CHAPTER V
PARAMETER SCREENING FOR IMPORTANT FACTORS INFLUENCING THE ARSENATE ADSORPTION USING A PLACKETT-BURMAN DESIGN

A screening experiment with five variables factor using a Plackett–Burman experimental design was conducted on As^{5+} removal. The variables factors include absorbent dose (g/L), pH, temperature (°C), initial concentration (µg/L), and adsorbents type. It has been found that adsorbents type, absorbent dose and initial concentration were statistically significant. Whereas, pH and temperature were insignificant but are important parameters in As^{5+} removal. A Plackett–Burman experimental design can serve as a useful tool for screening large numbers of variables and reducing the number of experiments.

5.1 Introduction

Arsenic, a possible carcinogenic element is present in natural-water systems as a result of both natural and anthropogenic activities. The problems concerning arsenic have been reported recently in many countries. World Health Organization's standard level in drinking water has been lowered to 10 µg/L ("WHO | Water sanitation and health", 2012.). Currently, the removal technologies have been developed to arsenic remove from drinking water such as membrane filtration, ion exchange, precipitation, and adsorption (Kartinen Jr., & Martin, 1995). However, many areas are still necessity suitable technologies like inexpensive, simple and easily applied. Diatomite, a common sedimentary rock-forming mineral, was used which it has low cost and high-potential adsorbents for the removal of heavy metals (Caliskan, Kul, Alkan, Sogut, & Alacabey, 2011). Nevertheless, the adsorption performance of diatomite for arsenic treatment was not satisfactory because it was the low adsorption capacity and the surface area of diatomite needs to be improved before use. The nano-zero-valence

This papere was published in Journal of Advanced Materials Research, 931-932, 178-182, May, 2014

iron (nZVI) has been reported to be very useful for the treatment of arsenic contamination in drinking water or groundwater by adsorption and reduction because of its large active surface area and high adsorption capacity. However, the agglomeration of nZVI during preparation was decreased the reactivity of the particle and also reduced mobility and transport of nZVI to the contaminated area. The researchers found that using nano zero-valent iron on activated carbon had the ability to arsenic absorb (Zhu, Jia, Wu, & Wang, 2009). While, activated carbon has expensive. Thus, diatomite was selected because it is suitable to be supporting material due to its property of catalysis and compositions according to the cheap and easily purchased material. To sum up, the nZVI was coated on the surface of diatomite in order to enhance the performance of arsenic adsorption and to reduce the adsorbent cost.

It has been reported that there were various parameters affecting the efficiency of arsenic adsorption. Chil-Sung Jeona et al. reported that the increase of adsorbent dose enhanced the adsorption efficiency (Jeon, Baek, Park, Oh, & Lee, 2009). The researchers showed that the concentration of As^{5+} increased the performance of adsorption were decreases (Gupta, Saini, & Jain, 2005).The pH value was reported that it effected on the adsorption efficiency (Jeon et al., 2009). The final interesting factor is the adsorption temperature. Caliskan et al. (2011). showed that the higher temperature gave the better Zn^{2+} adsorption than the room temperature using manganese-oxide-modified diatomite absorbent

5.2 Objectives

The objective of this chapter screened the important factors influencing the As^{5+} adsorption using a Plackett-Burman experimental design. The factor was interested as absorbent dose (g/L), pH, temperature (°C), initial As^{5+} concentrations (µg/L), and adsorbents type.

5.3 Materials and methods

5.3.1 Chemicals

A diatomite was achieved from northern part of Thailand. It consists of SiO_2 (79.76%), Al_2O_3 (9.61%) and Fe_2O_3 (2.49%) and specific surface area was 26.8 m^2/g. The fresh diatomite was prepared by washed several times with distilled water to remove the contaminants and then dried at 110°C in a drying oven for 24 h. After drying, it was kept in the polyethylene bags. An arsenic standard solution, H_3AsO_4 (Merch, Germany), was diluted with de-ionized water to the initial concentrations of As^{5+} in the range of 500-1,000 µg/L.

5.3.2 Experimental design and analysis method of arsenate adsorption

Plackett-Burman design, an efficient method to identify the important factors among a large number of variables (Zhou et al., 2011), was used in the present study to screen the important variables that significantly influenced on the As^{5+} adsorption. In this study, a 12-run Plackett-Burman design was applied to evaluate 5 variables factors. This technique provides the indications of how each component tends to affect the As^{5+} adsorption. An experimental design was employed to determine total effects of variables including: adsorbent dose (g/L), pH, the adsorption temperature (°C), initial concentration (µg/L), and adsorbent type. For the factor levels, the range of the variables was set from the lower to the upper limits encoded as -1 (lower) and +1 (higher), respectively. Thus, a total of 12 experimental run as shown in Table.5.1 were performed to complete the designs.

Table 5.1 Experimental range and levels of independent process variables for arsenate adsorption

Independence Variable	**Code**	**Level minimum (-1)**	**Level maximum (+1)**
Adsorbent dose (g/L)	X_1	0.25	0.75
pH	X_2	4	7
Temperature (°C)	X_3	30	50
Initial As^{5+} concentration (µg/L)	X_4	500	1000
Adsorbent type	X_5	D	ND

Symbols: D = diatomite, ND = nZVI-D_2

The actual As^{5+} adsorptions were carried out in a batch reactor, the mixture was stirred with the constant speed of 160 rpm for 10 min. The remaining concentration of arsenate was determined by graphite furnace atomic absorption spectrometry (GFAAS), Perkin Elmer series Analyst 880, United States. The percentages As^{5+} removal, (% As^{5+} removal) were calculated as follows:

$$Y = \frac{C_0 - C_t}{C_0} \times 100 \qquad (2.20)$$

where C_0 is the initial concentration of As^{5+} (mg/L) and C_t is the concentration of As^{5+} (mg/L) after adsorption at time. Y is the percentage As^{5+} removal.

The statistical analysis experimental results (response function, Y) were fitted to first order multiple regression equations (Eq.5.2) using coded level (-1 or +1) of the variables (x_i).

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \varepsilon \qquad (5.1)$$

Y is the response or dependent variable. The coefficients of the polynomial are represented by b_0 (constant term), b_i (linear effect) and ε (random error). X_i is the coded values of variables. These developed regression equations were used to develop the plots for the response functions. Therefore, the regression equation was used to predict the screen parameters.

5.4 Results and discussion of experimental analysis

5.4.1 Parameter screening

The experimental matrix design, the experimental values and predicted values based on experiments proposed by Plackett-Burman statistical design for the As^{5+} were all summarized in Table 5.2. The Pareto chart was used to identifying the important factors on the experimental displayed in Fig.5.1. It was found that the most significant effect was adsorbent type following by adsorbent type and initial concentration. Whereas, the pH and temperature factors were affect for As^{5+} adsorption. However, these factors were commonly applied in As^{5+} removal. Then, it can be concluding that the adsorbent type and followed by the adsorbent dose, the initial concentration, pH and temperature impacted on the removal As^{5+}, respectively.

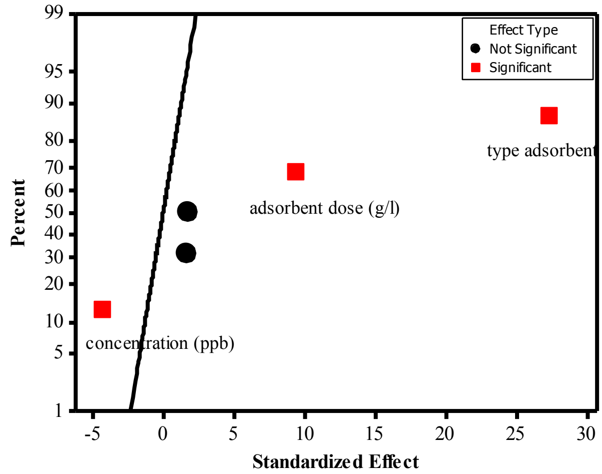

Figure 5.1 Pareto charts for the main factors effect on arsenate removal. The vertical line shows the P=0.05 level for statistical significant

A normality probability plot of effect was created from main effects of factors as shown in Fig.5.2. The results showed that pH and temperature was insignificant which were normally distributed with mean zero and the plot tends to near the straight line. The effect of adsorbent type, adsorbent dose and initial concentration were significant which were placed distant from the straight line.

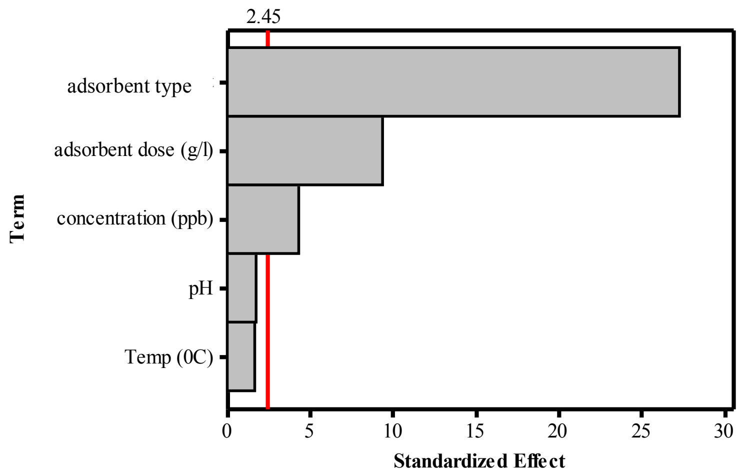

Figure 5.2 Normal probability plot of standardized effects for percentage arsenate removal (%*Y*)

The main effect was explains Fig.5.3 (Plot of main effects for As^{5+} removal). It was clear that increase in adsorbent dose, pH, and temperature leads to increase in As^{5+} removal, whereas the increase of initial concentration were resulted As^{5+} removal decrease. To sum up, the initial concentration displayed the negative-effect coefficients while the other four variables (adsorbent dose, pH, temperature and type adsorbent) showed the positive-effect coefficients

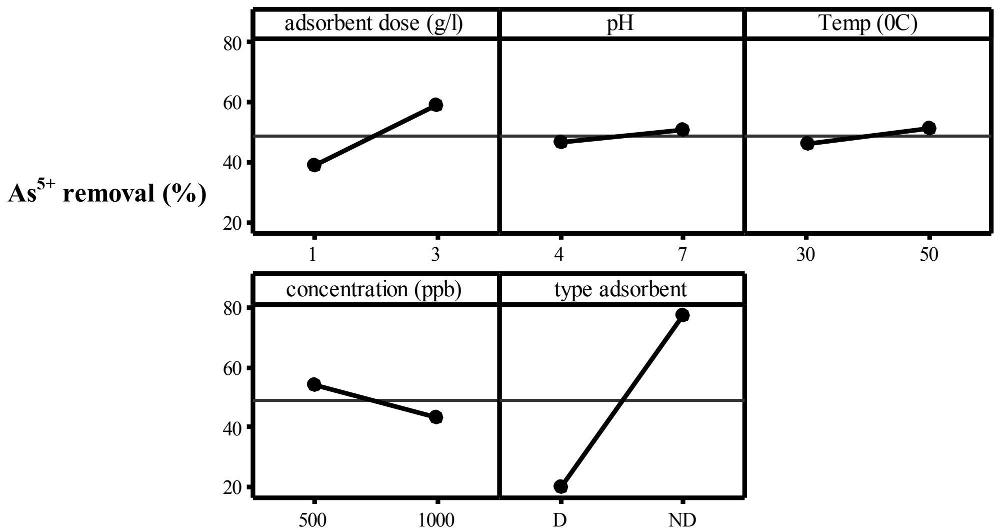

Figure 5.3 Main effect plots for percentage arsenate removal

The results of Fig 5.3 showed that the adsorbent type was the most affect for As^{5+} removal in all factor. The best adsorbent type was nZVI-D_2 because the aggregation of the nZVI decreasing its specific surface area and reaction activity. nZVI acts as certain material for removal of heavy metals from aqueous solution. The nZVI-D_2 has been achieved of As^{5+} removal more than diatomite because nZVI-D_2 was a stable material and dispersed of nZVI in surface of diatomite because of its large active surface area and high adsorption capacity. The second factor, the adsorbent dose was an important parameter to obtain efficiency removal of As^{5+} from wastewater. Fig 5.3 showed the influence of adsorbent dose, it can be seen that the removal of As^{5+} increases sharply with increase in adsorbent dose because the availability of more active site on the adsorbent surface and functional enhance (Pan, Chiou, & Lin, 2010). Next factor, the initial concentration indicated that removal efficiency of As^{5+} decreased when the initial concentration increased from the Fig 5.3.

Due to, the high initial concentration provided less driving force to overcome mass transfer resistances of As^{5+} into film surface of adsorbent. Another reason, the active site of adsorbent was limited while the initial concentration increased by reason of the removal reaction was intercepted and deceased. According to these results, the initial concentration plays an important role in the removal.

The effect of temperature on As^{5+} adsorption was displayed in Fig 5.3. The removal increased from about 45 to 55 % when the temperature increases from 30 to 50 °C, indicating that the adsorption was endothermic in nature (Pan et al., 2010). However, the temperature in this study was only slightly affected as a result temperature insignificantly effect on As^{5+} removal. The last factor was pH which insignificantly affected the As^{5+} treatment because of the range of pH in this chapter at pH range of 4–7 which located in a narrow range. The predominate As^{5+} species in aqueous solution is $H_2AsO_4^-$ in the range of pH 2 to 6 which the adsorbent surface display positive ion at pH solution below pH_{pzc}. An adsorption was occurred by the reaction and electrostatics attraction force between ions of As^{5+} and the surface of nZVI-D_2 and diatomite which leading to the formation of surface complexes. However, the pH of solution has been known as the most important with heavy metal adsorption onto adsorbent.

5.4.2 Regression analysis

The data in Table 5.2 were used to fit the linear model representing the removal percentage (response) as function of adsorbent dose, pH, temperature, initial concentration and adsorbent type. The regression coefficients (Table 5.3) were used to predict the response of each factor assisted by the linear regression equation as follow:

$$Y = 46.98 + 9.817X_1 + 1.803X_2 + 1.731X_3 - 4.513X_4 + 28.674X_5 \quad (5.2)$$

where Y (percentage As^{5+} removal) is the response denoted as the predicted percentage As^{5+} removal. X_1, X_2, X_3, X_4 and X_5 are the corresponding coded variables of amount of adsorbent dose, pH, temperature, initial concentration and adsorbent type, respectively.

Table 5.2 Placklett-Burman designs with experimental value and predicted value of arsenate removal

No.	Experimental design					Observed % *Y*	Predicted % *Y*
	X_1	X_2	X_3	X_4	X_5		
1	0.75	4	30	1000	ND	86.91	83.3767
2	0.25	4	30	500	D	14.70	15.4183
3	0.25	4	50	500	ND	73.63	76.2283
4	0.75	7	50	1000	D	32.44	34.9100
5	0.25	4	50	1000	D	10.52	9.8550
6	0.25	7	30	500	D	16.50	11.8133
7	0.75	7	30	500	ND	87.98	88.7967
8	0.25	7	30	1000	ND	56.25	60.1367
9	0.75	4	50	500	ND	97.78	95.8633
10	0.75	7	30	1000	ND	65.45	63.5983
11	0.75	7	30	1000	D	26.52	25.8850
12	0.75	4	50	1000	D	23.23	26.0283

Symbols: D = diatomite, ND = nZVI-D

Factors P-values (Table 5.3) of less than 0.05 were considered to have significant effects on the response include adsorbent type following adsorbent dose and initial concentration. However, in term of pH and temperature were discussed insignificant main effect as P-values are higher than 0.05.

Table 5.3 Estimated effects and coefficients for arsenate removal at 10 min (coded units)

Term	Code	Effect	Coef	P value
Constant			49.326	0.000
Adsorbent dose (g/L)	X_1	19.635	9.817	0.000
pH	X_2	3.605	1.803	0.137
Temperature (°C)	X_3	3.462	1.731	0.150
Initial concentration (μg/L)	X_4	-9.025	-4.513	0.005
Adsorbent type	X_5	57.348	28.674	0.000

The predicted values versus the observed values plot for As^{5+} removal was shown in Fig. 5.4. The fit of the models were controlled by the coefficient of determination R^2. Based on the ANOVA results, the models gave R^2 value of 99.31%. The value of R^2 is closed to 1.0, which was very high and advocates a high correlation between the observed values and the predicted values. This indicates that the regression model provides an excellent explanation of the relationship between the independent variables and the response.

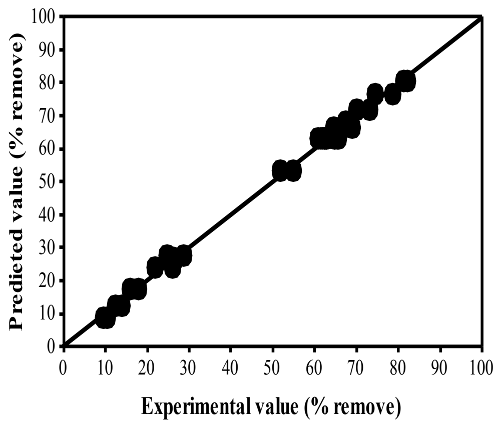

Figure 5.4 Correlation of experimental and predicted removal efficiency for arsenate with nZVI-D_2

The adequacy of fit was checked by graphical analysis of residuals. The differences of the experimental and the predicted values were used for calculation the residuals. The residual plots of this study for the quadratic regression model are shown in Fig. 5.5. The normal probability plot of residuals (Fig.5.5a) was along the straight line demonstrating the normality assumption is satisfied. A fig. 5.5b displayed the standardized residual and fitted value scatters randomly, the histogram chart, shown in Fig. 5.5c, indicated that the frequency of standardized residual was distributed in the normal curve. Fig. 5.5d showed a plot of the standardized residual versus run order, and the results present randomly scatters in the standard residual plots fluctuate around the center line. These results showed that the data was randomly distributed. It displayed that the data had accuracy and reliability. It has been explained that all experiment orders have no abnormality in this study. Therefore, it was concluded that the regression model was useful for screening the important parameter as well.

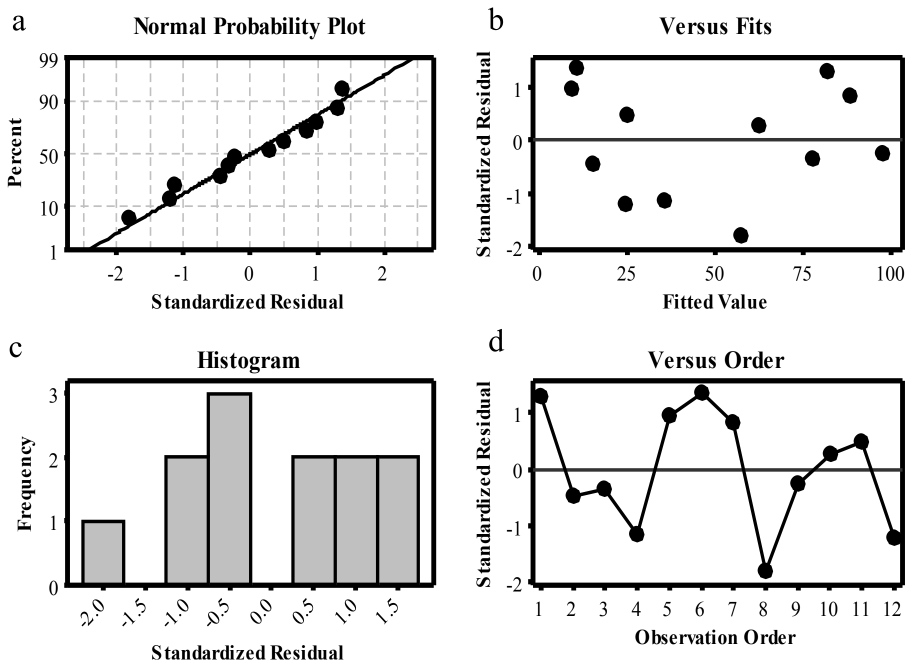

Figure 5.5 Internal standardized residual plots versus (a) normal probability, (b) fits, (c) histogram and (d) observation order for arsenate removal

5.5 Conclusions

The Plackett–Burman design can be applied to screen a large number of extrusion variables including discrete variables. The factors were chosen to be studied as absorbent dose (g/L), pH, temperature (°C), initial As^{5+} concentration (μg/L), and adsorbents type. The results showed that increase in adsorbent dose, pH, and temperature leads to increase in As^{5+} removal, whereas the As^{5+} removal decrease resulted from the initial concentration increase. It has been found that adsorbents type, absorbent dose and initial concentration were statistically significant whereas, pH and temperature were insignificant. A regression model for As^{5+} removal has R^2 (99.31%). The results indicated the suitability of the Plackett–Burman model for evaluating the effect of factor for As^{5+} removal.

5.6 List of abbreviations

Y	percentages arsenate removal
ε	coefficients of the polynomial, random error
b_0	coefficients of the polynomial, constant term
b_i	coefficients of the polynomial, linear effect
C_0	initial concentration (mg/L)
C_t	remaining concentration at any time (mg/L)
D	diatomite
ND	Nano zero-valent coated diatomite
R^2	determination coefficients
X_i	coded values of variables
X_1	adsorbent dose (g/L)
X_2	pH
X_3	temperature (°C)
X_4	initial arsenate concentration (μg/L)
X_5	adsorbent type
Y	response or dependent variable

5.7 References

Caliskan, N., Kul, A.R., Alkan, S., Sogut, E.G., & Alacabey, İ. (2011). Adsorption of Zinc(II) on diatomite and manganese-oxide-modified diatomite: A kinetic and equilibrium study. **Journal of Hazardous Materials, 193,** 27–36.

Gupta, V.K., Saini, V.K., & Jain, N. (2005). Adsorption of As(III) from aqueous solutions by iron oxide-coated sand. **Journal of Colloid and Interface Science, 288**(1), 55–60.

Jeon, C.S., Baek, K., Park, J.K., Oh, Y. K., & Lee, S.D. (2009). Adsorption characteristics of As(V) on iron-coated zeolite. **Journal of Hazardous Materials, 163**(2–3), 804–808.

Kartinen Jr., E.O., & Martin, C.J. (1995). An overview of arsenic removal processes. **Desalination, 103**(1–2), 79–88.

Pan, Y.F., Chiou, C.T., & Lin, T.F. (2010). Adsorption of arsenic(V) by iron-oxide-coated diatomite (IOCD). **Environmental Science and Pollution Research, 17**(8), 1401–1410.

WHO. (2012). **Water sanitation and health.** Retrieved October 15, 2013, from http://www.who.int/water_sanitation_health/en/

Zhou, J., Yu, X., Ding, C., Wang, Z., Zhou, Q., Pao, H. et al. (2011). Optimization of phenol degradation by Candida tropicalis Z-04 using Plackett-Burman design and response surface methodology. **Journal of Environmental Sciences, 23**(1), 22–30.

Zhu, H., Jia, Y., Wu, X., & Wang, H. (2009). Removal of arsenic from water by supported nano zero-valent iron on activated carbon. **Journal of Hazardous Materials, 172**(2–3), 1591–1596.