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ANALYSIS OF THE EFFECTS OF THE VARIABLES IN THE PROCESS OF CADMIUM SEPARATION BY SEASHELL WASTE

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ABSTRACT – The full experimental design approach was utilized for the investigation of Cd separation by seashell waste. The effect of process factors (seashell type, particle size, and initial metal concentration) was determined and compared for process efficiency and final pH value as system responses. Only main effects were significant ($p<0.05$), while the effects of their interactions were not statistically significant. Obtained Cd sorption capacity of seashell waste was in the range of 0.3 mg/g-150 mg/g, depending on the conditions. The results point to the promising way of utilizing waste seashells as a material suitable for the separation of Cd.

Keywords: Seashell Waste, Water Purification, Cd, Experimental Design.

INTRODUCTION

The significant task facing contemporary society is to find out innovative solutions for the recycling of different waste types to produce new materials or energy. Seashells are an example of abundant waste potentially hazardous to the environment of coastal areas, especially near shellfish farms and pre-processing plants. On the other hand, the shells are a rich secondary source of $CaCO_3$ [1], with wide potential applicability in construction materials, rubber, plastics, paper, etc. Additionally, carbonates are commonly applied as neutralizing agents for acidic industrial wastewaters and acidic soil.

The research conducted so far point to the possibility of seashells' application as sorbent material for the removal of heavy metals and radionuclides [2-4]. The divalent cations removal is based on the ion exchange with calcium, chemisorption, and precipitation. The complexity of systems containing seashells and metal solutions was previously highlighted, as they are highly dependent on experimental conditions, chemical properties of the pollutant, as well as on their interactions [1]. Furthermore, the metal removal efficiency was found to be dependent on the seashell type due to the differences in the physicochemical properties, including the contribution of $CaCO_3$ polymorphs like calcite and aragonite [5].

Bearing in mind the large influence of process conditions on metal separation efficiency, this study aimed to investigate and compare the effect of chosen factors on

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Cd separation. A full factorial design was used to identify significant factors and their interactions.

EXPERIMENTAL

The shells of *Mytilus galloprovincialis* (MG) and *Ostrea edulis* (OE) were sampled in Boka Kotorska Bay (Southeastern Adriatic Sea, Montenegro). About 10 kg of each seashell type were cleaned, washed, and dried in the oven at 60 °C for 48 h. The shells were subsequently milled and sieved into different particle size fractions (0.045–0.125 mm, 0.125–0.2 mm, and 0.2–1 mm).

Cadmium separation was investigated using solutions with initial Cd concentrations of 12.12 mg/L, 120.5 mg/L, and 1,150 mg/L, prepared from $Cd(NO_3)_2$. These simulated wastewater samples were equilibrated on a laboratory shaker with 0.1 g of MG or OE (solid/liquid ratio = 1:200 g/mL) for 24 h. The initial pH value of Cd solutions was 5±0.2.

Seashell type, initial metal concentration, and sorbent granulation were the selected process variables (Table 1). The experiments were conducted, and the data were analyzed according to the full factorial design matrix obtained by the MINITAB software (Table 2).

Table 1 Process variables and their levels

Symbol	Factor	Unit	Level 1	Level 2	Level 3
A	Cd concentration	mg/L	12.12	120.5	1,150
B	Particle size	mm	0.045-0.125	0.125-0.2	0.2-1
C	Seashell type	-	O.E	M.G	

After equilibration, the solid and liquid phases were separated by filtration, and the residual Cd concentrations were determined using Perkin Elmer 3100 Atomic Absorption Spectrometer. The pH values before and after the process were measured by WTW InoLab pH-meter, equipped with SenTix 81 glass electrode.

RESULTS AND DISCUSSION

The experimental results are presented with process conditions for each experimental run in Table 2.

The amounts of Cd removed by seashell waste varied in the wide range between 0.3 mg/g and 150.5 mg/g, demonstrating the significance of experimental factors and their levels (Table 2). The extreme values were observed when the most concentrated Cd solution was used in combination with the MG seashell type with different particle size fractions.

Furthermore, final pH values were in the range of 6.6 to 9.3 (Table 2). The values were commonly higher in respect to the initial pH due to the buffering properties of applied carbonate-based sorbents; however, they strongly depended on the experimental conditions.

In order to investigate the effects of process variables on system responses, the main effect plots were constructed. The main effect plot offers the information if the change of variable decreases or increases the selected system response. The mean for a given level of the variable is the average of all responses obtained for that level. In this plot, the means of responses for process variable levels are plotted and connected with the straight line. The overall mean response of the system for all levels of all factors is given with the horizontal line. Consequently, the strength of the effect of the chosen variable is indicated by the slope of the straight line in relation to the horizontal line.

Table 2 Experimental design matrix, and corresponding values of Cd sorption capacity, process efficiency and final pH values

	A	B	C	Sorption capacity (mg/g)	Final pH	Process efficiency (%)
1	1	2	1	2.4	9.2	99.7
2	2	2	2	22.4	8.4	96.1
3	2	1	1	21.3	7.6	88.9
4	2	2	1	16.7	7.3	69.4
5	1	2	2	2.1	9.1	93.9
6	2	1	2	22.9	8.6	98.3
7	1	1	1	2.4	9.3	99.7
8	3	2	1	23.4	6.6	10.2
9	3	3	1	3.6	6.5	1.6
10	3	2	2	70.4	6.6	33.3
11	1	3	1	2.4	9.1	98.4
12	2	3	2	13.6	7.3	58.5
13	1	1	2	2.2	9.3	98.5
14	3	1	1	19.4	6.6	8.5
15	1	3	2	2.2	9.1	96.5
16	2	3	1	5.4	7.1	22.6
17	3	3	2	0.3	6.5	0.2
18	3	1	2	150.5	6.9	71.3

The main effect plot (Figure 1,a) showed that the increase in solution final pH value was provoked both by the decrease in the initial metal concentration (Factor A), and by the decrease in the particle size fraction (Factor B), however, the effect of factor A was stronger. Furthermore, higher pH values were measured in the filtrates after contact with MG than OE.

The change in the levels of process variables had the same effect on Cd removal efficiency as on the final pH (Figure 1,c), which indicates a strong relationship between the final pH and the percentage of Cd removed from the solution.

The interaction plots for final pH (Figure 1,b) and for process efficiency (Figure 1,d) revealed that the interactions between process variables were negligible.

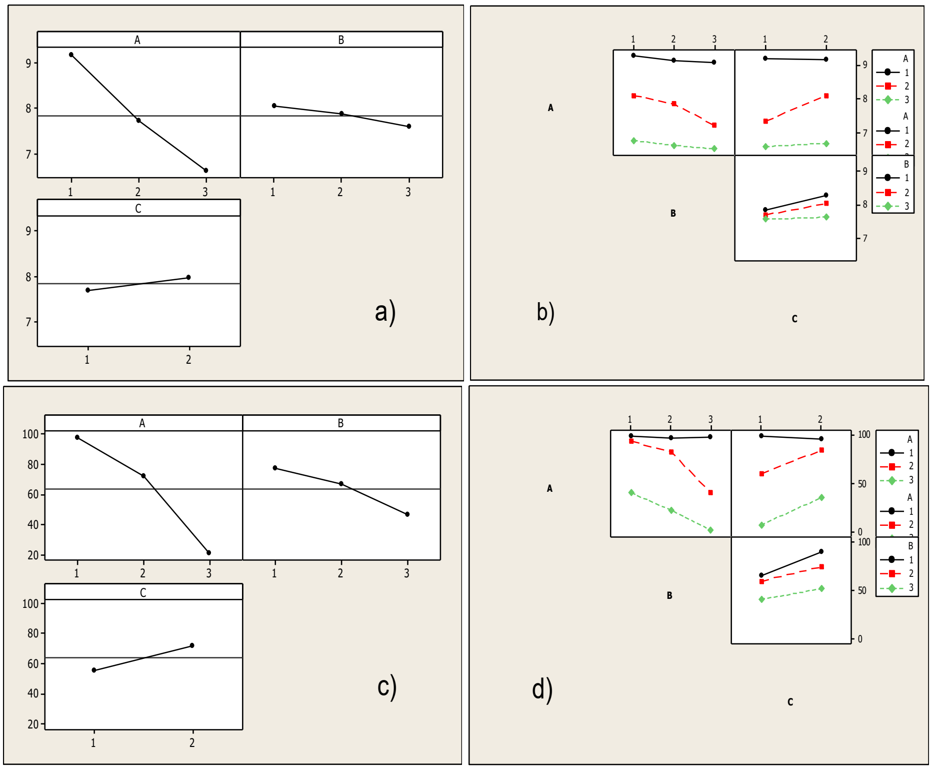

Figure 1 Main effect plots for a) final pH and c) process efficiency;
Interaction plots for b) final pH and d) process efficiency

STATISTICAL ANALYSIS

The behavior of the system can be expressed by multiple linear regression model given as:

$$Y_{predicted} = b_0 + \Sigma b_i x_i \quad (1)$$

where Y is predicted response, b_0 is the value of fitted response at the center point of the design, b_i are regression coefficients, and x_i are variables that can be expressed as main effects (x_i=A, B, C…) or any of their interactions (x_i=A·B, A·B·C, …). This model is linear in the sense that the unknown regression coefficients appear in the linear form [6].

The adequacy of the proposed linear regression was tested using Analysis of variance (ANOVA). ANOVA test (Table 3) approved that only main effects were statistically significant ($p<0.05$). Considering final pH as system response, the statistically significant factors are A, B and C at $p<0.05$. Otherwise, only factor A significantly influences process efficiency. The interaction of initial solution concentration and sorbent type was significant at $p<0.1$, which may indicate that different sorption mechanisms dominant at lower and higher metal concentrations for different seashell types.

Table 3 ANOVA test

Analysis of Variance for pH final						
Source	DF	Seq SS	Adj SS	Adj MS	F	P
A	2	19.8978	19.8978	9.9489	235.63	0.000
B	2	0.6144	0.6144	0.3072	7.28	0.046
C	1	0.3472	0.3472	0.3472	8.22	0.046
A*B	4	0.3556	0.3556	0.0889	2.11	0.244
A*C	2	0.5511	0.5511	0.2756	6.53	0.055
B*C	2	0.1078	0.1078	0.0539	1.28	0.373
Error	4	0.1689	0.1689	0.0422		
Total	17	22.0428				
S = 0.205480 R-Sq = 99.23% R-Sq(adj) = 96.74%						
Analysis of Variance for process efficiency						
Source	DF	Seq SS	Adj SS	Adj MS	F	P
A	2	18,430.5	18,430.5	9,215.2	33.29	0.003
B	2	3,034.0	3,034.0	1,517.0	5.48	0.071
C	1	1,210.3	1,210.3	1,210.3	4.37	0.105
A*B	4	1,636.9	1,636.9	409.2	1.48	0.357
A*C	2	856.9	856.9	428.5	1.55	0.318
B*C	2	129.6	129.6	64.8	0.23	0.801
Error	4	1,107.2	1,107.2	276.8		
Total	17	26,405.5				
S = 16.6373 R-Sq = 95.81% R-Sq(adj) = 82.18%						

CONCLUSION

The applicability of seashell waste for Cd removal was tested. The effect of applied sorbent type (Mytilus galloprovincialis (MG) and *Ostrea edulis* (OE)), the particle size fraction, and initial metal concentration was investigated in terms of sorption capacity, process efficiency, and final pH of the solution. The initial metal concentration is the most significant factor influencing system responses. The increase in initial metal concentration and seashell particle size led to a decrease in both the final pH and the process efficiency. The addition of MG to simulated wastewaters provoked higher values of system responses, indicating that seashell composition affects the process. In the investigated range of experimental conditions, significant interactions of the factors were not found. The results point to the possible use of seashell waste in Cd separation, as high efficiencies of water purification can be achieved by optimizing the levels of the factors. Furthermore, the experimental design approach was found a suitable and useful tool for the investigation of the sorption processes.

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