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Taguchi optimization for Cd(II) removal from aqueous solutions using oyster shell powders

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ABSTRACT

Waste oyster shells cause great environmental concerns and cadmium is a harmful heavy metal. Therefore, in this study, the Taguchi method was applied for removing Cd(II) from aqueous solutions using oyster shell powders (OSP) to optimize the controllable factors, which included pH (P), OSP-calcined temperature (T), Cd(II) concentration (C), OSP dose (D), and contact time (t). The percentage contribution of each factor in descending order was P (57.01%) > T (23.35%) > C (9.10%) > D (5.85%) > t (1.92%). The optimum removal conditions were pH of 10 and an OSP-calcined temperature of 900˚C, which resulted in a removal efficiency of 99.7%. At the higher OSP-calcined temperature of 900˚C, more adsorption occurred due to the large number of porosities created, as evident from the scanning electron microscope (SEM) observations. These porosities generated a large number of cavities, which significantly increased the surface area for adsorption. Further, a multiple linear regression equation was developed to correlate Cd(II) removal with the controllable factors: $\text{Cd(II) removal}(\%) = 9.4 \times P + 0.047 \times T - 1.28 \times C + 19.58 \times D + 0.08 \times t - 52.4$. The equation reasonably predicted the Cd(II) removal, and it could be used for estimating Cd(II) removal by OSP in the design stage.

Keywords: Oyster shell powders; Cadmium; Taguchi method; Adsorption; Precipitation

1. Introduction

Wastewater produced from the processes of welding, smelting, electroplating, and making alkaline batteries usually contains heavy metals, such as Cd(II) [1,2]. Cd(II) is harmful to both the environment and human health. Hence, wastewater containing Cd(II) is prohibited from discharging directly into rivers unless the effluent meets Taiwan's strictly enforced effluent standard regulation of 0.03 mg/L.

Cd(II) is one of the most difficult heavy metals to remove from wastewater by adsorption. Numerous adsorbents have been examined for its removal; some are efficient at high concentrations of Cd(II) and in high pH regions, and some are good at lower concentrations, even in acidic conditions [3]. Recently, removal technology of heavy metal ions by biosorption using agricultural waste is becoming popular because of the need for further environmental protection. For example, Cd(II) adsorption by orange peel powder [4], Cr(VI) adsorption by coir pith [5] and tobacco-leaf residuals [6], and Cu(II) adsorption by coconut shell [7] and gooseberry fruit [8] have been investigated. Moreover, Cd(II), Zn(II), Pb(II), and Cu(II) adsorption by spent coffee grounds has also been evaluated [9–11].

In addition to agricultural waste, mariculture waste also poses environmental concerns due to the rapid expansion of mariculture worldwide resulting from the depletion of natural marine resources. Among the various types of mariculture, oyster farms are popular in Asia; consequently, an enormous amount of oyster shells is produced. In Taiwan alone, the amount of oyster shells produced exceeds 0.16 million tons per year. Currently, oyster shell waste is dumped into coastal waters, land filled, or used as limestone in fertilizers and chicken feed. Hence, the applications of oyster shell waste as an adsorbent for heavy metals to benefit both mariculture and the environment were explored [12–15].

For oyster shells, most of the studies in the literature focused on the biological treatment, such as aerated filter medium treatment of municipal wastewater [16], nutrient and eutrophication control [17–19]. And for oyster shell powders (OSP), the studies on heavy metal adsorption were conducted [12,13,15]. However, none of them focused on the process optimization of OSP for heavy metal removal.

For process optimization, the Taguchi method established by Genichi Taguchi has been generally adopted because it can significantly reduce the overall testing cost and time. This method uses a specially designed orthogonal array consisting of controllable factors and their variation levels to optimize the experimental conditions [20]. It has been used in wastewater treatment, including modified mesoporous carbon for heavy metal adsorption [21], guava seed carbon for acid dye adsorption [22], zeolite fixed bed reactor for color removal [23], and vacuum membrane distillation for phenolic removal [24].

In this study, the Taguchi method was applied to establish the optimum conditions for the removal of Cd(II) from aqueous solutions. The controllable factors included the pH, the calcined temperature of OSP, the initial Cd(II) concentration, the OSP dose, and the contact time. The percentage contribution of each factor was also determined. Further, a multiple linear regression equation correlated with Cd(II) removal was developed for the purpose of prediction.

2. Material and methods

2.1. OSP preparation

Oyster shells were obtained from a local seashore area in Tainan City, Taiwan. The shells were cleaned with brushes after discarding the attached fresh remnant; they were then washed with deionized water (DI water), air-dried, and pulverized in a grinder (Yue Cherh, Taiwan). Then, the pulverized powders were sieved by a 42 mesh sieve to obtain the OSP for subsequent experiments. The OSP was calcined in a programmable furnace (DF-202, Deng Yng, Taiwan) at 300, 600, or 900°C for 2 h. The resulting powders were designated as OSP_{300}, OSP_{600}, and OSP_{900}, respectively. The surface structure of the OSP was analyzed by a scanning electron microscope (SEM) (S-3000 N, Hitachi, Japan).

2.2. Experimental procedure

Batch experiments were performed in a sealed, 250 mL conical flask at 150 rpm in a temperature-controlled mechanical shaking incubator (SB-7D Model, Deng Yng, Taiwan). The pH was controlled by either NaOH or HNO_3. The flask contained 200 mL of a Cd(II) solution. Each experiment was repeated three times, and the average value of the Cd(II) removal (%) was calculated. Prior to measuring the concentration of Cd(II), the water samples were centrifuged (CN-1040, Hsiangtai, Taiwan) and filtered through a 0.45 μm cellulose acetate membrane filter (ADVANTEC®, Japan). The stock solutions of Cd(II) (1,000 mg/L) were obtained from Merck (Germany) and diluted with DI water to the necessary concentration. The concentration of Cd(II) was measured by atomic absorption spectrometry (Hitachi, Z-8200, Japan).

2.3. Design of experiments using the Taguchi method

The Taguchi method applies an orthogonal array for experimental design and the signal to noise (S/N) ratio for quality assessment. In this study, five process-controllable factors were examined: pH, OSP-calcined temperature, Cd(II) concentration, OSP dose, and contact time, which were denoted by P, T, C, D, and t, respectively. By assigning three levels for each controllable factor, an L18 orthogonal array was developed as shown in Table 1. The levels in Table 1 indicate that the values were 5, 8, and 10 for P; 300, 600, and 900°C for T; 5, 10, and 20 mg/L for C; 0.25, 0.5, and 1 g/L for D; and 30, 60, and 120 min for t.

The details of the L18 experiments are shown in Table 2. With the L18 array, only 18 tests, rather than 243 (i.e. 3^5) full experimental runs, were conducted for the five controllable factors with three levels each, representing a great reduction in time and cost. The numerals 1, 2, and 3 in Table 2 denote Levels 1, 2, and 3, respectively.

The removal of Cd(II) is given by Eq. (1) as follows:

Table 1
Controllable factors and associated levels

Factor	Description	Level 1	Level 2	Level 3
P	pH	5	8	10
T	OSP-calcined temperature	300°C, 2 h (OSP_{300})	600°C, 2 h (OSP_{600})	900°C, 2 h (OSP_{900})
C	Cd(II) (mg/L)	5	10	20
D	OSP dose (g/L)	0.25	0.5	1
t	Time (min)	30	60	120

Table 2
Design of the experiments

	Factor				
Test identification	P	T	C	D	t
Test 1	1	1	1	1	1
Test 2	1	2	2	2	2
Test 3	1	3	3	3	3
Test 4	2	1	1	2	2
Test 5	2	2	2	3	3
Test 6	2	3	3	1	1
Test 7	3	1	2	1	3
Test 8	3	2	3	2	1
Test 9	3	3	1	3	2
Test 10	1	1	3	3	2
Test 11	1	2	1	1	3
Test 12	1	3	2	2	1
Test 13	2	1	2	3	1
Test 14	2	2	3	1	2
Test 15	2	3	1	2	3
Test 16	3	1	3	2	3
Test 17	3	2	1	3	1
Test 18	3	3	2	1	2

$$\text{Cd(II) removal}(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of Cd(II) (mg/L), respectively. In the Taguchi method, quality characteristics are categorized into larger-the-better, nominal-the-best, and smaller-the-better types. As the goal of this study was to remove Cd(II) from wastewater by OSP, the larger the better quality characteristic was selected. The related S/N ratio is given by Eq. (2):

$$S/N_{\mathrm{LB}} = -10 \log \frac{\sum_{i=1}^{n} \frac{1}{y_i^2}}{n} \tag{2}$$

where the subscript LB represents "larger-the-better", n is the number of repetitions under the same experimental conditions, and y_i is the result of each repeated measurement. In this study, each test was repeated three times, namely n was 3.

2.4. Optimization evaluation by analysis of means (ANOM)

The statistical approach begins with evaluating the average S/N ratio of factor F at level i, denoted by M_i^F, as shown in Eq. (3) [21,25].

$$M_i^F = \frac{\sum_{j=1}^{n_{Fi}} [(S/N)_i^F]_j}{n_{Fi}} \tag{3}$$

where $(S/N)_i^F$ represents the S/N ratio of the test for factor F at the ith level; the subscript j is the jth appearance of the ith level. In this study, each factor had three levels. For the 18 tests, each level for every factor appeared 6 times as shown in Table 2. Hence, j was, respectively, equal to 1, 2, 3, 4, 5, and $n_{Fi} = 6$. The optimum process condition for the maximum Cd(II) removal was identified based on the particular level for factor F with the maximum average S/N ratio.

2.5. Percentage contribution of each factor by analysis of variance (ANOVA)

ANOVA involves determining the percentage contribution of each controllable factor on Cd(II) removal, $\rho_{F,}$ as given by Eq. (4) [21,23]:

$$\rho_F = \left[\frac{\mathrm{SS}_F - (\mathrm{DoF}_F \times V_{\mathrm{ER}})}{\mathrm{SS}_T}\right] \times 100 \tag{4}$$

In the equation above, DoF_F signifies the degree of freedom for factor F. The sum of squares for factor F, SS_F, is given by Eq. (5):

$$\mathrm{SS}_F = \frac{mn}{L} \sum_{i=1}^{L} (R_i^F - R_T)^2 \tag{5}$$

where the symbols m, n, and L denote the total number of all experiments (i.e. 18), the number of repetitions (i.e. 3), and the number of levels (i.e. 3) of each factor, respectively. The symbol R_T represents the comprehensive average of Cd(II) removal for all of the tests and was computed by Eq. (6):

$$R_T = \frac{\sum_{j=1}^{m}(\sum_{i=1}^{n} R_i)_j}{mn} \tag{6}$$

where R_i is the Cd(II) removal obtained in the ith repetition of each test. Moreover, R_i^F denotes the average value of Ni(II) removal realized during the tests for factor F in the ith level and was evaluated by Eq. (7):

$$R_i^F = \frac{1}{n_{Fi}} \sum_{j=1}^{n_{Fi}} [(R_A)_i^F]_j \tag{7}$$

where $(R_A)_i^F$ represents the average Cd(II) removal of the test of factor F in the ith level and its corresponding jth appearance is represented as $[(R_A)_i^F]_j$. Hence, the total sum of squares SS_T of Eq. (4) was calculated by Eq. (8):

$$SS_T = \sum_{j=1}^{m}\left(\sum_{i=1}^{n} R_i^2\right)_j - mn(R_T)^2 \tag{8}$$

Finally, the variance of error, V_{ER}, of Eq. (4) was calculated by Eq. (9):

$$V_{ER} = (SS_T - \sum_{F=P}^{t} SS_F)/[m(n-1)] \tag{9}$$

3. Results and discussion

3.1. Optimization

The results of the 18 experiments are tabulated in Table 3. The average removal shown in Table 3 was the average of three repeated experiments, which were denoted by $R1$, $R2$, and $R3$. The S/N ratios were calculated by Eq. (2). The results showed that the average removal of Cd(II) varied from 17.5 to 99.7% and that the S/N ratios varied from 24.84 to 39.97, depending on the combination of the controllable factors. Subsequently, the S/N ratios were substituted into Eq. (3) to calculate the mean S/N ratio of factor F in the ith level, M_i^F. The results of M_i^F given in Table 4 showed that the best levels for each controllable factors were Level 3 for P, Level 3 for T, Level 1 for C, Level 3 for D, and Level 3 for t. Additionally, the average removal of each level for controllable factor F, denoted by R_i^F (given by Eq. (7) and tabulated in Table 4) revealed that the best levels for each controllable factor were exactly the same as those for M_i^F. These best

Table 3
Cd(II) removal and S/N ratio

	Factor					Removal (%)					
Tests	P	T	C	D	t	$R1$	$R2$	$R3$	Average removal (%)	Std.	S/N ratio
Test 1	5	300	5	0.25	30	17.1	17.5	17.8	17.5	0.29	24.84
Test 2	5	600	10	0.5	60	21.0	21.7	21.7	21.5	0.33	26.63
Test 3	5	900	20	1.0	120	45.2	44.6	46.4	45.4	0.75	33.14
Test 4	8	300	5	0.5	60	43.2	44.1	43.7	43.7	0.37	32.80
Test 5	8	600	10	1.0	120	52.3	51.5	52.1	52.0	0.34	34.31
Test 6	8	900	20	0.25	30	34.5	34.0	33.8	34.1	0.29	30.65
Test 7	10	300	10	0.25	120	54.1	54.7	55.4	54.7	0.53	34.76
Test 8	10	600	20	0.5	30	46.7	47.5	47.8	47.3	0.46	33.50
Test 9	10	900	5	1.0	60	99.8	99.5	99.7	99.7	0.12	39.97
Test 10	5	300	20	1.0	60	20.1	21.0	18.9	20.0	0.86	26.00
Test 11	5	600	5	0.25	120	17.7	18.3	19.2	18.4	0.62	25.28
Test 12	5	900	10	0.5	30	41.3	42.4	42.6	42.1	0.57	32.48
Test 13	8	300	10	1.0	30	39.2	37.9	39.0	38.7	0.57	31.75
Test 14	8	600	20	0.25	60	30.4	31.0	31.5	31.0	0.45	29.82
Test 15	8	900	5	0.5	120	87.4	86.2	88.3	87.3	0.86	38.82
Test 16	10	300	20	0.5	120	61.8	62.5	62.2	62.2	0.29	35.87
Test 17	10	600	5	1.0	30	91.2	90.5	91.1	90.9	0.31	39.17
Test 18	10	900	10	0.25	60	98.6	99.1	98.9	98.9	0.21	39.90

Note: std.: Standard Deviation.

Table 4
S/N ratio and Cd(II) removal response table

	$[(S/N)_i^F]_j$							$[(R_A)_i^F]_j$						
Factor/Level	$j=1$	$j=2$	$j=3$	$j=4$	$j=5$	$j=6$	M_i^F	$j=1$	$j=2$	$j=3$	$j=4$	$j=5$	$j=6$	R_i^F
$P/1$	24.84	26.63	33.14	26.00	25.28	32.48	28.06	17.5	21.5	45.5	20.0	18.4	42.1	27.50
$P/2$	32.80	34.31	30.65	31.75	29.82	38.82	33.03	43.7	52.0	34.1	38.7	31.0	87.3	47.80
$P/3$	**34.76**	**33.50**	**39.97**	**35.87**	**39.17**	**39.90**	**37.20**	**54.7**	**47.3**	**99.7**	**62.2**	**90.9**	**98.9**	**75.62**
$T/1$	24.84	32.80	34.76	26.00	31.75	35.87	31.00	17.5	43.7	54.7	20.0	38.7	62.2	39.47
$T/2$	26.63	34.31	33.50	25.28	29.82	39.17	31.45	21.5	52.0	47.3	18.4	31.0	90.9	43.52
$T/3$	**33.14**	**30.65**	**39.97**	**32.48**	**38.82**	**39.90**	**35.83**	**45.4**	**34.1**	**99.7**	**42.1**	**87.3**	**98.9**	**67.92**
$C/1$	**24.84**	**32.80**	**39.97**	**25.28**	**38.82**	**39.17**	**33.48**	**17.5**	**43.7**	**99.7**	**18.4**	**87.3**	**90.9**	**59.58**
$C/2$	26.63	34.31	34.76	32.48	31.75	39.90	33.31	21.5	52.0	54.7	42.1	38.7	98.9	51.32
$C/3$	33.14	30.65	33.50	26.00	29.82	35.87	31.50	45.4	34.1	47.3	20.0	31.0	62.2	40.00
$D/1$	24.84	30.65	34.76	25.28	29.82	39.90	30.88	17.5	34.1	54.7	18.4	31.0	98.9	42.43
$D/2$	26.63	32.80	33.50	32.48	38.82	35.87	33.35	21.5	43.7	47.3	42.1	87.3	62.2	50.68
$D/3$	**33.14**	**34.31**	**39.97**	**26.00**	**31.75**	**39.17**	**34.06**	**45.4**	**52.0**	**99.7**	**20.0**	**38.7**	**90.9**	**57.78**
$t/1$	24.84	30.65	33.50	32.48	31.75	39.17	32.07	17.5	34.1	47.3	42.1	38.7	90.9	45.10
$t/2$	26.63	32.80	39.97	26.00	29.82	39.90	32.52	21.5	43.7	99.7	20.0	31.0	98.9	52.47
$t/3$	**33.14**	**34.31**	**34.76**	**25.28**	**38.82**	**35.87**	**33.70**	**45.4**	**52.0**	**54.7**	**18.4**	**87.3**	**62.2**	**53.33**

levels are presented in boldface in Table 4. For each controllable factor, the best levels for maximum Cd(II) removal were pH 10, OSP_{900}, Cd(II) 5 mg/L, OSP dose 1 g/L, and contact time 120 min.

3.2. Effect of controllable factors on Cd(II) removal

From the above averages, the associated S/N ratio for each level of every controllable factor is presented in Fig. 1. It can be observed that the variation of the S/N ratios of pH is the largest, whereas that of the contact time is the smallest. Therefore, the most significant controllable factor was pH, while the least significant factor was contact time.

The significance of each controllable factor could be further quantified by the range of the S/N ratio (maximum S/N minus the minimum S/N) given in Table 5. A larger range indicated that the factor was more significant and should be utilized first. The range in descending order was $P > T > C > D > t$. It should also be noted that the range for P was the most significant among the variables.

To evaluate the percentage contribution of each controllable factor, ANOVA was performed using SPSS 17.0 to obtain SS_F (sum of square of individual controllable factor, Eq. (5)) and ρ_F (percentage contribution of each controllable factor, Eq. (4)). The results, which are also tabulated in Table 5, showed exactly the same order of influence of the controllable factors on Cd(II) removal as that indicated by the range of the S/N ratio. Moreover, as seen in Table 3, the optimum operating conditions for the present study, illustrated by the maximum Cd(II) removal of 99.7%, were $P3$, $T3$, $C1$, $D3$, and $t2$, which correspond to pH 10, Cd(II) concentration of 5 mg/L, OSP dose of 1 g, OSP_{900}, and contact time of 60 min.

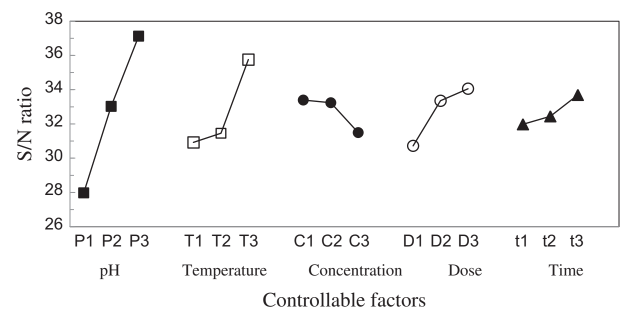

Fig. 1. Response distributions of S/N ratios.

3.3. Mechanism of Cd(II) removal by adsorption and precipitation

The solution pH is an important factor in governing adsorption or precipitation for metal removal. The dominant metal species are $M(OH)_2$ for pH > 6.0 and M^{2+} and $M(OH)^+$ for pH < 6.0 [26,27]. Literature reviews revealed that the optimum pH for Cd(II) adsorption is 5, including for absorption by sawdust [28], granular biomass [29] and modified chitosan [30,31]. The decreased Cd(II) adsorption caused by increasing pH is due to the formation of cadmium hydroxide, as illustrated by the following chemical precipitation [32,33]:

Table 5
Response table of S/N ratios and contribution of each controllable factor

	P	T	C	D	t
Level 1	28.06	31.00	33.48	30.88	32.07
Level 2	33.03	31.45	33.31	33.35	32.52
Level 3	37.20	35.83	31.50	34.06	33.701
Range	9.14	4.82	1.99	3.18	1.63
SS_F	21,030.74	8,525.63	3,477.41	2,126.07	733.03
ρ_F (%)	57.01	23.35	9.10	5.85	1.92
Rank	1	2	3	4	5
p	0.000[a]	0.000[a]	0.000[a]	0.000[a]	0.033
Significance	Yes	Yes	Yes	Yes	No

[a]$p < 0.001$.

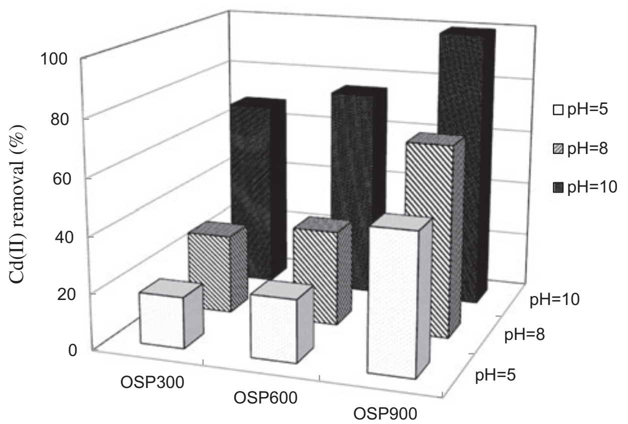

Fig. 2. The effect of pH and calcined OSP temperature on Cd(II) removal.

$$Cd^{2+} + OH^- \overset{K_{sp}}{\longleftrightarrow} Cd(OH)^+ + OH^- \longleftrightarrow Cd(OH)_{2(s)} \quad k_{sp} = 2 \times 10^{-14} \tag{10}$$

For solutions with a pH above 7, Cd(II) began to precipitate out from the solution. The increased Cd(II) removal for pH > 7 may result from a combination of both adsorption and precipitation on the surface of the adsorbent (Naiya et al.).

Based on the Taguchi results and the descriptions presented above, it was clear that pH is important factor in Cd(II) removal. However, it was not clear whether pH affected the adsorption and/or precipitation during Cd(II) removal by OSP. Therefore, further experiments were conducted to clarify this issue using a Cd(II) concentration of 10 mg/L, an OSP of 0.5 g/L, and a contact time of 2 h. The results shown in Fig. 2 obviously indicate that higher Cd(II) removal occurred with higher pH and higher calcined OSP temperature. From the data presented in Fig. 2, the relative proportions of adsorption and precipitation to Cd(II) removal were calculated by assuming that Cd(II) was removed by adsorption only at pH 5. The calculated results are tabulated in Table 6 in terms of mg of Cd(II) removal per g of OSP. It is clear that at pH 8 and pH 10, Cd(II) was removed by both adsorption and precipitation. Conversely, adsorption dominated at pH 8, and precipitation dominated at pH 10 except for OSP_{900}, which will be discussed later in terms of SEM photos. Additionally, two features could be observed: as the

Table 6
Relative proportions of adsorption and precipitation

OSP	Proportion (mg Cd(II)/g OSP)	pH 5	pH 8	pH 10
OSP_{300}	Total removal	0.732	0.892	1.992
	Adsorption	0.732 (100%)	0.732 (81.7%)	0.732 (36.7%)
	Precipitation	0 (0%)	0.160 (18.3%)	1.260 (63.3%)
OSP_{600}	Total removal	1.140	1.368	2.732
	Adsorption	1.140 (100%)	1.140 (83.3%)	1.140 (41.7%)
	Precipitation	0 (0%)	0.228 (16.7%)	1.592 (58.3%)
OSP_{900}	Total removal	2.728	3.016	3.992
	Adsorption	2.728 (100%)	2.728 (90.5%)	2.728 (68.3%)
	Precipitation	0 (0%)	0.288 (9.5%)	1.264 (31.7%)

Note: (): proportion in percentage.

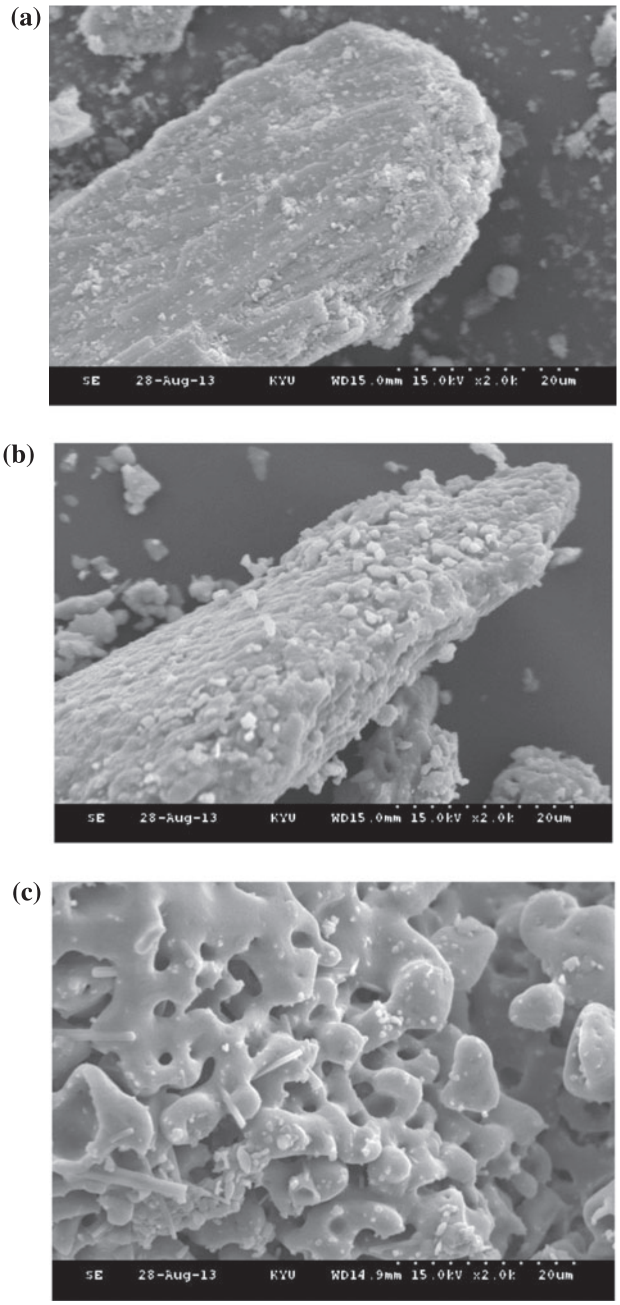

Fig. 3. SEM images of OSP (2,000×). (a) SEM image of OSP_{300}, (b) SEM images of OSP_{600}, and (c) SEM images of OSP_{900}.

pH increased, the precipitation of Cd(II) increased, and as the calcined OSP temperature increased, the adsorption also increased.

3.4. SEM observations

The 2000X surface micrographs of OSP_{300}, OSP_{600}, and OSP_{900} analyzed by SEM are shown in Fig. 3(a), (b), and (c) for 300, 600, and (c) 900˚C, respectively, for sample calcination for 2 h. As illustrated in Fig. 3(a), the surface of OSP_{300} consisted of fragments without any porosity, indicating that metal adsorption was limited to only a thin surface layer. At a calcination temperature of 600˚C, as shown in Fig. 3(b), some surface protrusions and small holes were created, which increased the adsorption surface, as illustrated in Fig. 2. In contrast, at 900˚C, a large number of porosities were created, as shown in Fig. 3(c). These porosities created a large number of cavities, which significantly increased the surface area for adsorption. Thus, metal adsorption increased dramatically, as portrayed in Fig. 2.

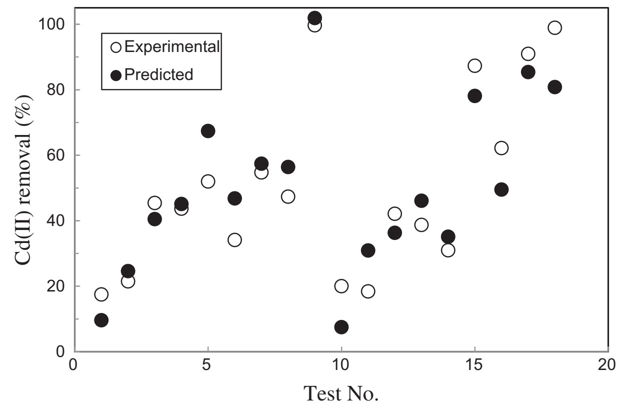

Fig. 4. Comparison of the predicted and experimental Cd(II) removal results.

3.5. Statistical regression modeling

A multiple linear regression equation was developed to correlate Cd(II) removal with the controllable factors under each experimental test using SPSS 17.0 statistical software. The mathematical model for Cd(II) removal through the statistical analysis is given by Eq. (11) ($R = 0.95$):

$$\text{Cd(II) removal}(\%) = 9.4 \times P + 0.047 \times T - 1.28 \times C + 19.58 \times D + 0.08 \times t - 52.4 \tag{11}$$

The predictability of Eq. (11) was compared with the experimental results, as depicted in Fig. 4. It can be seen from this figure that the model reasonably predicted the Cd(II) removal, considering the simplification of the Taguchi experimental design using a small number of experiments. Thus, the developed model could be used for Cd(II) removal estimations during the design stage of Cd(II) removal by OSP.

4. Conclusions

This study evaluated the feasibility of employing OSP for Cd(II) removal using the Taguchi method for process optimization. The average removal of the eighteen experimental results varied from 17.5 to 99.7%, depending on the combination of the controllable factors. The influence of the controllable factors in descending order was $P > T > C > D > t$. It is clear that pH was the most effective removal factor, followed by the calcined temperature of OSP; the least effective removal factor was the contact time. Both adsorption and precipitation mechanisms were observed in the removal process; their relative merits depended on the pH and the calcined temperature of OSP. The removal was best at pH 10 and OSP_{900}. The equation derived from the linear regression predicted the Cd(II) removal by OSP reasonably well and could be used as a tool for process evaluation.

References

[1] A.S. Sartape, A.M. Mandhare, P.P. Salvi, D.K. Pawar, S.S. Kolekar, Kinetic and equilibrium studies of the adsorption of Cd(II) from aqueous solutions by wood apple shell activated carbon, Desalin. Water Treat. 51 (2013) 4638–4650.

[2] L. Semerjian, Equilibrium and kinetics of cadmium adsorption from aqueous solutions using untreated Pinus halepensis sawdust, J. Hazard. Mater. 173 (2010) 236–242.

[3] M. Machida, B. Fotoohi, Y. Amamo, T. Ohba, H. Kanoh, L. Mercier, Cadmium(II) adsorption using functional mesoporous silica and activated carbon, J. Hazard. Mater. 221–222 (2012) 220–227.

[4] V.K. Gupta, A. Nayak, Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe_2O_3 nanoparticle, Chem. Eng. J. 180 (2012) 81–90.

[5] P. Suksabye, P. Thiravetyan, Cr(VI) adsorption from electroplating plating wastewater by chemically modified coir pith, J. Environ. Manage. 102 (2012) 1–8.

[6] Y. Chen, G. Tang, Q.J. Yu, T. Zhang, Y. Chen, Biosorption properties of hexavalent chromium on to biomass of tobacco-leaf residues, Environ. Technol. 30 (2009) 1003–1010.

[7] M.A. Acheampong, J.P. Pereira, R.J. Meulepas, P.N. Lens, Kinetics modelling of Cu(II) biosorption on to coconut shell and *Moringa oleifera* seeds from tropical regions, Environ. Technol. 33 (2012) 409–417.

[8] R.A.K. Rao, S. Ikram, Sorption studies of Cu(II) on gooseberry fruit (*emblica officinalis*) and its removal from electroplating wastewater, Desalination 277 (2011) 390–398.

[9] H. Djati Utomo, K.A. Hunter, Adsorption of divalent copper, zinc, cadmium and lead ions from aqueous solution by waste tea and coffee adsorbents, Environ. Technol. 27 (2006) 25–32.

[10] H. Djati Utomo, K.A. Hunter, Particle concentration effect: Adsorption of divalent metal ions on coffee grounds, Bioresour. Technol. 101 (2010) 1482–1486.

[11] K. Kaikake, K. Hoaki, H. Sunada, R.P. Dhakal, Y. Baba, Removal characteristics of metal ions using degreased coffee beans: Adsorption equilibrium of cadmium(II), Bioresour. Technol. 98 (2007) 2787–2791.

[12] Q. Wu, J. Chen, M. Clark, Y. Yu, Adsorption of copper to different biogenic oyster shell structures, Appl. Surf. Sci. 311 (2014) 264–272.

[13] D. Alidoust, M. Kawahigashi, S. Yoshizawa, H. Sumida, M. Watanabe, Mechanism of cadmium biosorption from aqueous solutions using calcined oyster shells, J. Environ. Manage. 150 (2015) 103–110.

[14] S.A. Odoemelam, N.O. Eddy, Studies on the use of oyster, snail and periwinkle shells as adsorbents for the removalof Pb^{2+} aqueous solution, J. Chem. 6 (2009) 213–222.

[15] T.C. Hsu, Experimental assessment of adsorption of Cu^{2+} and Ni^{2+} from aqueous solution by oyster shell powder, J. Hazard. Mater. 171 (2009) 995–1000.

[16] Y.X. Liu, T.O. Yang, D.X. Yuan, X.Y. Wu, Study of municipal wastewater treatment with oyster shell as biological aerated filter medium, Desalination 254 (2010) 149–153.

[17] W.T. Chen, C.W. Lin, P.K. Shih, W.L. Chang, Adsorption of phosphate into waste oyster shell: Thermodynamic parameters and reaction kinetics, Desalin. Water Treat. 47 (2012) 86–95.

[18] W.H. Park, C. Polprasert, Roles of oyster shells in an integrated constructed wetland system designed for P removal, Ecol. Eng. 34 (2008) 50–56.

[19] H.B. Kwon, C.W. Lee, B.S. Jun, J.d Yun, S.Y. Weon, B. Koopman, Recycling waste oyster shells for eutrophication control, Resour. Conserv. Recycl. 41 (2004) 75–82.

[20] G. Taguchi, Introduction to Quality Engineering, McGraw-Hill, New York, NY, 1990.

[21] G. Zolfaghari, A. Esmaili-Sari, M. Anbia, H. Younesi, S. Amirmahmoodi, A. Ghafari-Nazari, Taguchi optimization approach for Pb(II) and Hg(II) removal from aqueous solutions using modified mesoporous carbon, J. Hazard. Mater. 192 (2011) 1046–1055.

[22] M.P. Elizalde-González, V. Hernández-Montoya, Removal of acid orange 7 by guava seed carbon: A four parameter optimization study, J. Hazard. Mater. 168 (2009) 515–522.

[23] A.B. Engin, Ö. Özdemir, M. Turan, A.Z. Turan, Color removal from textile dyebath effluents in a zeolite fixed bed reactor: Determination of optimum process conditions using Taguchi method, J. Hazard. Mater. 159 (2008) 348–353.

[24] T. Mohammadi, P. Kazemi, Taguchi optimization approach for phenolic wastewater treatment by vacuum membrane distillation, Desalin. Water Treat. 52 (2014) 1341–1349.

[25] S. Kumar, G.H.V.C. Chary, M.G. Dastidar, Optimization studies on coal–oil agglomeration using Taguchi (L16) experimental design, Fuel 141 (2015) 9–16.

[26] G. Wulfsberg, Principles of Descriptive Inorganic Chemistry, University Science Books, Mill Valley, CA, 1991.

[27] C.N. Sawyer, P.L. McCarty, G.F. Parkin, Chemistry for Environmental Engineering and Science, fifth ed., McGraw-Hill, New York, NY, 2003, pp. 37–40.
[28] S.Q. Memon, N. Memon, S.W. Shah, M.Y. Khuhawar, M.I. Bhanger, Sawdust—A green and economical sorbent for the removal of cadmium (II) ions, J. Hazard. Mater. 139 (2007) 116–121.
[29] A.H. Hawari, C.N. Mulligan, Biosorption of lead(II), cadmium(II), copper(II) and nickel(II) by anaerobic granular biomass, Bioresour. Technol. 97 (2006) 692–700.
[30] R. Karthik, S. Meenakshi, Removal of Pb(II) and Cd(II) ions from aqueous solution using polyaniline grafted chitosan, Chem. Eng. J. 263 (2015) 168–177.
[31] G. Yang, L. Tang, X. Lei, G. Zeng, Y. Cai, X. Wei, Y. Zhou, S. Li, Y. Fang, Y. Zhang, Cd(II) removal from aqueous solution by adsorption on α-ketoglutaric acid-modified magnetic chitosan, Appl. Surf. Sci. 292 (2014) 710–716.
[32] T.K. Naiya, A.K. Bhattacharya, S.K. Das, Adsorption of Cd(II) and Pb(II) from aqueous solutions on activated alumina, J. Colloid Interface Sci. 333 (2009) 14–26.
[33] Y. Wang, X. Tang, Y. Chen, L. Zhan, Z. Li, Q. Tang, Adsorption behavior and mechanism of Cd(II) on loess soil from China, J. Hazard. Mater. 172 (2009) 30–37.