ENHANCING THE SURFACE REACTIVITY OF SEASHELLS BY THERMO-CHEMICAL METHODS

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Abstract

Phosphorus removal from wastewaters is a subject of intense scientific research. The present study proposes a new material with pollutants adsorbing properties, obtained by a combination of thermal and chemical approaches, applied to Black Sea shells' exoskeletons, which are considered to be a hazardous material in some situations. For the presented case, the XRD results revealed the fact that the chemical reaction was incomplete, the reagent being present in the sample investigated after the burning process.

Introduction

Phosphorus is an essential element for agriculture, being applied as fertilizer on a large scale. Its discharge limits in urban wastewater are set by the European law to 1-2 mg/L as total phosphorus, with the proposal to lower these values to 0.5 mg/L and also to include the nutrient recovery in the coming decades [1]. A large amount of phosphate in water is the result of human industrial and household activities, therefore the excess needs to be removed in order to protect the living organisms. The phosphate recovery has a positive impact on the preservation of the natural resources such as phosphate rocks or bodies of water [2]. Its extraction from wastewater by using renewable materials, ideally cheap and abundant, is intensively studied. One of the most promising such materials is the seashells exoskeletons, consisting mainly in calcium carbonate, which has proven its good adsorption properties [3]. Shells are mostly considered a waste which is produced in large amounts all over the world. The surface of seashells' exoskeletons can be modified by various chemical or thermal approaches, in order to increase their superficial reactivity and specific surface area. The improvement of these characteristics affect the properties of shells, and could lead to an increase in their adsorption potential and thus the efficiency regarding the processing of residual waters [4, 5].

In this paper, we present some preliminary work regarding an adsorbent material for water phosphate, obtained by using a combination of chemical and thermal treatments, both of them beneficial for surface modification. The efficiency regarding the removal of pollutants is expected to increase following this working hypothesis.

Experimental

Shells were collected from the Black Sea shore (the city of Mangalia, Romania) and were washed repeatedly with tap water, then with bidistilled water and were finally dried at 110 °C. Next, they were broken to pieces of various sizes and sieved, separating the different dimensional fractions.

Larger size shell fragments were tested in order to create a material with good adsorption properties on its surface, increased by a combination of thermal and chemical treatment. A high temperature was tested (> 800 °C) for a short time period, obtained by using a chemical reaction which generated a high amount of heat, i.e. the reaction between $KClO_3$ and sugars. Larger size

shell fragments were chosen because, when being used as a reactor bed, the larger size will facilitate the circulation of water to be treated and will reduce the equipment’s clogging.
The shells were weighed and mixed with various amounts of oxidizer ($KClO_3$) and fuel (sugar), then the mixture was directly ignited. Depending on the reagent type (specific sugar) and the stoichiometry, the reaction took place with different intensities, in some cases with a flame and the intended strong exothermic effect.
X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used in analyzing the modified exoskeleton’s surface and structure.

Results and discussion

The XRD pattern of one sample of shells modified by using the sugar/$KClO_3$ chemical reaction is presented in Figure 1:

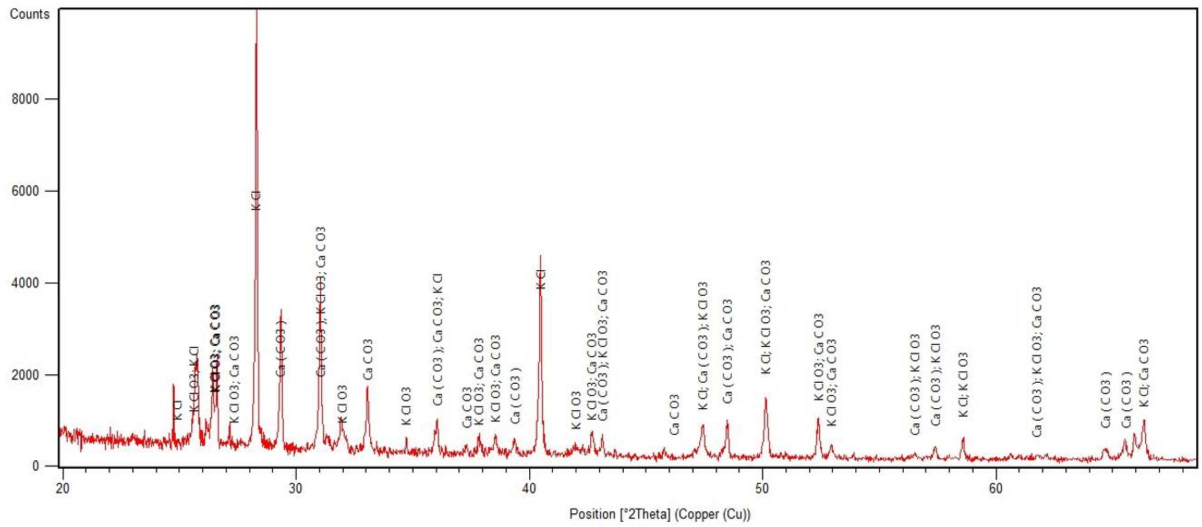

Figure 1. XRD pattern of a sample of shells and sugar/$KClO_3$ mixture after combustion

From the diffraction pattern it was noticed that KCl is present in the sample after the combustion, confirming that the assumed redox reaction took place. Calcium carbonate polymorphs aragonite and calcite are also present, meaning that the shells have at least partially retained their chemical identity and were not completely decomposed during the process. $KClO_3$ is also present in the diffraction pattern, suggesting an incomplete reaction, possibly due to the heterogeneity of the chemical system involved. The lack of calcium oxide in the pattern is probably due to its carbonation soon after air exposure.
The SEM investigation has shown that, post-combustion, the surface morphology resembles a sponge-like surface, with a number of pores of various dimensions, compared to the raw shells that have a different surface morphology. This means that the strong exothermal effect, which accompanied the chemical reaction, led to the partial decomposition of the seashell fragments, and that the method could be promising in tailoring the superficial properties of these materials, including the capability of removing the pollutants from waters.

Conclusion

Multiple tests were performed in order to transform a waste, i.e. shells exoskeletons, into an adsorption material for pollutants in wastewaters. Shells were mixed with various oxidant/fuel combinations, which were tested for combustion. Our results showed that a combination of thermal and chemical treatment has the potential to offer a useful material, considering the partial decomposition of calcium carbonate and the morphology of the shells fragments' surfaces after the decomposition chemical process.

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