Organo-mineral composites from the shells of *Crassostrea iredalei* (slipper cupped oyster), *Perna viridis* (green shell), and *Telescopium telescopium* (horned snail) in the removal of chromium (VI) from water

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Abstract

This paper presents and compares organo-mineral composites from *Crassostrea iredalei* (slipper cupped oyster), *Perna viridis* (green shell), and *Telescopium telescopium* (horned snail) in the removal of hexavalent chromium from water. Shells were oven-dried, ground, and sieved to fine powder size. Replicates of 10 ppm dichromate solution were individually treated with 1 mg of shell powder for 20 minutes. Following conversion of absorbance to concentration and % Cr^{6+} removed, *T. telescopium* was found to be most efficient in Cr^{6+} remediation with 9.632% removal, followed by *P. viridis* at 8.444%, and *C. iredalei* at 3.431%. Chromium removal is attributed to electronegativity differences between the metal and structural organic components of the shell composites, as well as the capacity of $CaCO_3$ to facilitate surface adsorption. Differences in the concentrations of Cr^{6+} removed result from variances in biomineralization among mollusk species, which dictate the characterization and concentration of $CaCO_3$ in their shell layers.

Keywords: *bioremediation, heavy metal removal, chromium (VI), mollusk shells, calcium carbonate*

Introduction. Heavy metals are increasingly emergent pollutants in bodies of water as a by-product of anthropogenic industrialization, and they continue to rise in concentration in recent years [1, 2]. These metals enter the aquatic ecosystem through waste disposed by industrial, commercial, and urban residential areas near bodies of water [3], as well as through direct contact or abrasion with road-deposited sediments usually displaced by storm run-off [2]. In trace amounts, these metals are essential to natural biogeochemical cycles [4]. Beyond safe concentrations, however, they disrupt the normal functions of the ecosystem, and are potentially hazardous to its organic components [5, 6].

Lead, cadmium, and chromium are among the most prevalent heavy metals in bodies of water, already exceeding safe limits in aquatic food products as demarcated by the United States Environmental Protection Agency (US-EPA), World Health Organization (WHO), Food and Agriculture Organization of the United Nations (FAO), and the Food and Drugs Administration (FDA) [4, 6]. Of these, chromium—a key material in the production of stainless steel, metal plating, and the manufacturing of industrial dyes and paints—has become alarmingly prevalent in water systems. Effluents containing chromium contribute to the existing heavy metal pollution in water, primarily hailing from chemical plants, tobacco smoke, and contaminated landfills [1, 7, 8].

Generally, heavy metals have cytotoxic, mutagenic, and carcinogenic effects to the health of organisms upon prolonged exposure [6]. In its hexavalent oxidation state, Cr (VI), chromium posits similar harmful effects: it is toxic to vital tissues of biotic organisms near contaminated water, a strong irritant, and a potential human carcinogen [1]. Moreover, the bioaccumulation of Cr^{6+} in humans can cause fatal complications in metabolism and regular bodily functions, resulting in acute organ failure and even death [8]. As a result, hexavalent chromium compounds are categorized by the Department of Environmental and Natural Resources (DENR) under its Priority Chemical List (PCL), for strict regulation and monitoring in the environment. Despite this, Cr^{6+} in the ecosystem continues to exceed the 0.1 ppm Philippine safe standard, reaching concentrations of up to 16 ppm [9].

Numerous technologies and treatments, which make use of various physical and chemical interactions in the environment, are currently employed to address heavy metal pollution in water. Among these strategies, the most favorable method of remediation is adsorption, a process involving the deposit of atoms and ions onto the surface of a highly porous, solid material [8]. Biological by-products are considered more novel, potential sources of good adsorbents, a facet of the method's cost-effectiveness, low energy demand, feasibility, accessibility, and sustainability [11].

Organic waste from agricultural activity were tested and proven efficacious as low-cost heavy metal adsorbents [11]. While land-based waste products are prevalently sourced and studied in adsorptive remediation research, the potential of

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waste products derived from aquatic resources are, in comparison, yet to be maximized. Nonetheless, the effective heavy metal removal of calcium carbonate ($CaCO_3$)—a mineral potently occurring in limestone, lime mud, eggshells, and mollusk shells—is well-established [12, 13, 14, 15].

Of these calcium reservoirs, mollusk shells—considered by-products of global shellfish consumption and big contributors to solid waste management problems in the country [17]—emerge as a more renewable and novel, albeit less explored $CaCO_3$-rich bioadsorbent [14, 16]. Generally, these shells are composites of several superimposed calcified layers structured by organic functional groups [15, 18]. A large percentage of the shell's chemical makeup is composed of either one of two naturally-occurring polymorphs of $CaCO_3$ [19]; however, the identity of the polymorph produced, as well as its percent composition, varies across mollusk species as a result of interspecies variations in shell formation [18, 20, 21, 22]. Thus, the capacities of shells derived from different mollusk species are expected to differ with respect to the identity and amount of heavy metal contaminant that the composites can remove [18].

However, there is a current lack of batch studies that consider differences in the remediation efficiencies of different speciated mollusk shells. To address this gap, this study investigated the short-term Cr^{6+} removal efficiencies of three of the most commonly consumed and produced mollusks in the Philippines [23]: *Crassostrea iredalei* (slipper cupped oyster), *Perna viridis* (green shell), and *Telescopium telescopium* (horned snail).

Specifically, the study aimed to:

(i) measure the initial and final absorbance of the Cr^{6+} solution before and after treatment of *C. iredalei*, *P. viridis*, and *T. telescopium* using UV-Visible spectrophotometry;

(ii) obtain the concentration of Cr^{6+} removed by *C. iredalei*, *P. viridis* and *T. telescopium* using a Cr^{6+} calibration curve; and

(iii) compare the concentration of Cr^{6+} removed by *C. iredalei*, *P. viridis* and *T. telescopium* using One-way ANOVA.

Methods. Prior to treatment, *C. iredalei*, *P. viridis*, and *T. telescopium* shell composites were oven-dried and processed to fine powder size. These treatments were then incorporated in 1 mg doses to three replicates of a 10 ppm Cr^{6+} solution per shell species. Treatments were incorporated to the solution for a contact time of 20 minutes. The absorbances of the solutions before and after treatment were measured using UV-Visible Spectrophotometry, from which Cr^{6+} concentration values were derived. One-way analysis of variance (ANOVA) was conducted to test for significant differences among and between treatments.

Preparation of shell samples. Samples were purchased from a local wet market, segregated by species, and boiled at 100°C for 10 minutes to remove unnecessary organic matter. Shell meat and flesh were removed prior to fragmentation, and the shells were shattered before rinsing with distilled water. Samples were subsequently oven dried at 105°C for a total of 24 hours, crushed to fine powder, and sieved to a particle size range of ≤ 63µm.

Treatment. Prior to testing, a 10 ppm Cr^{6+} solution was freshly prepared from the dilution of potassium dichromate ($K_2Cr_2O_7$) in distilled water. The initial absorbance of the stock solution was measured using a Shimadzu UV-Visible (UV-Vis) Spectrophotometer. The initial pH value was also recorded using a pH meter, and the solution was adjusted to a value below 3 through the addition of 1 M hydrochloric acid (HCl). Acidic conditions were maintained to prevent the reduction of Cr^{6+} ions to Cr^{3+} in solution, which occurs upon basification or with the incorporation of the organo-$CaCO_3$ treatment [24]. Setups corresponding to each of the three shell species were prepared, with three 100-mL replicates of the 10 ppm Cr^{6+} solution prepared per setup. A milligram of the corresponding treatment was incorporated to each replicate, and all set-ups were agitated for 20 minutes at 100 rpm, using a laboratory shaker. Shell powders were filtered out of the replicates using Whatman No. 40 filter papers. The absorbance of each replicate was measured, and final pH values per setup were recorded.

Data analysis. The concentration of Cr^{6+} removed, expressed in ppm, was obtained from the difference between the initial and final concentrations of the solution, while the adsorption efficiency (Q) of the three treatments was calculated from the formula:

$$Q = 100 \times \frac{(C_0 - C_1)}{C_0},$$

where C_0 and C_1 represent the initial and final concentrations of the Cr^{6+} solution, respectively. Tests for significant differences among the Cr^{6+} concentrations removed by each treatment using one-way Analysis of Variance (ANOVA) was conducted after data gathering, and post-Hoc Least Significant Difference (LSD) test was used in the further determination of significant differences between treatments. All statistical tests were run using the R statistical tool.

Safety Procedure. At all times, personal protective equipment (PPE) were used in the handling of laboratory reagents, apparatus, and equipment. Organic matter in samples were treated immediately to prevent unwanted interference in treatment and analysis. All used chemicals were collected in empty plastic bottles for collection and disposal.

Results and Discussion. *T. telescopium* removed 0.784 ppm chromium (VI) from a starting concentration of 10 ppm (9.632%), the highest amount among the three treatments, as seen in Table 1.

Table 1. A summary of adsorption efficiencies (Q), concentration (in ppm) of Cr^{6+} removed (C_o-C_l), initial, and final pH values for all treatments.

Treatment	C_o-C_l (ppm)	Q (%)	pH	
			initial	final
C. iredalei	0.279	3.431	2.12	2.14
P. viridis	0.687	8.444	2.12	2.16
T. telescopium	0.784	9.632	2.12	2.17

A significant difference was found among groups at the 95% confidence interval. Furthermore, following a post-Hoc test for least significant difference (LSD), significant differences were found to exist between *C. iredalei* and *T. telescopium,* and *C. iredalei* and *P. viridis.* However, no significant difference exists between *T. telescopium* and *P. viridis,* implying that the two treatments are not significantly different in effectivity and efficiency.

Increments in the final pH were observed for all treatments, given a starting value of 2.12 (Table 1), signifying that CO_3^{2-} ions in the shell powders were released and incorporated into the solution during the 20-minute contact period [10]. While these values have not exceeded the threshold of pH 3 to report significant basification, it was ensured that acidic conditions were maintained to prevent Cr^{6+} reduction [24].

These findings support the idea that differences in shell formation per species contribute to variances, if any, in the efficiency of organo-mineral composites in terms of chromium removal [18]. Localizations in the biomineralization process for each mollusk species result to variations in the dominant $CaCO_3$ polymorph formed and the quality of the compound expressed [25]. Moreover, differences in the percent composition of $CaCO_3$ and organic matter among mollusk shells have an apparent effect in the concentration of heavy metal removed by the material, as the former may not be the sole compound involved in surface adsorption [15].

Although *Crassostrea sp.* and *P. viridis* are reported to contain more $CaCO_3$ than *T. telescopium* [19, 21, 22], the latter surpassed the two in chromium removal and adsorption efficiency. This can be attributed to the larger percentage of structural biomolecules, which have larger electronegativity differences with Cr^{6+} than $CaCO_3$ and are responsible for the adsorption of carbonate salts formed by displacement reactions involving the species [15, 20, 26].

While no other batch study comparing the heavy metal removal efficiencies of *C. iredalei, P. viridis,* and *T. telescopium* exists, previous studies have established their individual capacities for other heavy metals. *Telescopium spp.* shells have a maximum adsorption capacity of 4.6 ppt for copper [20], *Perna spp.* shells can adsorb up to 89.23 ppm of zinc [27], and *Crassostrea spp.* shells are 96.2% efficient in removing cadmium from water [28].

Limitations. The results of this study support the claim rooted in literature that variances in chromium adsorption efficiency are largely accounted to differences in the organic and mineral composition of unique mollusk species. However, the researchers were not able to determine the specific functional groups active in the adsorption mechanism, as well as the amount and the identity of the $CaCO_3$ polymorph present in the samples used, as they required additional characterizations via scanning electron microscope with electron dispersive spectroscopy (SEM-EDS) and infrared (IR) spectroscopy. Apart from this, treatment periods were limited to 20 minutes per replicate; thus, the data presented by this study are only short-term removal efficiencies of these shell composites. Information on whether the *T. telescopium* treatment remains the most efficient among the three species at extended contact times cannot be provided or justified by this study. Lastly, while a concentration of 1 mg per replicate was used for all three treatments, this value serves exclusively as a baseline for comparison; optimizing the concentration of adsorbent used is beyond the scope of this study.

Conclusion. The shells of *Crassostrea iredalei, Perna viridis,* and *Telescopium telescopium* are all capable of removing Cr^{6+} from water, with the latter of the three reporting the highest amount of the metal removed and, subsequently, the highest removal efficiency. These findings are caused by both the chemical properties of the organo-mineral components of the shells and differences in the formation of each shell contribute to their variances in removed Cr^{6+}.

Recommendations. The study serves as a baseline for future comparative analyses of different mollusk shells in the removal of certain heavy metals from water. It is highly recommended that similar batch studies be undertaken to address the dearth of knowledge in this sector of water remediation. Future studies are advised to simulate real-time conditions of heavy metal pollution as a practical application of this line of research. Additionally, the researchers recommend that the amount of adsorbent added per unit volume of replicates be considered in determining the optimal removal efficiencies of the treatments used. Lastly, for a more accurate reflection of the shells' removal capacities, the effects of contact time to the concentrations of metal removed should be considered in the future, and that batch adsorption kinetics and equilibrium studies employ the adsorbents used in this study in the investigation of their long-term effects.

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