COMPARISON OF POTENTIAL OF FRUIT PROCESSING BY-PRODUCTS AND NATURAL ZEOLITE CLINOPTILOLITE IN TREATMENT OF ZINC(II)-CONTAMINATED WATER

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ABSTRACT

This preliminary research aimed to evaluate the potential of fruit processing by-products (cherry, sour cherry and olive pits) as biosorbents in the treatment of water contaminated with Zn(II), comparing their removal efficiency with that of natural zeolite clinoptilolite and its sodium-rich form. Surprisingly, natural zeolite in its native form did not show any better efficiency than the tested biosorbents, although their physicochemical properties and composition differ significantly. On the contrary, the sodium-rich natural zeolite showed up to 61% higher removal efficiency, which indicates the need for material modification in order to achieve satisfactory treatment. The obtained results indicate both, the tested biosorbents, as well as sodium-rich natural zeolite, as promising materials in cost-effective and sustainable wastewater treatment.

Key words: natural zeolite, biosorbents, zinc(II), wastewater treatment, modification.

INTRODUCTION

The current linear concept of development has proven to be unsustainable as it leads to depletion of natural resources, accumulation of waste materials and emission of various harmful substances on daily basis. The development of chemical industry and mining, as well as the application of modern agro technical measures using pesticides and artificial fertilizers in agricultural production, have led to significant emissions of heavy metals into the environment [1]. In addition to already existing water scarcity, water pollution has become an emerging environmental issue [2]. Sustainable, effective, and green water treatment technologies are key to securing sufficient clean water. The most common methods used for purification of wastewater loaded with heavy metals are ion exchange and adsorption. Recently, low-cost sorbents have been evaluated in order to make these methods more economically viable and environment-friendly [1-3]. Natural zeolites have been widely used in remediation of environment polluted with heavy metals, due to the high affinity for cationic species [4,5]. Nevertheless, depending on the characteristics of the targeted pollutant, different modification methods have been designed to enhance sorption capability and increase overall water treatment efficiency [5]. It is necessary to bear in mind every modification incurs additional costs and may potentially cause secondary pollution. Therefore, when selecting an appropriate modification method, it is crucial to consider not only the intended use but also its cost-effectiveness and environmental impact, prioritizing green solutions.

Nowadays, due to population growth and consequent intensification of food production and processing, the generated food processing by-products are also considered as applicable materials in wastewater treatment [6]. Therefore, a comparison of the effectiveness of natural zeolite with that of fruit processing by-products (biosorbents) in removing Zn(II) from wastewater was carried out in order to improve existing water treatment methods, as well as to gain insight into new avenues in development of innovative materials. Apart of zeolite usage, considering waste as a potential sorbent for treatment of heavy metal-contaminated water leads not only to more cost-effective water treatment, but also to more sustainable solid waste management. This approach will enable to meet zero waste concept and ultimately preserve the environment.

EXPERIMENTAL

Materials

A local processing plants provided wasted cherry (CP), sour cherry (SCP) and olive (OP) pits. The collected samples were washed in distilled water to remove impurities, dried in an oven at 40 °C to constant mass, and milled (Retsch MM 200) without separating the kernels from the outer shell. Afterwards the milled samples were sieved (Retsch AS200 basic) and the particle size fraction of 0.56-1.00 mm was chosen for current experiment.

The natural zeolite, NZ (Si/Al=4.08, ≤ 80% of clinoptilolite, CEC=1.42 meq/g, Ca-form, particle size 0.56-1.00 mm) originates from Zlatokop deposit in Serbia. Sodium- rich form of natural zeolite (Na-NZ) was prepared using 1 mol/L sodium chloride solution [7].

The aqueous solution containing ≈ 3 mmol Zn/L was prepared by dissolving $Zn(NO_3)_2 \cdot 6H_2O$ in ultrapure water. The initial Zn(II) concentration (c_o), as well as residual Zn(II) concentration after sorption (c_t) were determined by complexometric titration. All reagent used where of analytical grade.

Sorption study

The sorption of Zn(II) on NZ, Na-NZ and biosorbents CP, SCP and OP was carried out by batch method. Each sorbent was mixed with prepared aqueous Zn(II) solution in solid/liquid ratio of 1/100, on a laboratory shaker at 250 rpm, at room temperature for 24 h. In order to gain insight in sorbents behaviour over time, at chosen time intervals (t = 1 h, 2 h, 3 h, 4 h, 5 h, 7 h, 22 h and 24 h) the sorption was interrupted, the suspensions were filtered, and the residual Zn(II) concentration (c_t) in obtained filtrates was determined.

RESULTS AND DISCUSSION

The capacity of tested materials, i.e. the amount of Zn(II) bound per unit mass of the sorbent in time t (q_t, mmol/g) and removal efficiency (α_t, %) were calculated according to the following equations:

$$q_t = (c_o - c_t) \cdot \frac{V}{m} \quad (1)$$

$$\alpha_t = \frac{(c_o - c_t)}{c_o} \cdot 100 \quad (2)$$

where c_o is the initial Zn(II) concentration (mmol/L), c_t is the residual Zn(II) concentration in time t (mmol/L), V is volume of treated Zn(II) solution (L) and m is mass of the sorbent (g). The calculated capacity of sorbents, q_t, and removal efficiency, α_t, in time intervals within 24 h are given in Figure 1a and 1b.

Data presented in Figure 1a display that modified natural zeolite (Na-NZ) has the highest capacity toward Zn(II) over time, with maximum value of 0.246 mmol Zn/g, achieved after 24 h of sorption. Moreover, already after 2 h of contact, Na-NZ showed the capacity higher than 0.2 mmol/g, after which it continues to grow slightly over time. Contrary, much lower capacity has been obtained for other tested sorbents with maximum value reached after approximately 4 h of contact, followed by a slight decrease. These deviations in capacity and efficiency (Figure 1b) over time for natural zeolite and biosorbents are most likely due to simultaneous sorption/desorption processes caused by impurities and heterogeneous composition [5]. In the case of Na-NZ, deviations were not observed, which showed improved effective uptake capacity up to the 0.246 mmol/g (Figure 1a) compared to the NZ. According to the literature, this behaviour can be caused by many factors including differences in pore clogging, solution pH, zeta potential, surface charge etc. [8]. The modification of NZ with NaCl substantially improved Zn(II) uptake (Figure 1b) which resulted in almost 4 times higher removal efficiency (82.5% *vs*. 21.1%). It is worth noting that Na-NZ is obtained by a low-cost and green modification treatment.

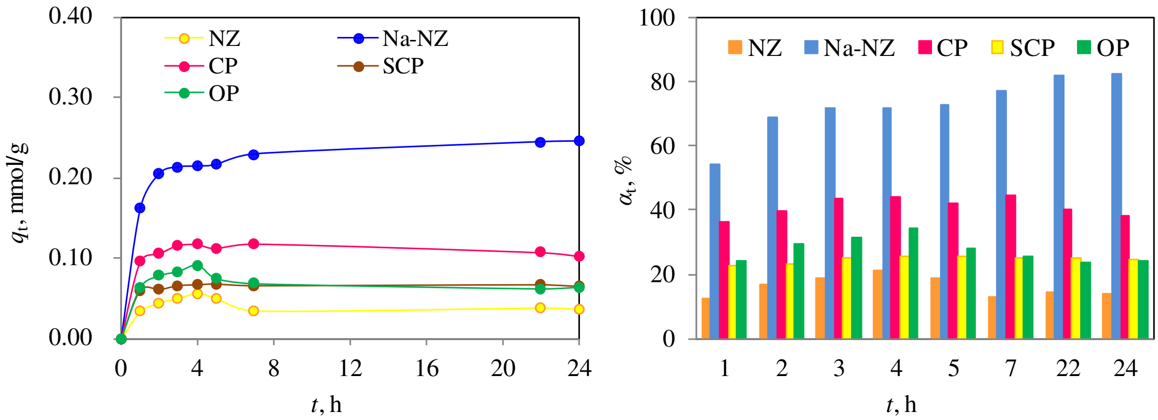

Figure 1. a) The capacity and b) removal efficiency of different sorbents in time intervals within 24 h.

The maximum values of capacity (and removal efficiency) were 0.057 mmol/g (21.1%) for NZ, 0.117 mmol/g (44.0%) for CP, 0.068 mmol/g (25.6%) for SCP, and 0.092 mmol/g (34.4%) for OP, respectively. The usage of NZ in its native form did not result in higher capacity compared to the biosorbents. Namely, there are significant differences in chemical composition of tested materials. While natural zeolite is alumosilicate mineral, containing exchangeable Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} in its framework voids, with well-known affinity toward heavy metal cations, used biosorbents contain mostly organic compounds (carbohydrates, lignin, cellulose, hemicellulose, proteins, lipids etc.) and a smaller amount of mineral content (K, Ca, Mg, Na and Fe) [9-11]. Due to the different chemical composition, it is expected that mechanism of Zn(II) binding to the tested sorbents differs, which will be the subject of future research. Nevertheless, this research showed that despite the unique properties of natural zeolite, especially affinity for heavy metal ions, its modification is needed in order to meet satisfying treatment effect. For example, natural zeolite clinoptilolite was insufficiently effective in remediation of mercury-contaminated soil and water, compared to the sulphur-impregnated natural zeolite [12,13] pointing to a very challenging selection of proper modification method. The choice of modification method primarily depends on the characteristics of the target pollutant, but also taking into account other criteria such as costs and negative environmental impact.

CONCLUSION

The sodium-rich natural zeolite showed the highest removal efficiency and the highest capacity among all tested sorbents, indicating modification as very effective tool in achieving satisfying remediation result. The minimum residual Zn(II) concentration achieved on Na-NZ equalled to 0.522 mmol/L (34.1 mg/L), which is above the permissible limits for zinc (2 mg/L). However, complete Zn(II) removal by one-step sorption was not expected considering the quite high initial concentration of 3 mmol/L (≈ 200 mg/L). According to the obtained preliminary results, fruit processing by-products have a promising potential for the treatment of wastewater contaminated with heavy metals, since they showed a higher capacity and efficiency of Zn(II) removal compared to the natural zeolite. Of course, further research is needed to increase their effectiveness, examine the binding mechanism and the ability to retain pollutants. Ultimately, any reuse of waste materials is more than welcome as the world faces an excessive accumulation of waste that is increasingly difficult to properly dispose of.

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