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Research Article

A Factorial Design Assessment of Marine Exoskeleton-Based Bio-sorption of Relevant Electroplating Metals

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Abstract: A preliminary assessment of the capacity of pulverized crab shells to function as bio-sorbents for the removal of selected metals, zinc, cadmium, and chromium was analyzed according to a factorial experimental design. These metals were chosen because they have little precedent in past sorption studies and represent metals discharged into receiving waters by the electroplating industry. The design was done to assess parameters that have the highest impact on adsorption capacity and removal efficiency. Validation with other heavy metal ion removals was performed for comparison followed by a factorial 33 DOE using JMP®. It was found that for zinc, adsorbent amount, pH, time and the interaction of adsorbent amount*time and pH*adsorbent amount have the highest significance. For cadmium, only adsorbent amount is significant. Finally, chromium uptake was strongly dependent on adsorbent amount and pH. According to ionic radius theory, the favorability for adsorption is according to the following trend: chromium > cadmium > zinc; however, under our set of experimental conditions, the order was: cadmium > zinc > chromium because the presence of calcium carbonate exerts a major role in their sequestration.

Keywords: Zinc; cadmium; chromium; bio-sorption; crab shells; factorial design

1. Introduction

Heavy metal ion removal from wastewater currently represents a vast and critical environmental challenge. Different methods are used for water remediation although adsorption is favored due its ease of operation, low energy consumption, and easy implementation [1]. However, the actual processing/operation for adsorption is often expensive when treating large amounts of water. Sequestration materials include zeolites, ion exchange resins, and activated carbon. Activated carbon, despite good performance, is often an unaffordable material for heavy metal ion removal due to a high energy demands for its production and associated low production yields.

The search for efficient and low-cost options to remediate metals in wastewater has targeted biologically derived materials. The process of removing contaminants from water using either living or dead organisms is known as bio-sorption. It is based on physico-chemical mechanisms which include adsorption, ion exchange, and precipitation. In general, adsorption can be categorized phenomenologically. Chemi-sorption involves use of a monolayer orchestrating sequestration interactions through ionic and covalent bond interactions, although it incurs high energy consumption. A physi-sorption process, however, requires no electron exchange and interactions are mainly motivated by electrostatic forces, hydrogen bonding, Van der waals, or dipole-dipole forces [2].

In the case of bio-sorption, both chemi- and physi-sorption mechanisms are observed simultaneously depending on the components in the bio-sorbent. An example of a bio-sorbent obeying both mechanisms is crustacean shells. Commonly discarded by the seafood industry, crab shells have been proven to efficiently

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remove a number of industrially relevant metal ions including lead [3–5], zinc [6,7], cadmium [6], copper (II) [5,6], chromium [6], cobalt (II) [8], and arsenic (V) [9–11] according to these latter two mechanisms.

The electroplating industry is a very important and very large industry that extensively uses zinc, cadmium, and chromium amongst many others. Its market size is USD 13.5 Billion in 2020 and projected to reach 16.9 billion by 2028 while maintaining a CAGR of 3.26% from 2021 to 2028. Its immediate impact is on corrosion prevention for buildings, cars, and appliances. It is involved in fabricating a protective barrier using many metals. The increasing use of electroplating in aerospace and defense sectors is driving this market currently and requires more detailed analysis of best abatement practices. In this industry, one hundred gallons of chromium electroplating solution are discharged despite being diluted by 200,000,000 gallons of stream water which can kill most aquatic species.

Therefore, our current study was among the first to study the efficacy of waste crab shells as bio-sorbents for the removal of electroplating metals such as chromium which have not received a detailed industrial wastewater study, but nonetheless remain of significance because of their toxicity.

2. Materials and Methods

2.1 Materials

Crab shells were obtained from a local seafood processing company. Sodium hydroxide (s) and hydrochloric acid (concentrated) were used for pH adjustments and lead nitrate was used for heavy metal stock solution preparation. All chemicals were purchased from Sigma-Aldrich (Saint Louis, MO, USA).

2.2 Methods

2.2.1 Shell Cleaning and Particle Size Reduction

Crab and shrimp shells were washed and cleaned using deionized water and then oven dried at 100 °C for 4 h. Particle size reduction was performed using a Wiley mill until 40 mesh particle size was achieved.

2.2.2 Shell performance as absorbent

Once the desired shell particle size was obtained, the milled shells were mixed into a 50 mL solution with initial heavy metal ion concentration as zinc and chromium 100 mg/L and cadmium 40 mg/L. Initial concentrations were determined based on typical concentration of heavy metals in water (add reference) WHO. Process parameters such as amount of adsorbent, solution pH and contact time were determined using a pre-determined experimental design.

2.2.3 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Metal ion concentration was measured using an ICP-MS (Inductively coupled plasma mass spectrometry) Perkin Elmer Elan DRCII before and after absorbent test. Metal uptake (mg/g) and removal percentage was used to assess material performance. This was calculated according to the following equations:

$$q_e = \frac{V \times (C_0 - C_e)}{W} \tag{3}$$

$$\%Removal = \frac{C_0 - C_e}{C_0} \times 100\% \tag{4}$$

Where qe is the metal uptake by the material (mg/g), V is the volume of the solution (mL), W is the weight of the adsorbent (g), C_0 is the concentration of metal ions before adsorption (mg/mL) and Ce is the concentration of metal ions after adsorption (mg/mL).

Preliminary Design: Preliminary experiments were done to determine the parameters that have the highest impact on adsorption capacity and removal efficiency by the crab shell. Also, validation against other metal ions was performed.

Experimental Design: After the preliminary design and validation were performed, a factorial 33 design of experiments was developed using JMP® (Cary, NC, USA). 33 experiments were done based on a comprehensive statistical design offered by JMP. JMP is a very powerful statistical software designed for scientists and engineers. It is equipped with a host of tools for data assimilation, review, and graphing whose overall power and ability can be found at https://www.jmp.com/en_ph/software/why-jmp.html. Figure 1 shows the parameters and evaluated levels for each heavy metal ion.

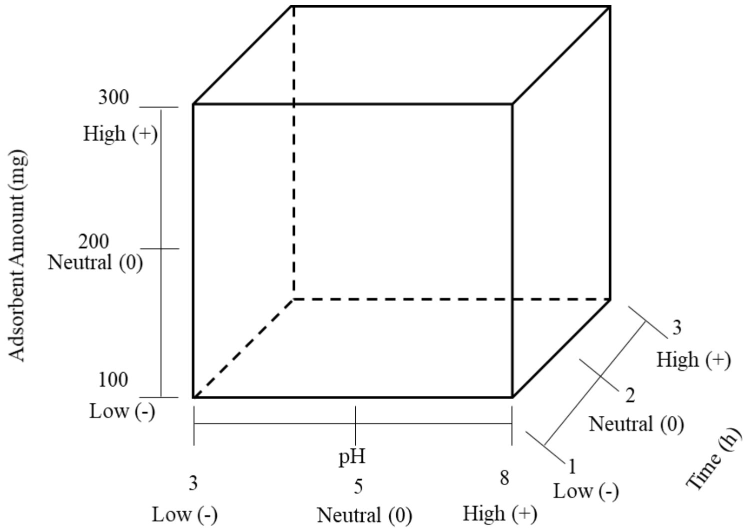

Figure 1. Factors and levels used in the factorial design. Absorbent amount: Low 100 mg, Neutral: 200 mg, Hight: 300 mg; pH: Low 3, Neutral 5, high 8; Time: Low 1 h, neutral 2 h, high 3 h.

3. Results and Discussion

3.1 Preliminary Results

Crab shell, chitin, and a commercially available ion exchange resin were placed in contact with different metals. The results for chromium, zinc, and cadmium are shown in Figure 2. It was found that crab shell was extremely competitive compared to commercially available products. For zinc, crab shell achieved a 97.99% of removal efficiency with an adsorption capacity ~ 23 mg/g; similar results were obtained for chromium. However, in the case of cadmium, chitin displayed a better performance compared to crab shell and ion exchange resin.

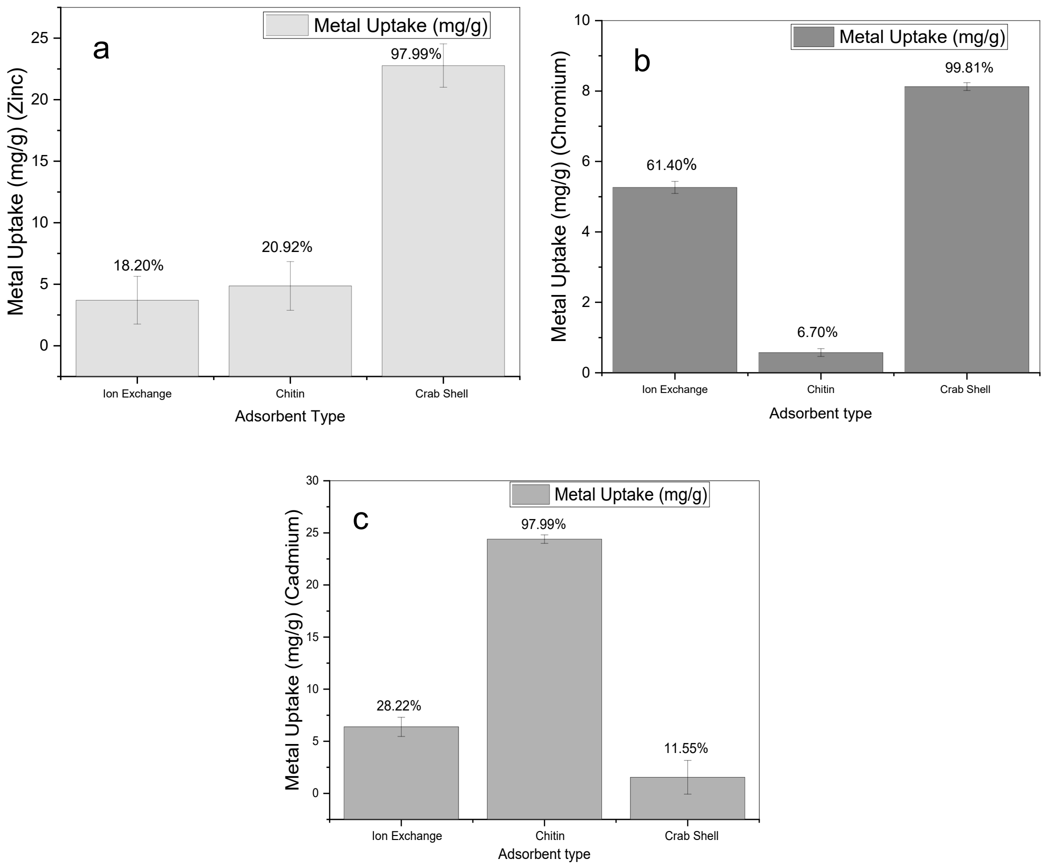

Figure 2. Performance evaluation of ion exchange resin, chitin, and pulverized crab shell for (**a**) zinc (**b**) chromium and (**c**) cadmium. For these test 50 mL of solution was used along with 0.2 g of adsorbent. The initial heavy metal ion concentration in solution is as follows: zinc and chromium 100 mg/L and cadmium 40 mg/L. All data has been calculated within +/- 5% deviation of error.

3.2 Experimental Design

Once preliminary experiments validated the performance of crab shell, an experimental design was executed. The purpose was to determine optimum conditions for each metal absorbed by the crab shell. The results are shown in Table 1 and demonstrate a higher efficiency for cadmium removal than originally determined. It was found that the highest removal was 99.73% under pH 8, 100 mg of adsorbent, and 3 h of residence time. Similarly for zinc, a 99.96% removal under pH 8, 300 mg of adsorbent and 3 h of residence time was uncovered. As for chromium, the highest removal achieved was 83.68% under pH 3, 300 mg of crab shell, and 3 h of residence time.

Table 1. Design matrix and the results for removal efficiency of the 33 full factorial design for each heavy metal analysed.

Run	pH		Adsorbent Amount (mg)		Time (h)		Average Removal Efficiency (%) Zn^{+2}	Average Removal Efficiency (%) Cd^{+2}	Average Removal Efficiency (%) Cr^{+3}
1	8	+	300	+	1	-	99.88%	99.30%	83.62%
2	3	-	100	-	3	+	72.93%	97.06%	52.54%
3	5	0	200	0	2	0	93.21%	99.57%	75.46%
4	3	-	300	+	1	-	92.08%	98.52%	83.38%
5	5	0	200	0	1	-	70.71%	98.74%	75.78%
6	3	-	100	-	1	-	47.28%	66.44%	51.50%
7	8	+	100	-	1	-	70.52%	99.74%	52.11%
8	8	+	300	+	3	+	99.96%	99.22%	83.59%
9	8	+	200	0	2	0	98.59%	99.79%	75.94%
10	3	-	300	+	3	+	83.76%	99.21%	83.68%
11	8	+	100	-	3	+	99.65%	99.73%	52.51%
12	5	0	200	0	2	0	92.64%	99.41%	75.93%
13	5	0	100	-	2	0	68.29%	98.36%	54.20%

The results were analyzed by JMP© and the main effects and interactions for each heavy metal ion were determined relative to the final concentration and metal uptake. A multi-variable analysis was done for each heavy metal ion. The significant factors in the regression model can be determined by performing analysis of variation (ANOVA) [12]. As shown in Table 2 for zinc, adsorbent mount, pH, time and the interaction of adsorbent amount*time and pH*adsorbent amount have a higher significance with P values below 0.05. On the other hand, for cadmium only adsorbent amount shows to be significant. As for chromium, there are two parameters that showed significance: adsorbent amount and pH. From the P-value, it appears that the main effect of each factor and interaction effects are statistically significant at P values < 0.05.

Table 2. Effect of different parameters in final response for the heavy metal ions studied. W = weight of the adsorbent.

Zinc		Cadmium		Chromium	
LogW	**P Value**	**LogW**	**P Value**	**LogW**	**P Value**
3.4730	0.0003	3.0040	0.0010	3.5080	0.0003
2.2010	0.0063	0.9830	0.1040	0.7400	0.1819
2.1840	0.0066	0.7490	0.1781	1.3580	0.0439
2.1070	0.0078	0.7400	0.1821	1.4290	0.0373
1.8400	0.0145	0.8960	0.1270	0.4640	0.3436
1.1160	0.0765	1.2620	0.0547	1.3020	0.0499
0.6110	0.2450	0.0460	0.8988	0.1470	0.7131
0.3560	0.4410	0.7330	0.1848	0.7150	0.1928
0.2880	0.5155	0.6580	0.2197	0.4810	0.3302

Following the main effects, model fitting was used to determine how the data deviated from the prediction established by the multivariate study. The purpose was to determine which variable is better described by the model. Metal uptake is measured as the difference between initial and final concentration per unit of adsorbent. The final concentration is the reading obtained by the ICP-MS reading. In conclusion, the model was better fitting at calculating the metal uptake than making an actual estimate of the final concentration of the heavy metal in the solution. As shown in Figure 3, higher deviations were observed for cadmium and chromium compared to zinc in which their adsorption behavior was predicted by the statistical model.

According to ionic radius theory [6], the favorability for the crab shell adsorption is given according to the following order: chromium > cadmium > zinc; however, under the experimental conditions for this study, the order was cadmium > zinc > chromium. This order is due to the ability to exchange ions with calcium carbonate in addition to the ability to form ion complexes in the presence of the calcium carbonate at different pH. Thus, calcium carbonate plays a key role in the capture of these heavy metal ions in which a chemisorption process prevails over physisorption. Finally, under these pH conditions, cadmium is more likely to form such complexes, consequently precipitate, and be removed. Such a study bodes well for consideration as a remediation technology by the electroplating industry.

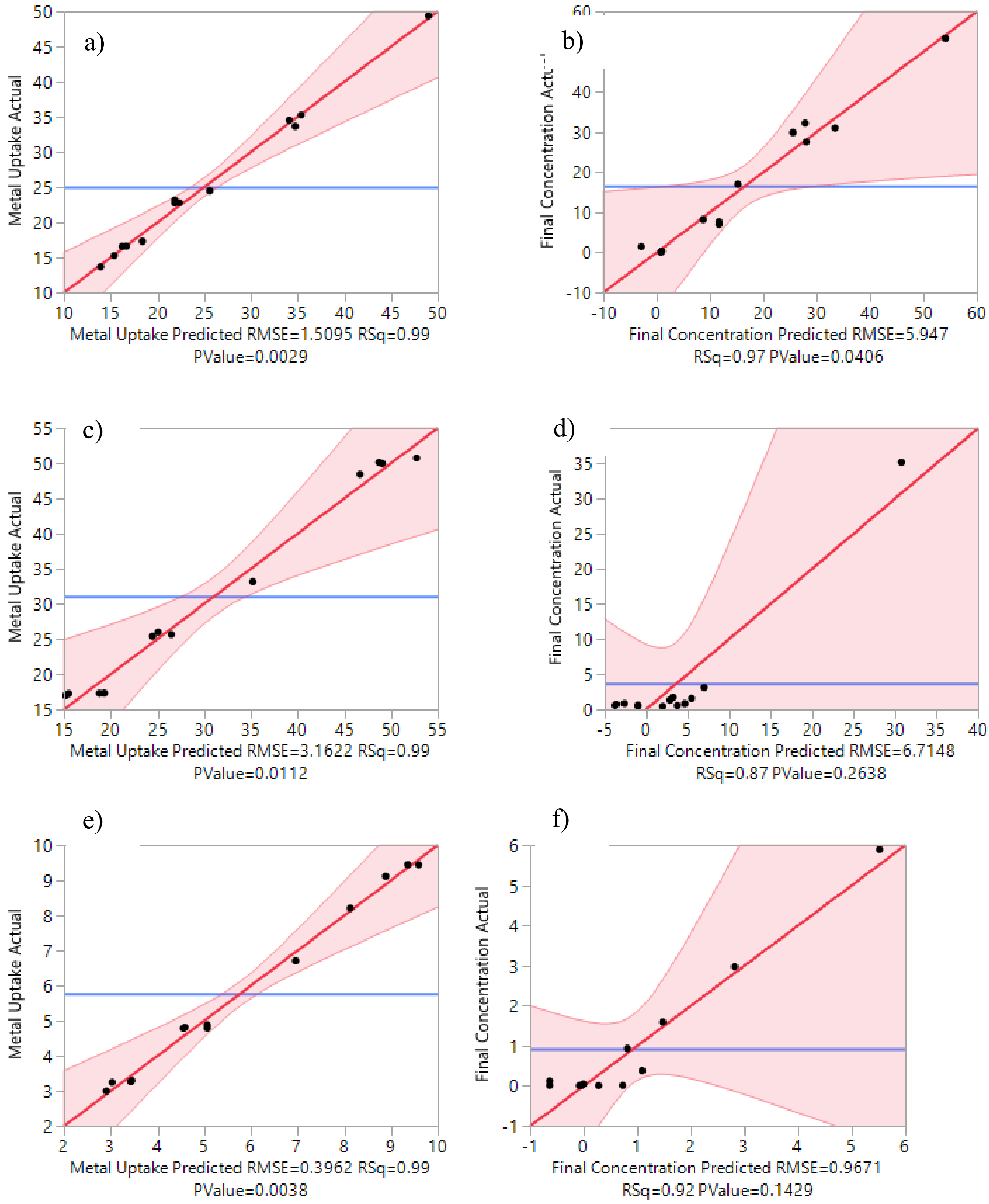

Figure 3. Prediction plots for metal uptake and final concentration (**a**) Metal uptake for zinc, (**b**) Final concentration for zinc, (**c**) Metal uptake for cadmium, (**d**) Final concentration for cadmium, (**e**) Metal uptake for chromium, (**f**) Final concentration for chromium.

5. Conclusions

According to the experimental design, the best adsorption was found for cadmium in most cases followed by zinc, and chromium being the least. It is important to highlight that although the parameters for adsorption were determined to be as close as possible to the optimum, pH conditions were not at exact values to obtain maximum removal for some of the metals due to long equilibration times. In sum, waste crab shell was found to be a very attractive biomaterial for heavy metal ion removal and may have a place in the electroplating industry.

Author Contributions

The contribution of the Authors is as follows: CLZ—data collection and drafting the article; HJ—conception or design; RWG—conception or design; GY—data analysis and interpretation and critical revision of the article; LL—critical revision of the article and final approval of the version to be published.

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Conflict of interest

There are no conflicts of interest to declare for our study.

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