

**UNIVERSITY OF BELGRADE
TECHNICAL FACULTY IN BOR
CHAMBER OF COMMERCE AND
INDUSTRY OF SERBIA**

PROCEEDINGS



**XIII International
MINERAL PROCESSING and
RECYCLING CONFERENCE**

Editors:

Grozdanka Bogdanović

Milan Trumić

Belgrade, Serbia, 8 – 10 May 2019



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ZINC AND STRONTIUM REMOVAL EFFICIENCY BY THERMALLY MODIFIED SEASHELL WASTE

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ABSTRACT - The efficiency of thermally modified marine seashells in the separation of Zn and Sr cations was investigated, as a way to valorize and utilize carbonate-rich seafood industry waste. Crushed seashells were heated at different temperatures (300 - 900 °C) and exposed to 0.01 mol/L metal solutions. The percentage of Zn removal increased up to 99.7 % with the increase in temperature, whereas Sr removal gained a maximum of 42.2 % after contact with the specimen heated at 500 °C. Removal efficiency was analyzed in line with the temperature induced transformations of seashells mineral matrix, solution pH values, and Ca concentrations. As revealed by X-ray diffraction analysis, optimal removal of Sr and Zn achieved using pure calcite and pure calcium oxide samples, respectively, was principally a result of the precipitation mechanism.

Key words: seashell waste, temperature treatments, water treatment, Zn, Sr.

INTRODUCTION

Natural limestone is a mineral with immense utilization as an essential component or a raw material for the production of construction materials, ceramics, glass, paper, plastic, rubber, paints, pharmaceuticals, etc. [1]. Furthermore, as an alkaline material with sorption/precipitation properties, it is frequently utilized in water treatment and soil remediation. Given that contemporary society is facing the depletion of non-renewable mineral resources and simultaneously generates vast amounts of solid waste, development of technologies that exploit carbonate-rich waste materials as a secondary resource is a concept that brings multiple benefits.

A typical example of a bio-waste that could be valorized owing to a high content of calcium carbonate is the seashell material of marine mollusks. Empty seashells are identified as a major solid waste arising from a rapidly growing fishery industry, and the research on their applicability aims at reducing ecological problems in coastal areas caused by excessive accumulation [2]. To this point, seashells were successfully utilized in soil treatment, animal feed production, neutralization of acid mine drainage and the production of construction materials [3-5]. Recent studies have also revealed the ability of seashell material to separate a variety of heavy metals and

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radionuclide ions from the aqueous phase [6-8]. The thermal treatments contribute to the combustion of the organic phase present in the seashell material (<5 % w/w), which mitigates the issues associated with seashell storage and use. Furthermore, enhanced removal of Hg and Cu cations [9, 10], as well as of phosphate anions [11], was detected after proper thermal treatment of seashells.

In the present study, the influence of temperature treatments onto seashell waste ability to separate Zn and Sr ions from aqueous media was investigated, to consider the prospects of using seafood industry waste instead of traditional agents – natural limestone and lime. The Zn was chosen as a representative heavy metal commonly found in industrial wastewaters, whereas radioactive ⁹⁰Sr is a human-made contaminant found in liquid radioactive waste and natural waters after nuclear accidents.

MATERIALS AND METHODS

The seashell waste (SW) used in the study was a composite sample collected at the North Greek Aegean Sea coast in 2016, comprised of several bivalvia species [8]. The soluble impurities and sand particles were removed by rinsing the shells with hot water. Cleaned shells were dried at 50 °C, ground in the laboratory mill and the fraction with a particle size < 1 mm was used in further experiments. Thermally treated samples were produced by heating the SW in the electrical furnace for 4 h at the constant temperature in the range 300-900 °C. The obtained powders were correspondingly denoted as SW300 - SW900.

Temperature-induced alteration of SW capacity to separate metal ions was studied in the batch conditions, at room temperature (21 ± 2 °C). Working solutions of 0.01 mol/L Zn and Sr cation were prepared from their nitrate salts (Zn(NO₃)₂×6H₂O and Sr(NO₃)₂, Fisher Scientific) and deionized water. The initial pH of both Sr and Zn solutions were adjusted to 5.0 ± 0.1 using 0.01 mol/L solutions of either NaOH or HNO₃. SW or SW300 - SW900 samples (0.1 g) were mixed with 20 mL of metal solutions in 50 mL centrifuge tubes, and suspensions were agitated for 24 h at 10 rpm using the Reax 20 Heidolph overhead laboratory shaker. After 24 h of contact, liquid phases were separated from the solid using Heraeus Megafuge 16, set at 9000 rpm for 10 minutes.

Residual concentrations of Zn and Sr, as well as the amounts of Ca ions released from the seashell material, were determined by Perkin Elmer 3100 Atomic Absorption Spectrophotometer, while the final pH values were measured by InoLab WTW pH meter. Metal removal experiments were performed in duplicate. Selected solid residues which showed the highest percentage of removed Zn or Sr ions (SW900-Zn and SW500-Sr) were additionally analyzed by X-ray diffraction (XRD) within 10-60 2θ range on the Rigaku Smartlab SAXS diffractometer.

RESULTS AND DISCUSSION

Treatments of SW have affected the cation removal efficiency to a great extent, and the removal patterns were quite different for the two investigated cations (Fig. 1). Separation of Zn ions was generally higher compared to the Sr removal efficiency, in agreement with the behavior of raw SW. Namely, the study of SW selectivity towards various divalent cations has disclosed the highest removal capacity of Zn

ions in comparison to Sr, Cu and Pb [8]. Furthermore, Zn removal continuously increased with the increase in temperature, from 79.9 % using SW300 to even 99.7 % using SW900. On the other hand, Sr removal exhibited an increase from 22.2 % to 42.2 % using samples SW300 - SW500. A slight decrease in process efficiency was observed using specimen heated at 600 °C, whereas the increase in temperature above 600 °C resulted in the abrupt decline in Sr removal.

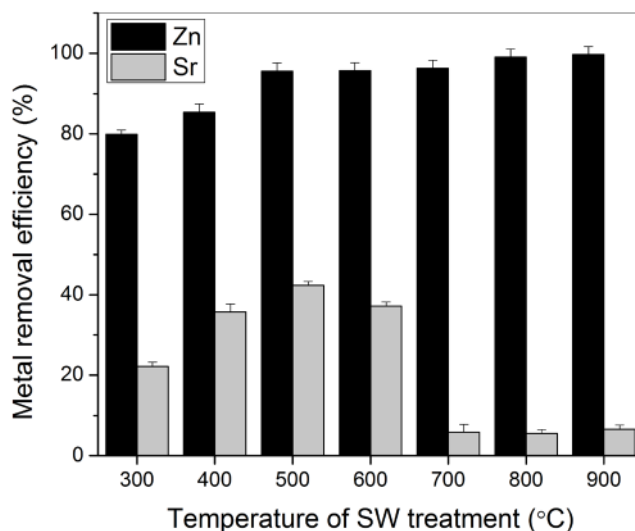


Figure 1. Effect of SW temperature treatments onto Zn and Sr removal efficiency

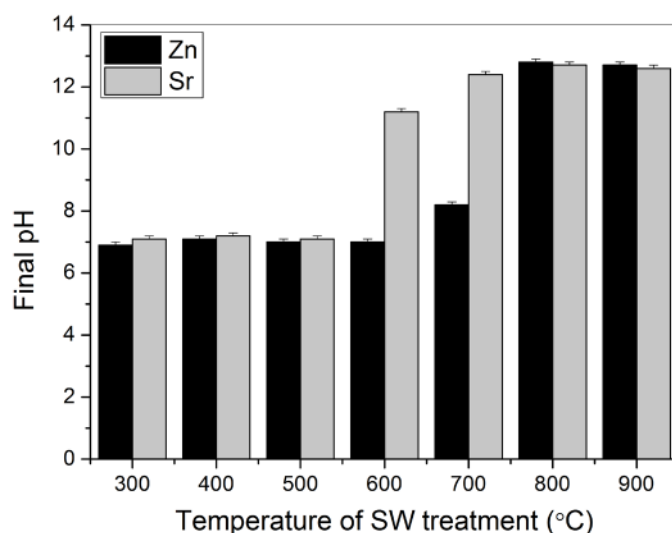


Figure 2. Final pH values of the Sr and Zn solution after interaction with temperature treated SW particles

The contact of variously treated SW samples and metal-containing solutions was accompanied by the solution pH changes and the variations in the amounts Ca ions released from the seashell material (Fig. 2 and Fig. 3). Equilibrium pH values were commonly in the neutral range after mixing both metal solutions with SW300 - SW500 samples, while the increase in solution pH was associated with the further rise in temperature. The amounts of released Ca ions were higher in Zn solutions (Fig. 3b) than in Sr solution (Fig. 3a), in line with higher removal rates of Zn. Actually, molar ratio between removed and released cations was practically 1:1 in the wide range of temperatures (300 – 600 °C), whereas using SW samples calcined at $T \geq 700$ °C the solubility of the SW residues increased and the amounts of released Ca exceeded the amounts of removed Sr or Zn ions.

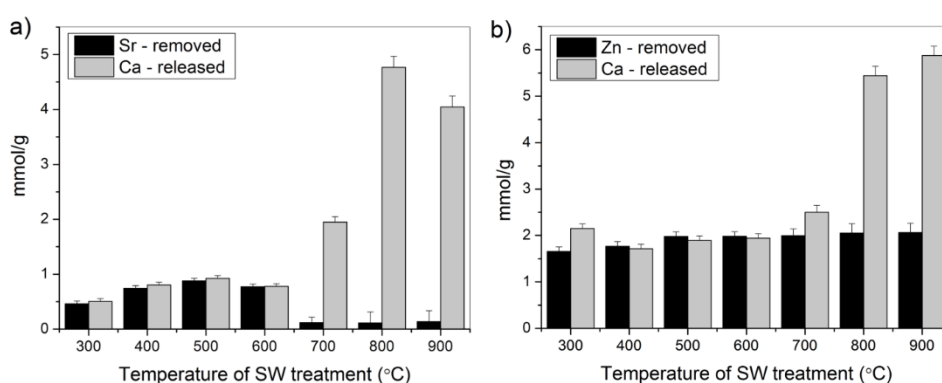


Figure 3. Amounts of Ca ions released and metal cations removed after interaction of temperature treated SW particles with Sr-solution (a) and Zn-solution (b)

The variations in SW potential to separate the investigated cations from the solution can be explained based on the temperature-induced changes in SW properties. Raw SW sample was composed of calcium carbonate in the form of aragonite [8]. As revealed by previous XRD analysis, the transformation of SW mineral matrix occurs in several stages [10]: (i) between 300 °C and 400 °C aragonite is being transformed into more stable calcite polymorph, (ii) in the range 700 °C – 800 °C the diffraction maximums of lime (CaO) appear in addition to calcite peaks, and finally (iii) at 900 °C the calcite decomposition process is completed giving pure CaO. Based on the thermogravimetric analysis, the weight loss of 3.3 % detected up to 600 °C was associated with the loss of the organic phase.

Consequently, removal of Zn and Sr accompanied with the release of equimolar Ca amounts is characteristic for all treated SW samples that retained carbonate structure of either aragonite or calcite polymorph, whereas increased removal of Zn and reduced removal of Sr coincide with the CaCO_3 conversion to CaO. As the reaction of CaO with water results in the pH increase, the hydrolysis and the precipitation of Zn ions contribute to its efficient removal. Quite the opposite, Sr ions do not hydrolyze in observed pH range and the increase in CaO content and concentrations of dissolved Ca ions in the SW samples calcined at $T \geq 700$ °C inhibited Sr removal. Due to the chemical similarity between the two cations, a strong competing effect of Ca on Sr removal was observed using different inorganic materials [12].

Depending on the composition of raw seashells, their pretreatment history, initial concentration of metals in the solution and other experimental conditions, removal of cationic pollutants such as Pb, Cu, Cd, Zn, Hg, Sr, etc. was found to be governed by several operating mechanisms, such as adsorption, ion exchange, coprecipitation, precipitation, etc. [6-10]. To detect the mineral phase changes induced by Zn and Sr removal, temperature treated SW samples which exhibited maximum removal efficiency were analyzed by XRD. The results implied that the precipitation mechanism governs the metal removal by the temperature activated SW (Fig. 4). The main crystalline phase in system SW900-Zn was portlandite ($\text{Ca}(\text{OH})_2$). The appearance of calcite peaks may be explained by the reaction of $\text{Ca}(\text{OH})_2$ with atmospheric CO_2 . Formation of portlandite and calcite in the presence of Zn ions may be the mode of metal incorporation into the solid phase. Besides, new Zn-containing crystalline product was identified - calcium hexahydroxodizincate dihydrate ($\text{CaZn}_2(\text{OH})_6 \times 2\text{H}_2\text{O}$).

SW500 sample after exposure to Sr-solution was analyzed to consider the role of calcite phase in the sequestering mechanism (Fig. 4). Although Sr retention by adsorption, ion-exchange and solid-solution formation cannot be excluded, incorporation of Sr in a new discrete crystalline phase - strontianite (SrCO_3) was identified. The same reaction product was detected after interaction of raw SW with Sr-solution [8], therefore, at the applied initial concentration of Sr, utilization of both aragonite and calcite polymorphs lead to the precipitation of strontianite. The highest removal efficiency of SW treated at 500 °C in respect to other carbonate-based SW samples (i.e., SW300, SW400, and SW600) may be connected with the organic phase exclusion and increased reactivity of the remaining solid.

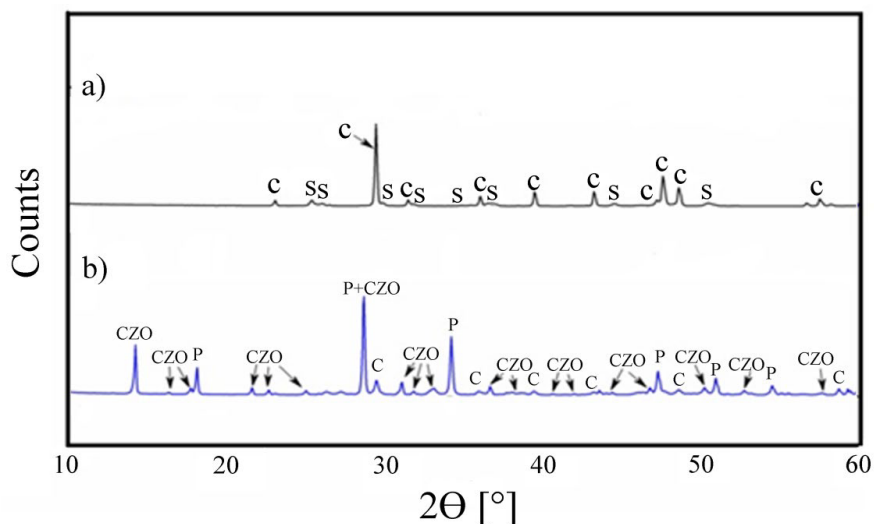


Figure 4. Diffractograms of seashell samples after heat treatment at different temperature and removal of divalent metal ions: a) 500 °C, Sr; b) 900 °C, Zn. Different phases are labeled with capital letters: C - calcite (CaCO_3), S - strontianite (SrCO_3), P - Portlandite ($\text{Ca}(\text{OH})_2$), CZO - Calcium Hexahydroxodizincate Dihydrate ($\text{CaZn}_2(\text{OH})_6 \times 2\text{H}_2\text{O}$)

CONCLUSION

Temperature treatments of the SW were found beneficial concerning both Zn and Sr removal from the aqueous phase. Temperatures 700-900 °C which resulted in partial or complete calcination of calcite to lime were favorable for sequestering Zn ions, and at the same time, adverse regarding Sr separation. By heating the SW at 500 °C pure calcite was obtained, the organic phase was removed, and such sample exhibited the highest potential for Sr removal. Even though cation immobilization via surface adsorption, ion-exchange, and solid-solution formation cannot be excluded, the precipitation of distinct crystalline solids of Sr and Zn was confirmed using the SW samples heated at optimal temperatures, i.e., SW500 and SW900, respectively. The results demonstrate the potential for using seashells as an alternative to limestone and lime for the removal of metal cations while at the same time reducing the negative impact and risks coming from accumulated waste.

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