Modern Applied Science; Vol. 10, No. 1; 2016
ISSN 1913-1844 E-ISSN 1913-1852
Published by Canadian Center of Science and Education

Factorial Design Analysis of Zn(II) Ions Adsorption on Thermally Treated Rice Husk

Keat Khim Ong[1], A. T. Ahmad Farhan[2], W. M. Z. Wan Yunus[2], Ahmad Mujahid Ahmad Zaidi[3], M. L. Jabit[4], A. Fitrianto[5], K. M. Safidin[4], U. F. Abdul Rauf[1], F. Che Ros[1], A. G. Hussin[2] & M. B. Ahmad[6]

[1] Department of Chemistry and Biology, Centre for Defence Foundation Studies, Universiti Pertahanan Nasional Malaysia, Malaysia

[2] Department of Defence Science, Faculty of Defence Science and Technology, Universiti Pertahanan Nasional Malaysia, Malaysia

[3] Department of Mechanical Engineering, Faculty of Engineering, Universiti Pertahanan Nasional Malaysia, Malaysia

[4] Technical Services Centre, Malaysian Agricuktural Research and Development Institute Headquarter, Malaysia

[5] Department of Mathematics, Faculty of Science, Universiti Putra Malaysia, Malaysia.

[6] Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, Malaysia

Correspondence: Keat Khim Ong, Department of Chemistry and Biology, Centre for Defence Foundation Studies, Universiti Pertahanan Nasional Malaysia, Kem Sungai Besi, 57000 Kuala Lumpur, Malaysia. Tel: 603-9051-3400. E-mail: ongkhim@upnm.edu.my

Received: September 17, 2015 Accepted: October 26, 2015 Online Published: December 18, 2015

doi:10.5539/mas.v10n1p121 URL: http://dx.doi.org/10.5539/mas.v10n1p121

The research is financed by Universiti Pertahanan Nasional Malaysia.

Abstract

Adsorption of Zn(II) ions from aqueous solutions by thermally treated rice husk was investigated using factorial experimental design to study effects of heating temperature and period of rice husk, pH, initial Zn(II) ion concentration, adsorption temperature and contact time, and adsorbent dosage. Main and interaction effects of these factors were analyzed using statistical techniques and the results were analyzed statistically using the Student's t-analysis and analysis of variance which were used to determine significant factors that affect the percentage removal of Zn(II). These significant factors were heating temperature of rice husk, pH, initial metal concentration, contact time, and adsorbent dosage. The interaction between two different effects also affects the percentage removal of Zn(II) ions. These include the interactions between heating temperature of rice husk and initial metal concentration, pH and initial metal concentration, and pH and the adsorbent dosage.

Keywords: adsorption, factorial design analysis, Zn(II), thermally treated rice husk

1. Introduction

Rapid development of industrial and agricultural sectors coupled with the growth of population increase hazardous heavy metals released into our environment. Heavy metals such as lead, chromium, copper, cadmium, nickel, silver, mercury, and zinc are harmful but, in many instances, they are discharged without proper treatment by manufacturers and/or users, therefore, become a major cause of water pollutions (Kilic et al., 2013). Without proper disposal methods, these metals endanger public and environment health (Sheela et al., 2012) as they are stable ions which can be accumulated by living organisms (Demirbas, 2008).

Malaysian Environmental Quality Act 1974 sets the permissible limit of Zn in drinking water is 2.0 mg/l (Wahi et al., 2010). Excessive intake of Zn in human bodies will cause nausea, diarrhoea, depression, lethargy, and neurological signs, such as seizures and ataxia (Malamis & Katsou, 2013). Zinc is frequently detected in wastewaters of acid mine drainage, galvanizing, natural ore processing, and municipal wastewater treatment plants (Hawari et al., 2009).

Many methods have been developed to extract zinc ion from water. These methods include adsorption, complexation, chemical oxidation or reduction, chemical precipitation, reverse osmosis, ion exchange, solvent extraction, membrane filtration, coagulation, phytoextraction and evaporation (Lim et al., 2012). However, the methods such us chemical precipitation, ion exchange and membrane filtration are expensive, ineffective at low concentration (i.e. < 100 mg/L), and produce toxic sludge/ waste materials that also need to be disposed (Kilic et al., 2013).

Recently, several studies have been carried out to explore the usage of agricultural wastes as heavy metal ion adsorbents. Hydroxyl groups of cellulose, hemi-cellulose and lignin, which are major components of these wastes, have the abilities to bind the heavy metals (Nguyen et al., 2013). The adsorption capacity of these wastes to adsorb heavy metals could be increased with the pre-treatment (Bhattacharya et al., 2006). Agricultural wastes such as hazelnut shell (Jamali et al., 2009), pomegranate husk (El Nemr, 2009), sugarcane bagasse (Garg et al., 2009), banana peel (Anwar et al., 2010), and rice husk (Bansal et al., 2009) have been studied for these purposes.

Rice husk is a waste material from rice milling process. Based on the statistical data from Malaysian Ministry of Agriculture, there is 408 000 metric tons of rice husk generated in Malaysia annually (Syuhadah and Rohasliniey, 2013). The presence of abundant floristic fiber, protein and some functional groups such as carboxyl, hydroxyl and amidogen in rice husk increase the possibility of adsorption process to occur. Modification on the textures of rice husk, either chemical and/or thermal treatment/s, could enhance its adsorption capacity (Ye et al., 2010). Rice husk has the potential to be used as raw material to produce activated carbon. Hence, it will be a cheaper alternative compared to existing commercial activated carbons. Activated carbon produced from rice husk has highly porous structure and high specific area (Taha et al., 2011). Rice husk ash which is produced from thermal treated rice husk, was previously used to absorb oil on hard surfaces, filter arsenic from water, adsorption of gold thiourea, and adsorption of metal ions (Mane et al., 2007).

In this study, a 2^{7-1} fractional factorial design was used to evaluate the effects of heating temperature and period of rice husk, pH of metal ion solution, initial metal concentration, adsorption temperature and contact time, and an adsorbent dosage on the removal of Zn(II) ions from aqueous solutions by thermally treated rice husk as running full factorial design is too expensive due to large number of experiments have to be performed. Moreover, higher order interactions are negligible.

2. Method

Rice husk was collected from a local rice mill in Selangor, Malaysia. All chemicals and reagents used were of analytical grade and purchased from Merck Malaysia. The ultrapure water was obtained from a Milli-Q water purification system (Millipore, Germany) for preparation of solutions and rinsing purposes throughout the experiments.

2.1 Preparation of Thermal Treated Rice Husk

The rice husk obtained was ground and washed with ultrapure water several times until constant pH was obtained. The powder was then dried in an oven at 105^{O}C for 24 h, sieved to obtain particles of less than 2 mm, heated in a furnace at selected temperature and period (Table 1) and then cooled in a desiccator and stored in a polyethylene bottle.

2.2 Preparation of Metal Solution

Solutions of Zn(II) ion were prepared by diluting appropriate amounts of 1000 mg/L of $Zn(NO_3)_2$ with ultrapure water (resistivity of 18.2 MΩ.cm). The pH was adjusted to the desired pH using 1.0 M of NaOH and HCl.

2.3 Adsorption Study

The mixture of 100 mL of $Zn(NO_3)_2$ solution and 1 g of thermally treated rice husk (RH) sample was agitated at 150 rpm for a particular period (Table 2). The mixture was filtered using a 0.45 µm cellulose nitrate membrane filter and the solution was then analyzed using an inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin Elmer, OPTIMA 5300 DV). All experiments were conducted in duplicates.

Table 1. Experimental range and levels of the factors used for the optimization of adsorption of Zn(II) ions

Factor	Coded symbol	Low level (-1)	High level (+1)
Heating temperature (^{O}C)	x_1	500	800
Heating period (hour)	x_2	2	4
pH	x_3	2	6
Initial concentration (mg/L)	x_4	30	150

Temperature (℃)	x_5	30	60
Contact time (minute)	x_6	30	180
Adsorbent dosage (g)	x_7	2	10

3. Results and Discussion

Table 2 shows the experimental results of the adsorption study of Zn(II) ions using factors in coded unit. The percentage removal of Zn(II) was calculated as shown below:

$$[(Co-Ce)/Co] \times 100\% \quad (1)$$

where *Co* is initial concentration and *Ce* is final concentration of Zn(II) solutions. Analysis of results was performed using MINITAB 17 for windows.

Table 2. Experimental results of the adsorption of Zn(II) ions using factors in coded unit

Run	Heating Temperature	Heating Time	pH	Initial Concentration	Temperature	Contact time	Adsorbent Dosage	% removal
1	1	-1	-1	1	1	-1	-1	23.81
2	1	-1	1	-1	1	1	1	99.23
3	-1	1	-1	-1	-1	-1	-1	18.61
4	-1	-1	-1	-1	-1	-1	1	58.02
5	-1	1	-1	1	-1	-1	1	40.33
6	1	-1	-1	-1	-1	1	1	98.81
7	1	1	-1	-1	1	1	1	99.58
8	-1	-1	1	-1	1	1	-1	88.19
9	-1	-1	-1	-1	1	-1	-1	18.33
10	-1	1	1	-1	1	-1	-1	79.54
11	1	1	1	-1	-1	1	1	98.45
12	-1	-1	1	-1	1	-1	1	98.61
13	1	-1	-1	-1	1	1	-1	10.77
14	-1	1	-1	1	1	-1	-1	2.80
15	-1	-1	1	1	1	1	1	96.51
16	1	-1	-1	-1	1	-1	1	99.32
17	-1	-1	1	1	1	-1	-1	29.6
18	1	-1	-1	1	1	1	1	99.73
19	-1	-1	-1	1	-1	-1	-1	0.41
20	-1	1	-1	-1	1	-1	1	75.00
21	-1	1	-1	1	-1	1	-1	11.98
22	1	1	1	-1	1	1	-1	99.62
23	1	1	-1	1	-1	1	1	99.41
24	1	1	1	-1	1	-1	1	98.33
25	-1	-1	1	1	-1	1	-1	36.98
26	-1	-1	-1	1	1	1	-1	8.37
27	-1	-1	-1	-1	-1	1	-1	0.74
28	1	-1	1	-1	1	-1	-1	99.84
29	1	-1	1	-1	-1	1	-1	99.76
30	-1	1	1	1	1	-1	1	92.42
31	1	1	-1	1	-1	-1	-1	44.61
32	1	1	-1	-1	-1	-1	1	99.31
33	1	-1	-1	1	-1	1	-1	25.83
34	1	1	-1	-1	1	-1	-1	9.46
35	1	1	-1	-1	-1	1	-1	97.67
36	1	1	1	1	-1	1	-1	99.66
37	-1	1	1	1	1	1	-1	27.81
38	-1	1	-1	1	1	1	1	89.72
39	1	-1	1	1	-1	-1	-1	82.86
40	-1	1	1	1	-1	-1	-1	20.37

41	-1	-1	-1	1	1	-1	1	44.06
42	-1	1	1	-1	1	1	1	99.76
43	1	-1	-1	-1	-1	-1	-1	25.07
44	1	-1	1	1	1	1	-1	90.40
45	1	1	1	1	-1	-1	1	99.07
46	-1	1	1	1	-1	1	1	98.88
47	-1	1	1	-1	-1	-1	1	99.43
48	-1	-1	-1	1	-1	1	1	82.30
49	-1	1	-1	-1	1	1	-1	17.50
50	1	1	-1	1	1	-1	1	99.87
51	-1	1	1	-1	-1	1	-1	90.00
52	-1	1	-1	-1	-1	1	1	97.69
53	-1	-1	1	1	-1	-1	1	83.85
54	-1	-1	1	-1	-1	1	1	98.90
55	-1	-1	1	-1	-1	-1	-1	78.29
56	1	-1	1	1	1	-1	1	99.90
57	1	-1	1	1	-1	1	1	99.65
58	1	-1	-1	1	-1	-1	1	99.91
59	1	1	1	1	1	-1	-1	82.43
60	-1	-1	-1	-1	1	1	1	96.73
61	1	1	1	1	1	1	1	99.46
62	1	1	1	-1	-1	-1	-1	97.45
63	1	1	-1	1	1	1	-1	57.56
64	1	-1	1	-1	-1	-1	1	99.88

The determination of main effects and interaction between factors were employed. Percentage removal of Zn(II), which act as the response in this experiment was produced by a change in the level of a factor, heating temperature, heating period, pH, initial concentration of Zn(II), temperature of reaction, contact time, or adsorbent dosage varied from lower to higher level. The 2^{7-1} factorial design was employed as codified model stated below:

$$\eta = A_0 + A_1x_1 + A_2x_2 + A_3x_3 + A_4x_4 + A_5x_5 + A_6x_6 + A_7x_7 + A_8x_1x_2 + A_9x_1x_3 + A_{10}x_1x_4 + A_{11}x_1x_5 + A_{12}x_1x_6 + A_{13}x_1x_7 + A_{14}x_2x_3 + A_{15}x_2x_4 + A_{16}x_2x_5 + A_{17}x_2x_6 + A_{18}x_2x_7 + A_{19}x_3x_4 + A_{20}x_3x_5 + A_{21}x_3x_6 + A_{22}x_3x_7 + A_{23}x_4X_5 + A_{24}x_4x_6 + A_{25}x_4x_7 + A_{26}x_5x_6 + A_{27}x_5x_7 + A_{28}x_6x_7 \quad (2)$$

where A_0 is the global mean and A_i is the regression coefficient related to the main factor effects and interactions. Table 3 displays the effects, regression coefficients, standard errors, *t* statistics and *p*-value, by which it may be concluded that, the removal efficiency increased as the effect of the factor is positive which changed from low to high. Otherwise, the removal efficiency decreased when the effect of the factor is negative. The results revealed that the effects of all main effects is positive except initial concentration as indicated by the effect of its is -10.09, showing that increasing initial concentration from low to high level (30 mg/L to 150 mg/L) cause decreased in the removal efficiency of Zn(II) ions. Interaction between x_1x_7 shows that effect of heating temperature (x_1) depends of the level of adsorbent dosage (x_7). When the heating temperature increases from low to high, changing the adsorbent dosage from low level to high level will decrease the percentage of removal by about 7 units.

Table 3. Estimated regression coefficient using coded level of factors in 2^{7-1} factorial design used for adsorption of Zn(II) ions

Term	Effects	Coefficient	Standard Error	*t*-Value	*p*-Value
Constant		69.75	1.83	38.11	0.000
x_1	21.89	10.95	1.83	5.98	0.000
x_2	3.58	1.79	1.83	0.98	0.335
x_3	33.32	16.66	1.83	9.10	0.000
x_4	-10.09	-5.04	1.83	-2.76	0.009
x_5	0.14	0.07	1.83	0.04	0.969
x_6	8.20	4.10	1.83	2.24	0.032

x_7	44.38	22.19	1.83	12.12	0.000
x_1x_2	0.96	0.48	1.83	0.26	0.794
x_1x_3	-1.46	-0.73	1.83	-0.40	0.692
x_1x_4	11.72	5.86	1.83	3.20	0.003
x_1x_5	-2.87	-1.43	1.83	-0.78	0.439
x_1x_6	-4.45	-2.22	1.83	-1.22	0.233
x_1x_7	-7.03	-3.52	1.83	-1.92	0.063
x_2x_3	-3.57	-1.78	1.83	-0.97	0.337
x_2x_4	0.31	0.15	1.83	0.08	0.934
x_2x_5	-1.87	-0.93	1.83	-0.51	0.613
x_2x_6	2.50	1.25	1.83	0.68	0.499
x_2x_7	-1.63	-0.81	1.83	-0.44	0.660
x_3x_4	-7.75	-3.87	1.83	-2.12	0.042
x_3x_5	-0.26	-0.13	1.83	-0.07	0.945
x_3x_6	-3.11	-1.56	1.83	-0.85	0.401
x_3x_7	-21.91	-10.96	1.83	-5.99	0.000
x_4x_5	1.00	0.50	1.83	0.27	0.785
x_4x_6	2.92	1.46	1.83	0.80	0.430
x_4x_7	4.34	2.17	1.83	1.19	0.244
x_5x_6	-0.22	-0.11	1.83	-0.06	0.952
x_5x_7	2.00	1.00	1.83	0.55	0.588
x_6x_7	2.27	1.13	1.83	0.62	0.540

The equation model for Zn(II) removal efficiency is stated below, by substituting the regression coefficients in Eq. (2):

$$\eta = 69.75 + 10.95x_1 + 1.79x_2 + 16.66x_3 - 5.04x_4 + 0.07x_5 + 4.10x_6 + 22.19x_7 + 0.48x_1x_2 - 0.73x_1x_3 + 5.86x_1x_4 - 1.43x_1x_5 - 2.22x_1x_6 - 3.52x_1x_7 - 1.78x_2x_3 + 0.15x_2x_4 - 0.93x_2x_5 + 1.25x_2x_6 - 0.81x_2x_7 - 3.87x_3x_4 - 0.13x_3x_5 - 1.56x_3x_6 - 10.96x_3x_7 + 0.50x_4x_5 + 1.46x_4x_6 + 2.17x_4x_7 - 0.11x_5x_6 + 1.00x_5x_7 + 1.13x_6x_7 \quad (3)$$

The relative importance of the individual and interaction effects is shown in Pareto chart, Figure 1. The chart shows the difference between the calculated effects from zero and it was determined based on student's t -test. For a 95% confidence level, the corresponding critical t-value at 29 degrees of freedom is equal to 2.03 as indicated by the vertical line in the chart which shows the minimum statistically significant effect magnitude for that particular confidence level. Figure 1 shows Pareto chart of standardized effects on removal efficiency for Zn(II) of full model. The effects of adsorbent dosage, pH, heating temperature, initial concentration, contact time, interaction between pH and adsorbent dosage, heating temperature and initial concentration, and pH and initial concentration are significant as the standardized effects exceed the t-value, while heating time and temperature are insignificant.

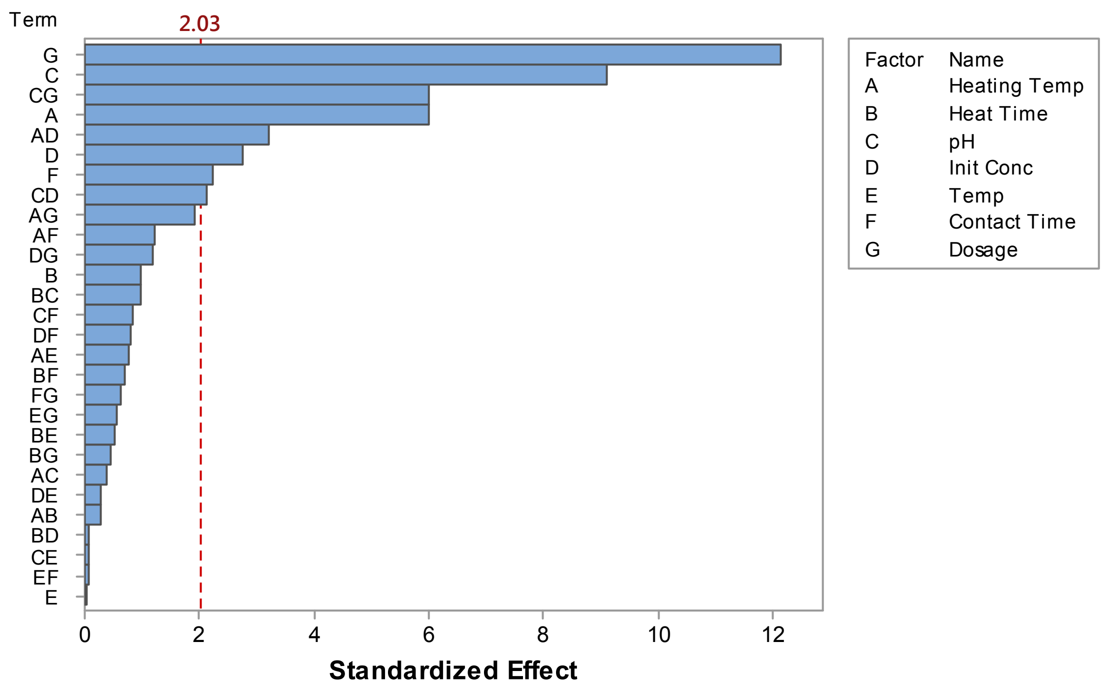

Figure 1. Pareto chart of standardized effects on removal efficiency for Zn(II) – full model

3.1 Analysis of Variance (ANOVA)

The sum of squares used to estimate the each term up to second order polynomial model is shown in Table 4. Fisher's *F*-ratios and *p*-values are also shown in the table. A particular effect in the model is statistically significant when *p*-value is less than 0.05, where *p*-value is the smallest level of significance leading to rejection of null hypothesis.

Table 4. Analysis of variance- full model fitting

Source	Degrees of freedom	Sum of squares(SS)	Mean square(MS)	F-Value	*p*-Value
x_1	1	7454.6	7454.6	35.76	0.000
x_2	1	199.7	199.7	0.96	0.335
x_3	1	17271.5	17271.5	82.85	0.000
x_4	1	1583.7	1583.7	7.60	0.009
x_5	1	0.3	0.3	0.00	0.969
x_6	1	1045.9	1045.9	5.02	0.032
x_7	1	30642.4	30642.4	146.99	0.000
x_1x_2	1	14.4	14.4	0.07	0.794
x_1x_3	1	33.3	33.3	0.16	0.692
x_1x_4	1	2136.5	2136.5	10.25	0.003
x_1x_5	1	128.0	128.0	0.61	0.439
x_1x_6	1	308.0	308.0	1.48	0.233
x_1x_7	1	769.8	769.8	3.69	0.063
x_2x_3	1	198.1	198.1	0.95	0.337
x_2x_4	1	1.4	1.4	0.01	0.934
x_2x_5	1	54.2	54.2	0.26	0.613
x_2x_6	1	97.5	97.5	0.47	0.499
x_2x_7	1	41.2	41.2	0.20	0.660
x_3x_4	1	934.2	934.2	4.48	0.042
x_3x_5	1	1.0	1.0	0.00	0.945
x_3x_6	1	150.7	150.7	0.72	0.401

x_3x_7	1	7469.2	7469.2	35.83	0.000
x_4x_5	1	15.7	15.7	0.08	0.785
x_4x_6	1	132.8	132.8	0.64	0.430
x_4x_7	1	293.2	293.2	1.41	0.244
x_5x_6	1	0.8	0.8	0.00	0.952
x_5x_7	1	62.5	62.5	0.30	0.588
x_6x_7	1	80.1	80.1	0.38	0.540
Error	34	7087.7	208.5		
Total	62	79524.7			

Note. S= 14.4382; R^2= 91.09%; $R^2_{(adj)}$= 83.75%

Table 4 shows that heating time (x_2) and temperature (x_5) are not significant as the *p*-value which are larger than 0.05, with the values of 0.335 and 0.969, respectively. Hence, these insignificant effects are neglected and removed. The effects, regression coefficients, standard error, *t* statistics and *p*-value were recalculated for the significant effects to refit the model and the results are presented in Table 5.

Table 5. Statistical parameters for 2^{7-1} fractional factorial design – reduced model

Term	Effects	Coefficient	Standard Error	*t*-Value	*p*-Value
Constant		69.51	1.68	41.44	
x_1	21.42	10.71	1.68	6.39	0.000
x_3	33.79	16.90	1.68	10.07	0.000
x_4	-9.62	-4.81	1.68	-2.87	0.006
x_6	7.73	3.87	1.68	2.30	0.025
x_7	44.85	22.43	1.68	13.37	0.000
x_1x_4	12.19	6.09	1.68	3.63	0.001
x_3x_4	-8.22	-4.11	1.68	-2.45	0.018
x_3x_7	-22.38	-11.19	1.68	-6.67	0.000

Figure 2 shows the Pareto chart for reduced model and displays the student's *t*-test results. The results also indicated that heating temperature, pH, initial concentration, contact time, and adsorbent dosage are significantly affects the removal efficiency of Zn(II) ions.

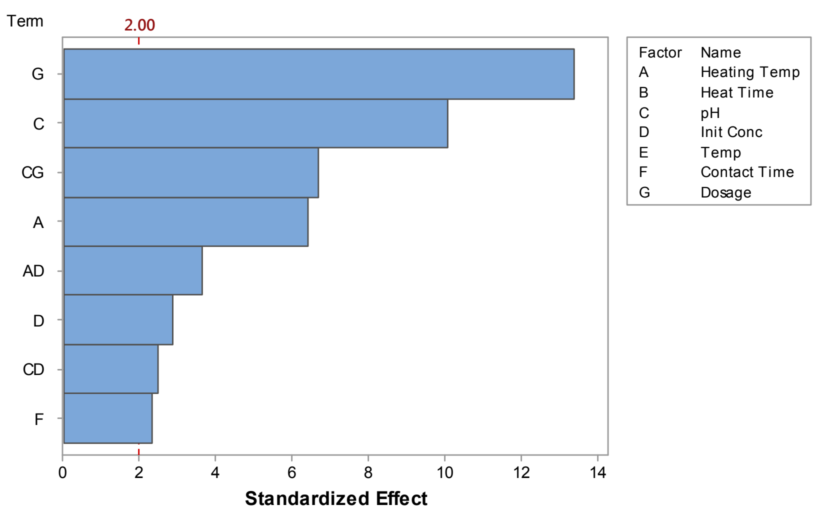

Figure 2. Pareto chart of standardized effects on the removal efficiency for Zn(II) – reduced model

The reduced model equation of Zn(II) removal efficiency is expressed as below:

$$\eta = 69.51 + 10.71x_1 + 16.90x_3 - 4.81x_4 + 3.87x_6 + 22.43x_7 + 6.09x_1x_4 - 4.11x_3x_4 - 11.19x_3x \quad (4)$$

The results of ANOVA for the reduced model are presented in Table 6, only shows the significant factors that affecting the removal efficiency of Zn(II) with *p*-value less than 0.05. The significant factors were heating temperature of rice husk, pH, initial metal concentration, contact time, adsorbent dosage, and two ways interaction between heating temperature of rice husk and initial concentration, pH and initial concentration, and pH and adsorbent dosage.

Table 6. Analysis of variance – reduced model

Source	Degrees of freedom	Sum of squares(SS)	Mean square(MS)	*F*-Value	*p*-Value
x_1	1	7211.1	7211.1	40.77	0.000
x_3	1	17942.9	17942.9	101.45	0.000
x_4	1	1454.4	1454.4	8.22	0.006
x_6	1	939.1	939.1	5.31	0.025
x_7	1	31613.4	31613.4	178.75	0.000
x_1x_4	1	2334.7	2334.7	13.20	0.001
x_3x_4	1	1061.5	1061.5	6.00	0.018
x_3x_7	1	7872.2	7872.2	44.51	0.000
Error	54	9550.3	176.9		
Total	62	79524.7			

Note. S= 13.2987; R^2= 87.99%; $R^2_{(adj)}$= 86.21%

Various previous works have been reported regarding factorial design analysis to determine significant factors that affect the removal of heavy metals ions using different adsorbents. For example, the effects of pH, adsorbent dosage and initial silver ions concentration on adsorption silver ions from water onto montmorillonite was investigated by Geyikçi and Büyükgüngör (2013) using factorial design analysis at two levels. The results were analyzed statistically using the Student's t-test, analysis of variance, F-test and lack of fit to define most important process variables affecting the percentage silver ions adsorption. The most significant effect was found to be initial concentration.

An experimental design technique has been used to study the biosorption of Cr^{3+} and Cr^{6+} ions from water solutions, simulating typical tanning effluents using the factorial design 2^3. The effects of three factors pH, temperature, and metal concentration were evaluated at two levels. The results were analyzed statistically and found that the most significant effect affecting Cr^{3+} sorption was attributed to interaction between metal concentration and pH, while the most significant effect of Cr^{6+} uptake was ascribed to metal concentration (Carmona et al., 2005).

Meski et al. (2011) used a factorial design to study the quantitative removal of zinc from aqueous solutions on synthesized hydroxyapatite. The factors investigated were initial zinc concentration in solution, adsorbent dosage, Ca/P molar ratio and calcination temperature of hydroxyapatite. Based on the analysis of variance and the factorial design of experiments, adsorbent dosage has a positive effect on the removal of zinc, whereas zinc concentration, Ca/P molar ratio and calcination temperature have a negative effect on the removal process.

The main effects plot is shown in Figure 3 which clearly indicated that there was huge difference in Zn(II) percentage removal between low and high levels for all significant factors (heating temperature of rice husk, pH, initial metal concentration, contact time, and adsorbent dosage) as indicated by the steep plots in the figure, which shows that the factors are highly significant.

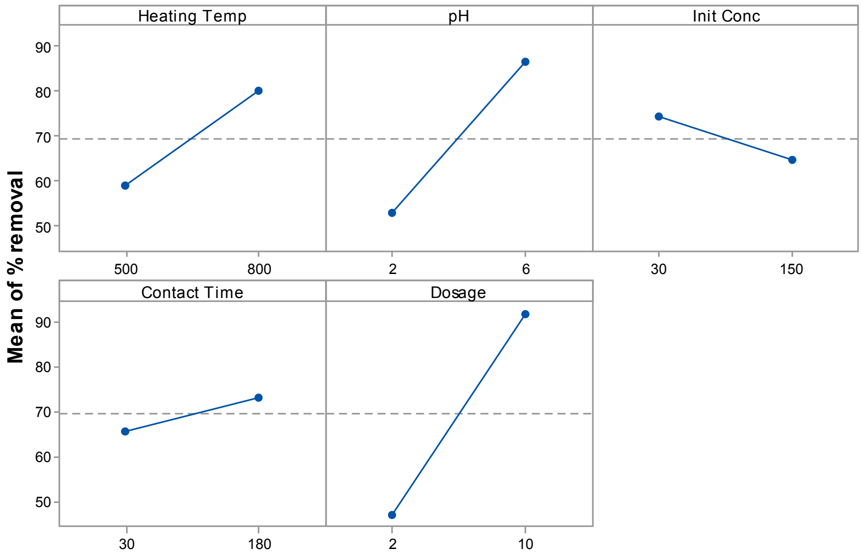

Figure 3. Main effects plot for Zn(II) percentage removal

Figure 4 shows the interaction plot of effects and revealed that there were interactions between some factors affecting the percentage removal of Zn(II). The interactions occur between two different factors consist of heating temperature of rice husk and initial metal concentration, pH and initial metal concentration as well as pH and adsorbent dosage. The results showed that increasing each factor would increase percentage removal of Zn(II).

Figure 5 shows normal probability plot of residuals. The plot shows that the experimental points were reasonably distributed randomly around the straight line which suggests the data is normal distributed. Meanwhile, plot of fitted response variable versus standardized residuals is displayed in Figure 6. The plot is important not only for checking constant variances assumption but also to identify possible outlier. All points are in the range +2 to -2, except for a point run number 35 which slightly out of the range.

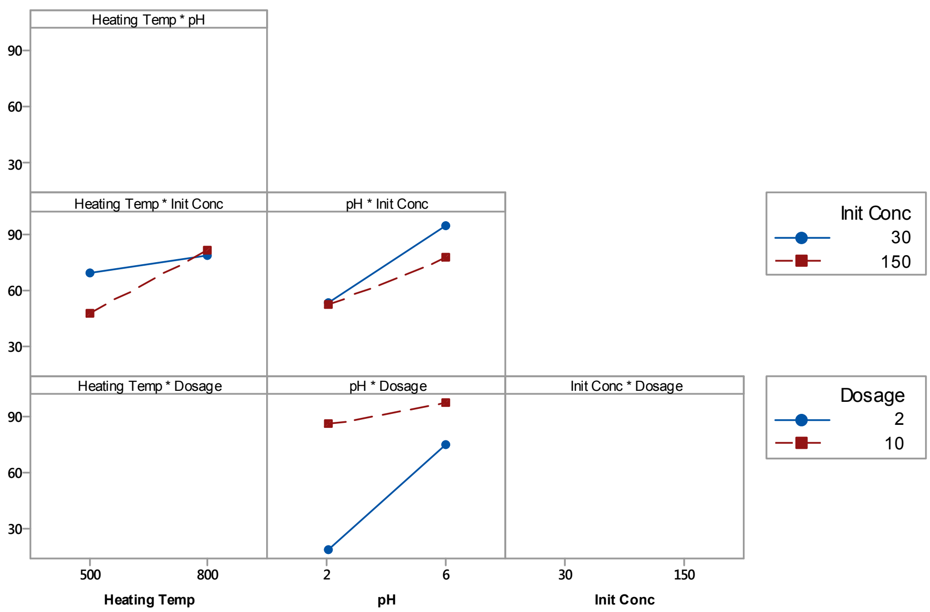

Figure 4. Interaction effects for Zn(II) percentage removal

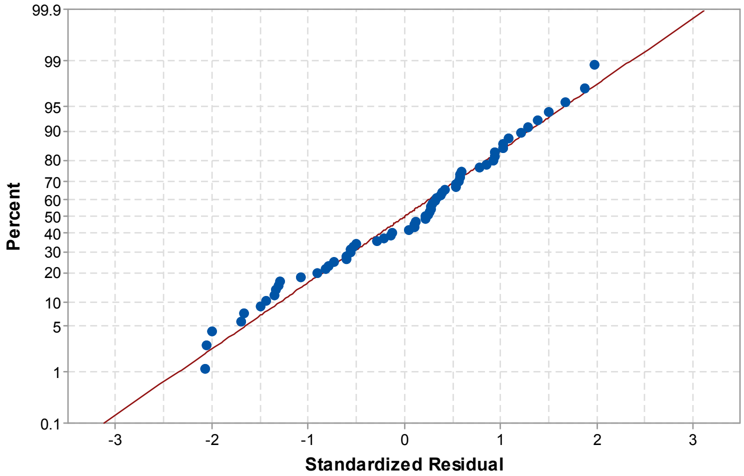

Figure 5. Normal probability plot of residual values for removal efficiency of Zn(II) versus their expected values when the distribution is normal

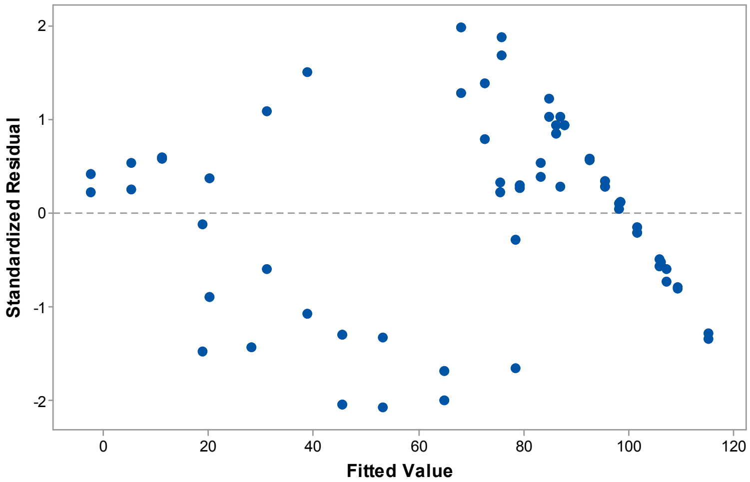

Figure 6. Zn(II) percentage removal (predicted) versus residual

3.2 Effect of PH

Removal of heavy metals from aqueous solution was greatly influenced by the pH of the solution. In Table 3, the p-value for pH is less than 0.05 indicated that pH has a significant effect on removal of Zn(II) ions. The removal efficiency of Zn(II) ions increased by 33.79% when pH increased from 2 to 6, similar trend was reported by Elham et al. (2010) and Wahi et al. (2010). This may due to that at lower pH, more hydronium ions form and compete with Zn(II) ions for the bonding sites, hence, the removal of Zn(II) was lower at lower pH. As the pH increased, the concentration of hydronium ions decreased resulting in more availability of binding sites, therefore increased the removal efficiency of Zn(II) ions.

3.3 Effect of Heating Temperature of Rice Husk

In this study, thermal treated rice husk was prepared at two different heating temperatures i.e. 500 and 800^{O}C. The removal efficiency of Zn(II) increased by 21.42 % with increasing heating temperature. According to Taha et al., (2011), the increase in removal efficiency was influenced by higher porosity in the rice husk which obtained at higher temperature.

3.4 Effect of Contact Time

Removal efficiency of Zn(II) ions was enhanced when the contact time increased from 30 to 180 minutes. At 30 minutes, 65.65% of Zn(II) ions was removed while 73.38% was removed at 180 minutes. During the early stage of adsorption, there are a large number of vacant binding sites available to bind with Zn(II) ions. As the contact time increased, the binding sites are occupied by Zn(II) ions and become more saturated until it reached equilibrium.

3.5 Effects of Adsorbent Dosage and Initial Zn(II) Concentration

Removal efficiency of Zn(II) increased with increasing adsorbent dosage. The removal of Zn(II) was 47.09% when the adsorbent dosage was 2 g, whilst, 91.94% of Zn(II) ions was removed when the adsorbent dosage increased to 10 g, with an increase of 44.85%. The removal efficiency of Zn(II) was greater when higher amount of adsorbent dosage used was due to the presence of large amount of binding sites available for adsorption. On the contrary, the removal efficiency of Zn(II) declined as the initial Zn(II) concentration increased. Increase in initial Zn(II) concentration from 30 to 150 mg/L resulted in decrease of Zn(II) removal efficiency by 9.62%. The decreasing removal efficiency of Zn(II) was due to saturation of all binding sites for adsorption at higher Zn(II) concentration.

3.6 Interaction Effects of Heating Temperature of Rice Husk and Initial Metal Concentration, PH and Initial Metal Concentration, PH and Adsorbent Dosage

Heating temperature of rice husk and initial metal concentration, pH and initial metal concentration as well as pH and adsorbent dosage were found to be the significant interaction effects that affect removal of Zn(II) ions. When the heating temperature of rice husk increased from 500 to 800^{O}C, removal efficiency of Zn(II) increased from 69.71 to 78.94% at 30 mg/L initial concentration and 47.90 to 81.51% at 150 mg/L. Similar trend was observed for the interaction between pH and initial concentration, where removal efficiency of Zn(II) increased from 53.32 to 95.33% from pH 2 to 6 at 30 mg/L initial concentration, while 51.92 to 77.49% was recorded at 150 mg/L, respectively. For the interaction between pH and adsorbent dosage, the increase in pH from 2 to 6 resulted in increase of Zn(II) removal efficiency from 19.00 to 75.18% for 2 g adsorbent dosage, and 86.24 to 97.65% for 10 g adsorbent dosage, respectively.

4. Conclusion

The results from this study indicated that thermal treated rice husk is effective to be used for removing Zn(II) ions from aqueous solutions. Out of seven factors that have been investigated on the percentage removal of Zn(II) ions, t only five factors were found to be significant. They are heating temperature of rice husk, pH, initial metal concentration, contact time, and adsorbent dosage. The removal efficiency of Zn(II) increases with increasing heating temperature, pH, contact time and adsorbent dosage, while increasing initial metal concentration results in decreasing removal efficiency of Zn(II) ions. The interaction between two different effects also significantly affect the percentage removal of Zn(II). They are interactions of heating temperature of rice husk and initial metal concentration, pH and initial metal concentration, and pH and adsorbent dosage.

Acknowledgments

The authors are thankful to Universiti Pertahanan Nasional Malaysia and Malaysian Agricultural Research and Development Institute for providing research facilities.

References

Anwar, J., Shafique, U., Waheed, U. Z., Salman, M., Dar, A., & Anwar, S. (2010). Removal of Pb(II) and Cd(II) from water by adsorption on peels of banana. *Bioresource Technology, 101*, 1752-1755. http://dx.doi.org/10.1016/j.biortech.2009.10.021

Bansal, M., Garg, U., Singh, D., & Garg, V. K. (2009). Removal of Cr(VI) from aqueous solutions using pre-consumer processing agricultural waste: A case study of rice husk. *Journal of Hazardous Materials, 162*, 312-320. http://dx.doi.org/10.1016/j.jhazmat.2008.05.037

Bhattacharya, A. K., Mandal, S. N., & Das, S. K. (2006). Adsorption of Zn(II) from aqueous solution by using different adsorbents. *Chemical Engineering Journal, 123*, 43-51. http://dx.doi.org/10.1016/j.cej.2006.06.012

Carmona, M. E. R., Da Silva, M. A. P., & Leite, S. G. F. (2005). Biosorption of chromium using factorial experimental design. *Process Biochemistry, 40*, 779–788. http://dx.doi.org/10.1016/j.procbio.2004.02.024

Demirbas, A. (2008). Heavy metal adsorption onto agro-based waste materials: A review. *Journal of Hazardous Materials, 157*, 220-229. http://dx.doi.org/10.1016/j.jhazmat.2008.01.024

Elham, A., Hossein, T., & Mahnoosh, H. (2010). Removal of Zn(II) and Pb (II) ions Using Rice Husk in Food Industrial Wastewater. *Journal of Applied Sciences and Environmental Management, 14*(4), 159-162. http://dx.doi.org/10.4314/jasem.v14i4.63306

Feza, G., & Hanife, B. (2013). Factorial experimental design for adsorption silver ions from water onto montmorillonite. *Acta Geodynamica et Geomaterialia, 3*(171), 363–370.

http://dx.doi.org/10.13168/AGG.2013.0035

Garg, U. K., Kaur, M. P., Garg, V. K., & Sud, D. (2008). Removal of Nickel(II) from aqueous solution by adsorption on agricultural waste biomass using a response surface methodological approach. *Bioresource Technology, 99*, 1325-1331. http://dx.doi.org/10.1016/j.biortech.2007.02.011

Hawari, A., Rawajfih, Z., & Nsour, N. (2009). Equilibrium and thermodynamic analysis of zinc ions adsorption by olive oil mill solid residues. *Journal of Hazardous Materials, 168*, 1284-1289. http://dx.doi.org/10.1016/j.jhazmat.2009.03.014

Jamali, H. A., Mahvi, A. H., & Nazmara, S. (2009). Removal of Cadmium from Aqueous Solutions by Hazel Nut Shell. *World Applied Sciences Journal, 5(Special Issue for Environment)*, 16-20. Retrieved from http://www.idosi.org/wasj/wasj5(s)/3.pdf

Kilic, M., Kirbiyik, C., Cepelio˘gullar, Ö., & Pütün, A. E. (2013). Adsorption of heavy metal ions from aqueous solutions by bio-char, a by-product of pyrolysis. *Applied Surface Science, 283*, 856-862. http://dx.doi.org/10.1016/j.apsusc.2013.07.033

Lim, H. K., Teng, T. T., Ibrahim, M. H., Ahmad, A., & Chee, H. T. (2012). Adsorption and Removal of Zinc (II) from Aqueous Solution Using Powdered Fish Bones. *APCBEE Procedia, 1*, 96-102. http://dx.doi.org/10.1016/j.apcbee.2012.03.017

Malamis, S., & Katsou, E. (2013). A review on zinc and nickel adsorption on natural and modified zeolite, bentonite and vermiculite: Examination of process parameters, kinetics and isotherms. *Journal of Hazardous Materials*, 252- 253, 428- 461. http://dx.doi.org/10.1016/j.jhazmat.2013.03.024

Mane, V. S., Mall, I. D., & Srivastava, V. C. (2007). Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash. *Journal of Environmental Management, 84*, 390-400. http://dx.doi.org/10.1016/j.jenvman.2006.06.024

Meski, S., Ziani, S., Khireddine, H., Boudboub, S., & Zaidi, S. (2011). Factorial Design Analysis for sorption of zinc on hydroxyapatite. *Journal of Hazardous Materials, 186*(2-3), 1007-17. http://dx.doi.org/10.1016/j.jhazmat.2010.11.087

Nemr, A. E. (2009). Potential of pomegranate husk carbon for Cr(VI) removal from wastewater: Kinetic and isotherm studies. *Journal of Hazardous Materials, 161*, 132-141. http://dx.doi.org/10.1016/j.jhazmat.2008.03.093

Nguyen, T. A. H., Ngo, H. H., Guo, W. S., Zhang, J., Liang, S., & Yue, Q. Y. (2013). Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. *Bioresource Technology, 148*, 574-585. http://dx.doi.org/10.1016/j.biortech.2013.08.124

Sheela, T., Nayaka, Y. A., Viswanatha, R., Basavanna, S., & Venkatesha, T. G. (2012). Kinetics and thermodynamics studies on the adsorption of Zn(II), Cd(II) and Hg(II) from aqueous solution using zinc oxide nanoparticles. *Powder Technology, 217*, 163-170. http://dx.doi.org/10.1016/j.powtec.2011.10.023

Syuhadah, N. (2012). Rice Husk as Biosorbent: A Review. *Health and the Environment Journal, 3*(1).

Taha, M. F., Kiat, C. F., Shaharun, M. S., & Ramli, A. (2011). Removal of Ni(II), Zn(II) and Pb(II) ions from Single Metal Aqueous Solution using Activated Carbon Prepared from Rice Husk. *World Academy of Science, Engineering and Technology, 5*(12), 1473-1478.

Wahi, R., Kanakaraju, D., & Yusuf, N. A. (2010). Preliminary Study on Zinc Removal from Aqueous Solution by Sago Wastes. *Global Journal of Environmental Research, 4*(2), 127-134. Retrieved from http://www.idosi.org/gjer/gjer4(2)10/10.pdf

Ye, H., Zhu, Q., & Du, D. (2010). Adsorptive removal of Cd(II) from aqueous solution using natural and modified rice husk. *Bioresource Technology, 101*, 5175-5179. http://dx.doi.org/10.1016/j.biortech.2010.02.027