to fractional factorial design with randomize runs. Table below shows the parameters with its variation which was used in the removal of heavy metal (zinc) experiment. The run orders of experiment were determined by using Design Expert software. The equations were developed to predict the theoretical values of removal of zinc so that it can be compared with the experimental values. This was followed by analysis of the regression equation by statistical tools; Analysis of Variance (ANOVA), F test.

Table 1 : Parameters for removal heavy metal (zinc)

Factors	-1	0	+1
Chitosan dosage (mg)	10	20	30
Agitation (rpm)	50	125	200
Contact Time (min)	2	7	12
pH	3	5	7

Chitosan dosage, pH, contact time: Karthikeyan. et.al (2003), Agitation: Roussy. et.al (2005)

The percentage of heavy metals removal was taken as the dependent variables or response (Y). A second order polynomial equation was then fitted to the data by multiple regression procedure. This result in empirical model that relate the response measured in the independent variables to the experiment. For a four factor system, the model equation is:

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{44} x_4^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{34} x_3 x_4 \quad ...... (1)$$

Where Y is the percentage of zinc removal (%, mg/L), predicted response; β_0, intercept; β_1, β_2, β_3, β_4, linear coefficient; β_{11}, β_{22}, β_{33}, β_{44}, squared coefficients; β_{12}, β_{13}, β_{14}, β_{15}, β_{23}, β_{24}, β_{34}, β_4

Table 2: Process design optimization of zinc removal

Run	Dosage (mg)	Contact Time (min)	pH	Agitation speed (rpm)
1	35.00	7.00	5.00	125.00
2	30.00	2.00	3.00	200.00
3	30.00	12.00	3.00	50.00
4	20.00	7.00	5.00	125.00
5	10.00	2.00	3.00	50.00
6	20.00	7.00	5.00	125.00
7	20.00	7.00	8.00	125.00
8	10.00	12.00	3.00	200.00
9	20.00	7.00	5.00	125.00
10	30.00	12.00	7.00	50.00
11	10.00	12.00	7.00	200.00
12	20.00	13.00	5.00	125.00
13	20.00	1.00	5.00	125.00
14	20.00	7.00	2.00	125.00
15	20.00	7.00	5.00	250.00
16	30.00	2.00	7.00	200.00
17	20.00	7.00	5.00	125.00
18	20.00	7.00	5.00	125.00
19	20.00	7.00	5.00	0.00
20	10.00	2.00	7.00	50.00
21	5.00	7.00	5.00	125.00

33. Results and Discussion

3.1 ANOVA Response

According to the results from the ANOVA response; Table 2, the mean square gave total 20 runs but only nine runs were measured, 13 runs were rejected due to lack of fit and pure error calculation. Then, there were seven runs, which could be considered as significant because the P values were less than 0.05. The term significant was represented the value of probability "Prob > F" which less than 0.05.

According to the results, the factors A, B, C, D, AB, AC, and BD were significant. However, the values still not equal to zero meanwhile the values of zero mean very good. Thus, from the results, there were four factors that had a good result which the P values were almost equal to zero. Those four factors were A, C, D, AB and AC which equal to 0.001.

3.2 Factors Influencing the Adsorption of Zinc

3.2.1 Effect of Dosage

The dependence of zinc adsorption on dosage was studied by applied three different amounts of adsorbent (10, 20 and 30 mg/L), those values were randomly sorted with other three parameters which produced a varied data for the experiment. Figure1 represents the percentage removal of zinc in water at a varied concentration of adsorbent. From the figure, it can be observed that removal efficiency of the adsorbent generally improved with increasing dosage.

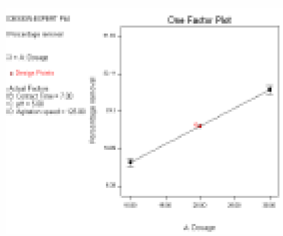

Figure 1: Percentage removal of zinc vs Dosage

3.2.2 Effect of Contact Time

Result of Figure 2 indicates that removal efficiency increased with an increase in contact time. Other parameters such as the dosage of adsorbent, pH of solution and agitation speed was kept optimum, while temperature was kept at room temperature. It can be seen that removal efficiency increased as the contact time increased. However, after sometimes, the percentage removal was slow with the increasing of time.

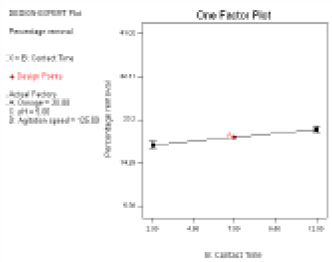

Figure 2: Percentage removal of zinc vs contact time.

3.2.3 Effect of pH

To study the effect of pH on the zinc removal efficiency, pH value was set at three different levels according to the design which were 3, 5 and 7. As shown in Figure 3, the uptake of free ionic zinc depends on pH, where optimal metal removal efficiency occurs at pH7. Figure 3 also indicated that the percentage removal of zinc in the water was increased as the pH value was increased. Therefore, it showed that the increasing of pH will eventually increase the percentage removal of zinc value.

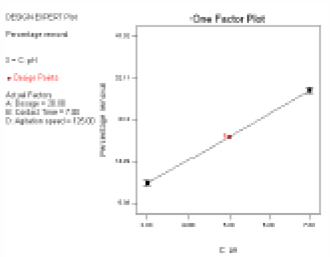

Figure 3: Percentage removal of zinc vs pH

3.2.4 Effect of agitation speed

Agitation speed is one of the parameter used in the experiment and it was also design at three different levels. Then, the effect of agitation speed on removal efficiency of zinc was studied by applying three different speeds of agitation which is 50rpm, 125rpm and 200rpm. As can be seen from Figure 4, the percentage of zinc removal efficiency generally increased with increasing of agitation speed.

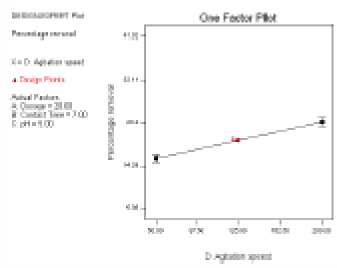

Figure 4: Percentage removal of zinc vs agitation speed

3.2.5 Factors affecting the efficiency of zinc removal

3.2.5.1 Dosage and contact time

Result of Figure 5 shows that the removal efficiency was also affected by interaction of two factors which are dosage and contact time. The figure indicated that, the percentage of zinc removal was increased with increasing dosage and contact time.

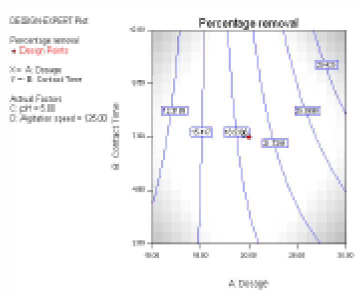

Figure 5: Percentage removals of zinc vs contact time and dosage.

3.2.5.2 Dosage and pH

The efficiency of zinc removal also depends on two interaction factors which are dosage of absorbent and pH. As shown in the Fig. 6-6, the percentage of zinc removal was increased when the amount of absorbent increased together with the increasing of pH value

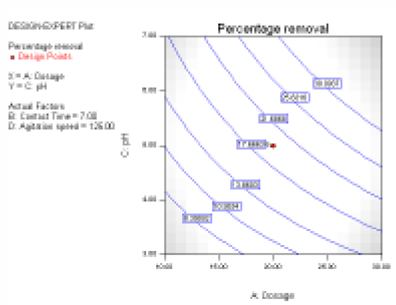

Figure 6: Percentage removal of zinc vs dosage and pH.

3.2.5.3 Contact time and Agitation speed

The percentage of zinc removal from water was also depends on two interactions; contact time and agitation speed. Figure 7, showed that the zinc removal percentage was increased when the factors of agitation speed and contact time were increased.

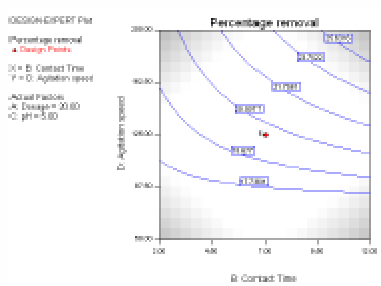

Figure 7: Percentage removal of zinc vs contact time and agitation speed

3.3 Optimization

According to the numerical solution in optimization part, (Tables 3-5 below), there were 10 solutions for the optimized condition. However, the first solution was selected because it had a better result of zinc removal and also suggested by the Design Expert software. The optimum conditions suggested were at pH7, 30mg dosage, 12 minutes of contact time, and 190 rpm agitation speed.

Table 3: Process design optimization of zinc removal

Run	Dosage (mg)	Contact Time (min)	pH	Agitation speed (rpm)	Percentage removal (%)
1	35	7	5	125	34.89
2	30	12	3	50	12.83
3	20	7	5	125	19.59
4	30	2	3	200	10.56
5	30	12	7	50	41.02
6	20	7	5	125	19.59
7	5	7	5	125	8.97
8	20	7	8	125	33.92
9	20	7	5	0	12.27
10	20	7	5	125	19.59
11	10	2	3	50	5.38
12	20	7	5	125	19.59
13	10	12	7	200	22.26
14	20	7	8	125	33.92
15	20	7	5	250	24.98
16	30	2	3	200	10.56
17	10	12	3	200	7.55
18	20	7	5	125	19.59
19	10	2	7	50	17.52
20	20	7	2	125	6.13

21	20	7	5	125	19.59

Table 4: ANOVA for Response Surface Reduce 2FI Model (Response: Zinc concentration)

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	2023.06	7	269.01	200.00	< 0.0001	Sign.
A	335.92	1	335.92	232.47	< 0.0001	
B	17.52	1	17.52	12.12	0.0041	
C	1255.66	1	1255.66	868.95	< 0.0001	
D	80.77	1	80.77	55.90	< 0.0001	
AB	41.66	1	41.66	28.83	0.0001	
AC	80.29	1	80.29	55.56	< 0.0001	
BD	16.90	1	16.90	11.69	0.0046	
Residu.	18.79	13	1.45			
Lack of Fit	18.79	6	3.13			
Pure Error	0.000	7	0.000			
Cor Total	2041.85	20				

The Model F-value of 200.00 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. The term A represent a dosage of *chitosan*, B represent contact time, C and D represent pH and agitation speed respectively. In this case, A, B, C, D, AB, AC, BD are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

Table 5: Optimization Results

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Dosage	is in range	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Contact Time	is in range	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
pH	is in range	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Agitation speed	is in range	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Percentage remov...	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Solutions

Number	Dosage	Contact Time	pH	Agitation speed	Percentage removal	Desirability	
1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Selected
2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
5	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
6	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
8	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
9	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
10	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	

[illegible] Solutions found

Number of Starting Points: [illegible]

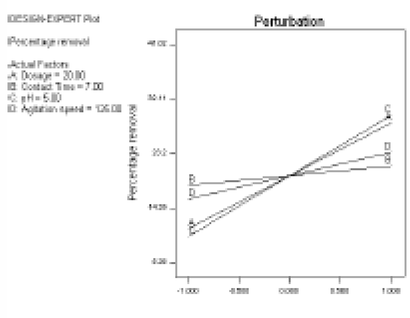

Figure 8: Perturbation plot

The perturbation plot above (Figure 8) used to compare the effect of all the factors at a particular point in the design space. The response was plotted by changing only one factor over its range while holding of the other factors constant. It helps in analyzing all independent variables that influence adsorption capacity of *chitosan*. This model will consider all parameters and conditions required and come out with adsorption capacity equation. Referred to the Figure 9 below, the value of actual and predicted were closed. Thus, it means that all the factors are affecting the zinc removal efficiency by using the *chitosan*. The output for multiple regressions for average removal is shown in figure 9.

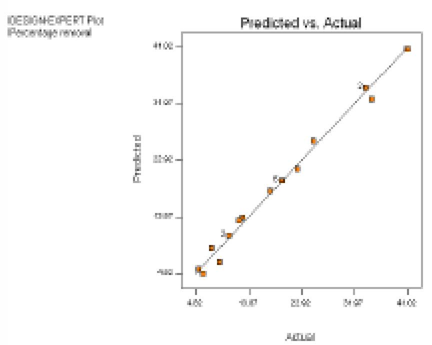

Figure 9: Predicted value vs actual value

This output shows the results of linear regression to describe the relationship between average percentage removal with initial pH, dosage of adsorbent, agitation speed and contact time. The equation of the fitted model as following:

Percentage Removal = 3.24218 - 0.55399*A - 1.97752*B + 1.32147*C + 4.50646E003*D + 0.073303*AB + 0.18097*AC + 6.61908E-003* BD

Where: A = Dosage (mg); B= Contact time (minute); C = pH; D= Agitation speed (rpm)

Then, from the results of central composite design (CCD), it can be concluded that removal efficiency will be increased with the increasing of all parameters involved.

3.4 Removal Efficiency

The influences of several operational parameters such as dose of adsorbent, agitation speed, pH and contact time were investigated. Based on the optimization result (with optimum condition; pH7, 30mg dosage, 12 minutes of contact time, and 190 rpm agitation speed), the final optimize concentration of zinc was produced. Then, from the results, the percentage of removal efficiency (E) of the adsorbent on zinc was calculated (52.40%) and it means only 52.40% concentration of zinc that had been removed from the model water by using *chitosan* under the optimum conditions. Calculations were done according to equation (3)

$$E(\%) = \frac{C0 - C1}{C0} \times 100 \quad \ldots\ldots\ldots \quad (3)$$

C_0 = initial concentration of zinc solution (mg/L)

C1 = equilibrium concentration of zinc solution (mg/L), respectively.

34. Conclusions

In the continuing search to find more effective adsorbents, this was a good opportunity for the biological absorbent; *chitosan* to make a breakthrough in the environmental aspects. Even though their truly potential usages are unknown, *chitosan* had shown possible applications in various fields. and perhaps, this is one of them. Basically, *chitosan* required several factors to influence their adsorption process. Similar to other adsorbents, the efficiency of *chitosan* as a flocculating agent are greatly dependent on pH, agitation speed, dosage, and contact time. From the results, it was clearly shown that removal efficiency for zinc was increased with the increasing of all parameters. The sequence of dominant factors that will make a great difference had been also successfully identified. It began with pH, dosage of *chitosan*, agitation speed, and followed by time. Therefore, from the results obtained, it was approved the capacity of *chitosan* as flocculating agent to remove zinc from model water. Even though the highest maximum removal was achieved to be only ≈52.40 % (with optimum condition; pH7, 30mg dosage, 12 minutes of contact time, and 190 rpm agitation speed). So, it was enough to indicate that *chitosan* is competent to be the next alternative adsorbent. All parameters responsible in influencing removal of zinc have been identified. Furthermore, a general adsorption equation based on parameters selection had also been obtained. (Percentage removal = 3.24218 - 0.55399*A - 1.97752* B + 1.32147* C + 4.50646E - 003*D +0.073303 *AB + 0.18097*AC +6.61908E-003* BD).

Acknowledgement

This work is supported by Ministry of Higher Education Malaysia Fundamental Research Grant Scheme (Grant no FRGS0308-88) and we gratefully acknowledge the support.

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