Waste Valorisation into Zeolite and Their Potential Application in Water Treatment

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Abstract. Serious environmental issues have escalated as a result of urbanization, industrialization, and global population growth, caused by solid waste accumulation and water pollution. Tackling these challenges requires innovative strategies for waste reuse and pollution control, such as using solid wastes with high concentrations of Si and Al as raw materials for the development of emerging materials used for decontamination of waters (i.e. zeolites). Therefore, within this study two zeolites were synthesized using an easy, environmentally friendly and inexpensive method (sol-gel). The precursors were metallic waste (aluminium cans) for the sodium aluminate, and both pure precursor (pure sodium silicate) and agricultural waste (rice husks) for the sodium silicate. The synthesized samples were analyzed using different techniques, such as XRF, XRD, DTA and SEM. The results showed that the developed zeolites are faujasite and sodalite types, which are adequate for eliminating heavy metal ions from water. Additionally, the heavy metal removal efficiency for the two developed zeolites was higher than 95% for Cd, Ni after 24h testing, and only ~35% after 24h for Pb, emphasizing their good capacity to retain heavy elements. Thus, these findings demonstrate the great potential of waste-derived zeolites as sustainable adsorbents for reducing heavy metal pollution in aquatic environments, contributing to the advancement of resource recovery, waste reduction, and green remediation methods and aligning with the circular economy principles.

1 Introduction

Aquatic ecosystems are continuously impacted by a range of pollutants, including nutrients, heavy metals, organic micropollutants, micro- and nanoplastics, and pathogens [1, 2]. Also, emerging contaminants like PFAS, bisphenols, and surfactants pose significant threats at trace concentrations to the ecosystem and eventually to human health [3]. Although, current pollutant removal techniques, such as physical and chemical methods

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(coagulation/flocculation and electrocoagulation), chemical precipitation, adsorption, and biological treatments, are effective up to a certain point, they pose some limitations, such as incomplete pollutant removal, secondary pollution and byproducts, high energy and operational costs, environmental disruption, lack of adaptability [4]. Additionally, as climate change and urbanization exacerbate pollution issues the newly proposed removal techniques should consider detecting and treating new pollutants, integrating treatment systems into existing infrastructure, and balancing cost-effectiveness and environmental impact.

Recent studies have highlighted a trend toward multifunctional, environmentally friendly, and scalable materials that can be used for water purification, and are also in line with the principles of the circular economy and global sustainability objectives. Among these types of materials, it should be mentioned nanomaterials (such as nano zero-valent iron, titanium dioxide, and zinc oxide for retaining emerging pollutants), metal-organic frameworks (MOFs) for the elimination of persistent organic pollutants and heavy metals, ion-exchange resins for specific ions, and zeolites that have ion-exchange capacity for heavy metals [5, 6]. The latter are aluminosilicate structures, categorized into natural and synthetic materials, that presentpores in their structure, which facilitate the adsorption of various organic molecules, functioning as molecular sieves [7]. Recently, numerous studies focused on cost-effective zeolite synthesis using industrial wastes like fly ash, porcelain, paper sludge, lithium slag, and agro-wastes to reduce costs. This approach combines environmental remediation, sustainable materials science, and circular economy practices, as it reduces the pressures associated with solid waste accumulation by valorizing industrial residues as both silicon and aluminum sources, minimizing thus the need for high-purity chemical reagents commonly used in conventional zeolite synthesis [8].

Synthetic zeolites are typically prepared using hydrothermal or solvothermal methods, and the process usually involves the formation of aluminosilicate gel, aging, and crystallization, followed by mixing the solutions [2, 5]. The obtained zeolites may remove hazardous pollutants, such as heavy metals, organic substances, PFAS, microplastics, and pathogens [9, 10]. For example, NaY and NaX zeolites obtained through a conventional hydrothermal method using aluminium foil waste as precursor, showed the following affinity: Hg (II) < Cu (II) < Cd (II), and the ion-exchange was in accordance with the second-order pseudo-kinetic model [11]. Additionally, Ziejewska et al. have obtained three types of zeolites (sodalite, gismondine and Linde Type A) using fly ash as precursor for silicon and aluminium oxides. The results showed high efficiency in removing cationic contaminants from wastewater, with a range of 85% to 97% for methylene blue, and 89% to 100% for lead ions [12].

The present study contributes to sustainable environmental management by assessing the valorisation of agricultural and metallic waste to obtain crystalline aluminosilicates with applicability in water treatment. By following an atypical synthesis method for zeolites, namely, the sol-gel method, this work highlights an environmentally friendly and resource-efficient approach for obtaining innovative advanced materials through waste-valorisation (aligned with the circular economy principles). After synthesis and characterization, the materials' retention capacity for three heavy metals (Cd, Ni, and Pb) in a concurrent system will be tested to assess their viability as a solution for water remediation.

2 Experimental

2.1 Materials

The zeolites were synthesized using both pure precursors (pure sodium silicate, Merck reagent) and agricultural (rice husks) and metallic (aluminium cans) waste. Rice husks were

washed with distilled water and dried at 70 °C before being combined with 1 M HCl at 85 °C for 3 hours. The mixture is filtered with distilled water until it reached a neutral pH, then dried and calcined for 2 hours at 700 °C before being mixed with 1 M NaOH to produce sodium silicate (Na_2O_3Si) [13]. Metal cans were dissolved in a 10M NaOH solution to obtain sodium aluminate ($NaAlO_2$). NaOH was used to improve alkalinity during synthesis, as it is crucial for controlling zeolite crystallization, determining composition, and influencing the type of crystallizing zeolite. The obtained sodium aluminate solution was filtered to remove impurities, including paint and protective coatings. The synthesis method for the two zeolites (Zw1 and Zw2) involved the use of 30 mL of $NaAlO_2$, mixed with 40 / 15mL of Na_2O_3Si (synthesized / pure precursor) for 1h at room temperature. The obtained gel was left to crystallize for 1 day at room temperature, and then dried for 24 hours at 80°C. The resulting material was ground, washed with excess distilled water and alcohol, and dried at 80 °C.

2.2 Methods

The oxide composition of the synthesized Zw1 and Zw2 zeolites was determined by X-ray fluorescence (XRF) using a Rigaku Supermini fluorescence spectrometer, and the X-ray diffraction (XRD) spectra were obtained using a Bruker D8-Advance diffractometer with Cu-Kα radiation (λ = 1.5406 Å) at a scanning range between 5° and 80°. To assess the thermal stability of the zeolite materials obtained by valorizing different types of waste, thermogravimetric analyses (DTA) were performed using a Netzsch STA 449 F5 Jupiter thermal analyzer, with a treatment temperature of up to 1000°C and a heating rate of 10°C/min. Additionally, a Hitachi SU-70 scanning electron microscope (SEM) was used to examine the structural morphologies of the samples, which had previously been metalized with a thin AuPd coating using the SC7620 Mini Sputter Coater/Glow Discharge System.

To assess heavy metal retention efficiency, a laboratory solution with known concentrations of Cd, Ni, and Pb ions was prepared. The synthesized zeolites were vigorously mixed with the respective solution, and 5 mL of solution was collected at established intervals (1, 2, 6, and 24 hours) to determine the existing Cd, Ni, and Pb concentration by using the Analytik Jena GmbH- contrAA700 atomic absorption spectrometer. The retention efficiency (Ef, %) of the analyzed heavy metals was determined using Eq 1 [14]:

$$E_f = [(C_0 - C_f) / C_0] * 100 \quad (1)$$

where: C_0 represents the initial concentration of the analyzed metal in the solution; C_f is the concentration after the laboratory tests.

3 Results and discussion

3.1 Structural characterization

Table 1 shows the chemical compositions of the obtained zeolites, determined by X-ray fluorescence. As it can be noticed, both Zw1 and Zw2 zeolites have as predominant phases: sodium oxide (Na_2O), alumina (Al_2O_3), and silica (SiO_2), along with a variety of minor oxides that originate from the used precursors.

Table1. Chemical composition of synthesized zeolites

Zeolite	Na_2O	Al_2O_3	SiO_2	TiO_2	V_2O_5	BaO	CeO_2	Pr_6O_{11}
Zw1	21,9	39,7	36,3	0,31	0,2	0,6	0,8	0,3
Zw2	24,1	36,9	38,4	0,46	0,2			

The XRF results are correlated with those from XRD, as shown in Figure 1.

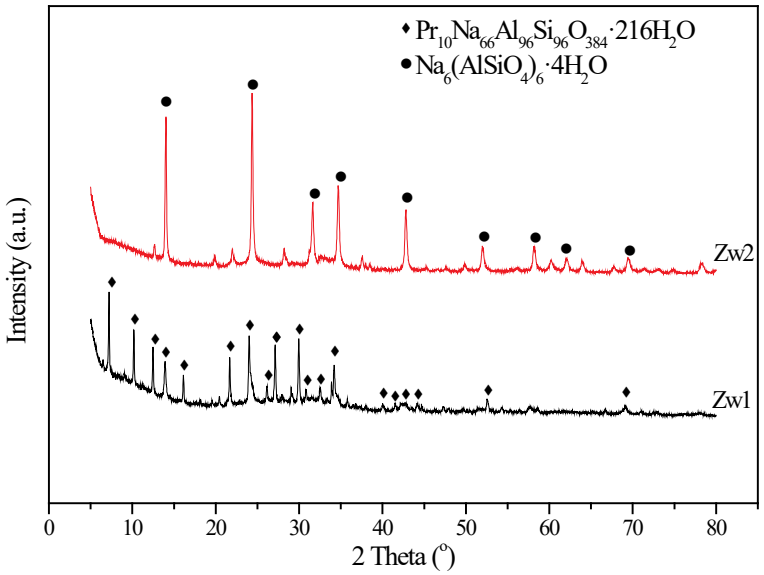


Fig.1. Diffraction spectra of Zw1 and Zw2 zeolites

Figure 1 shows the diffraction spectrum of Zw1, which highlights the formation of Sodium Aluminum Praseodymium Silicate Hydrate (PDF 00-057-0133), with all diffraction peaks attributed to this structure, and with the highest intensities at 2θ = 7.25°, 10.23°, 12.52°, 14.48°, 16.17°, 21.74°, 24.05°, 26.17°, 27.17°, 29.99°, 34.24°, and 52.63°.This is characteristic of low-silica faujasite (Zeolite X). No other crystalline phases corresponding to other compounds are detected. Thus, the XRD analysis highlights the possibility of obtaining zeolite materials with an advanced degree of purity, using aluminum and agricultural waste as raw materials.

A different composition of precursors determines distinct zeolites with varying structures. Thus, the diffraction spectrum of Zw2 shows a different pattern than Zw1, due to the silica source, as well as its concentration in the mixture. The Zw2 zeolite obtained by using extra pure sodium silicate exhibits a predominantly crystalline structure with sharp and thin peaks at 2θ = 13.94°, 24.32°, 31.55°, 34.65°, 42.8°, 51.97°, and 58.15°, which correspond to Sodium Aluminum Silicate Hydrate (PDF 00-042-0216), a sodalite type zeolite.

To evaluate the thermal stability of the developed zeolite materials, thermogravimetric analyses were performed, and the TG and DTA curves of Zw1 and Zw2 samples were plotted (Figure 2).

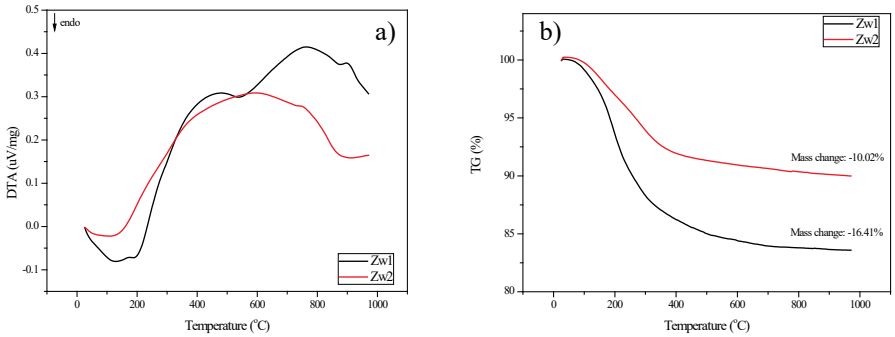
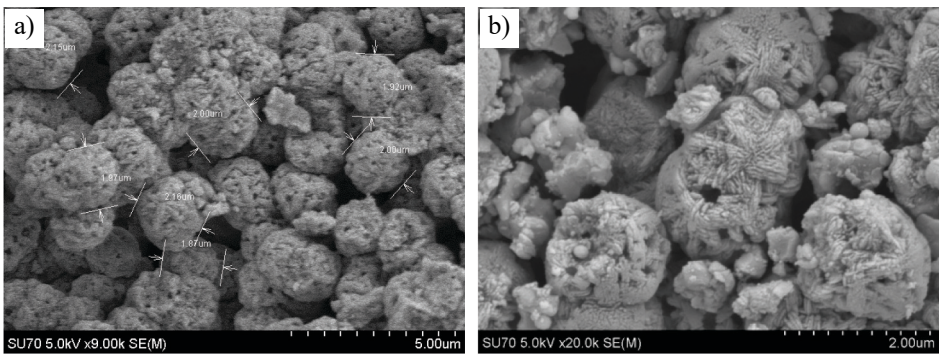


Fig.2. a) DTA and b) TG curves for Zw1 and Zw2 zeolites

Thermogravimetric analyses indicate similar behaviour for the two zeolites Zw1 and Zw2. A primary endothermic effect highlighted by the DTA curves is the loss of water physically bound or absorbed in the porous structure of the zeolites, in the temperature range of 40 - 210°C (Figure 2a), a phenomenon associated with a mass loss of ~4% for Zw2, and ~8% for Zw1 (Figure 2b). An explanation for this behavior is the existence of a higher stability of the pure sodium silicate used in the development of Zw2. A particular interest is represented by the exothermic DTA signal recorded around 760°C for Zw2, and around 820°C for Zw1, a phenomenon associated with the collapse of the zeolitic structure since at these temperatures, the densification of the structure occurs.

Scanning electron microscopy (SEM) was used to investigate the morphology and size of the synthesized zeolite crystals, as shown in Figure 3. The formed Zw1 zeolite is very well-structured, composed of spherical crystalline units that tend to cluster, with the diameter of the spheres being ~2µm (Figure 3a). Also, crystalline lamellar formations, interconnected, are formed on the surface of the microspheres (Figure 3b), corresponding to low-silica faujasite - Zeolite X.

SEM images of Zw2 show heterogenous structures of spherical aggregates, with "desert rose" formation, typical of the sodalite zeolite (Figure 3c and d), with a skeletal and porous structure, having particles with sizes < 5µm.



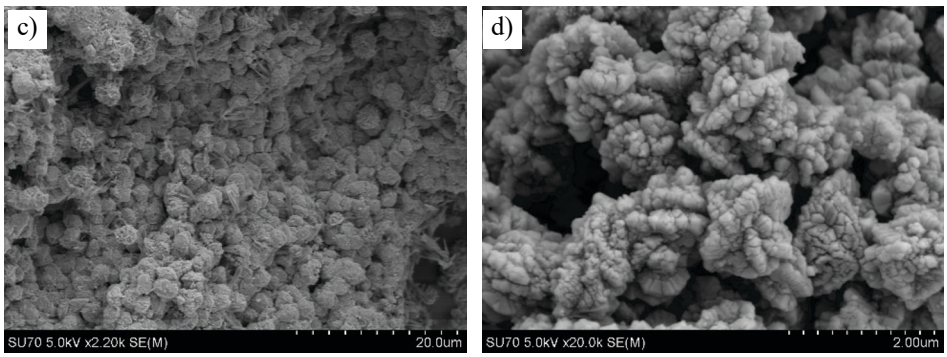


Fig. 3. SEM images of a, b) Zw1 and c, d) Zw2 zeolites

3.2 Removal efficiency

As can be seen from Figure 4, in general, the synthesized zeolites exhibit reduced concentrations of heavy metal ions (Cd, Ni, Pb) even after the first hour of mixing, their concentrations being minimal. Figure 5 shows the retention efficiencies of the analysed heavy metals. A high capacity for adsorbing Cd and Ni metal ions from the used solution was observed for both developed zeolites (>95%) after just 1h of contact. Slightly better efficiencies were observed for the Zw2 zeolite, as sodalite compared to faujasite is more structurally stable, has higher binding affinity, a better surface adsorption mechanism, and improved precipitation effects. Its small cage environments promote stronger electrostatic interactions and favorable ion site distribution. Additionally, sodalite may act as a nucleation site for surface precipitation, enhancing removal without relying solely on ion exchange [15].

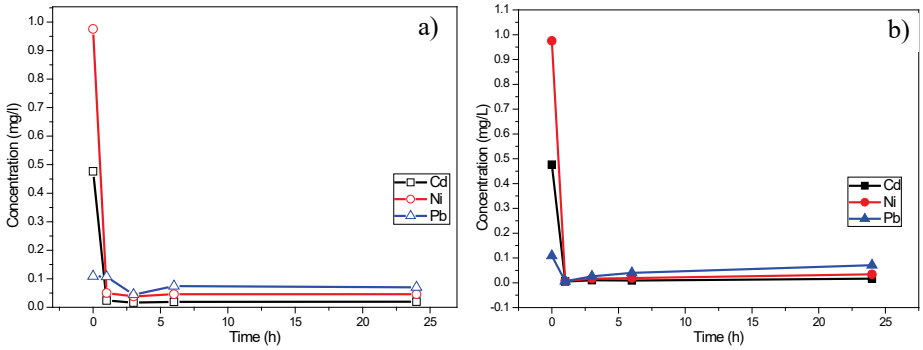


Fig. 4. Heavy metal concentrations after 0, 1, 3, 6, and 24h for a) Zw1 and b) Zw2 zeolites

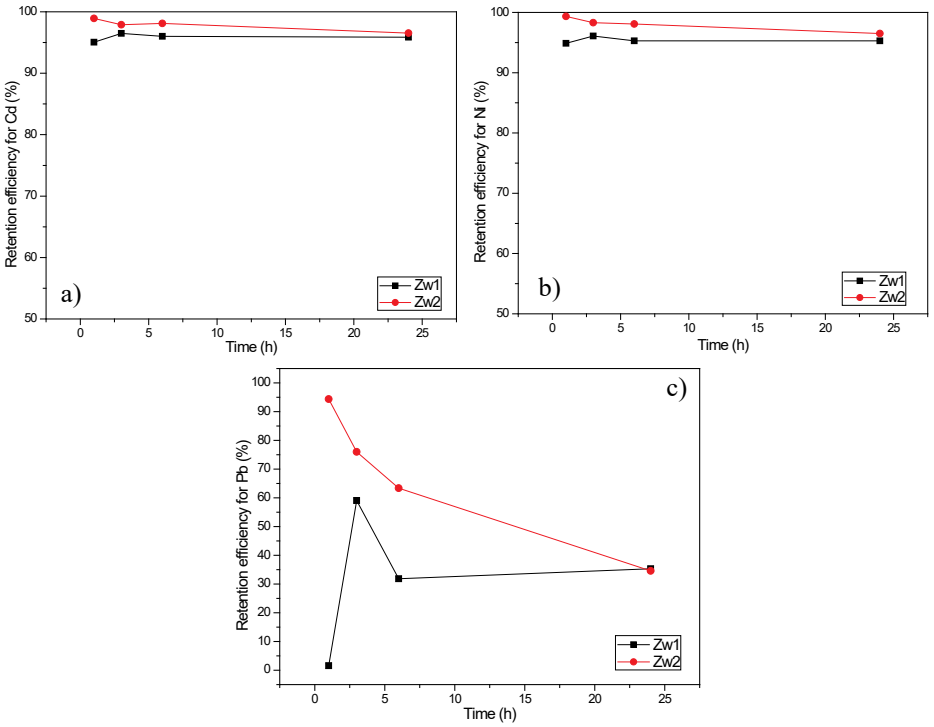


Fig. 5. Comparative retention efficiencies for heavy metals: a) Cd, b) Ni, and c) Pb

4 Conclusions

Two zeolites were synthesized using a simple, low-cost method (sol-gel), starting from pure and waste precursors, aligned to the principles of circular economy, waste valorisation and pollution control. The XRD spectra of Zw1 and Zw2 samples highlight the formation of faujasite - Sodium Aluminum Praseodymium Silicate Hydrate and sodalite - Sodium Aluminum Silicate Hydrate, with all diffraction peaks corresponding to those structures. To evaluate the thermal stability of zeolitic materials under regeneration conditions through thermal treatment, thermogravimetric analyses were performed, with treatments up to 1000 °C. The TG – ATD curves show a maximum mass loss of 16% for Zw1 (characterized by a higher porosity and therefore a greater amount of water present in the structure) and up to 10% for Zw2.

SEM assessed the morphology and size of the synthesized zeolites to determine the chemical species in the zeolite structures. Zeolite Zw1 is very well structured, composed of spherical crystalline units, corresponding to the faujasite type zeolite. The SEM images of zeolite Zw2 highlight the formation of sodalite zeolite, with a skeletal and porous structure, having particles with sizes < 5µm. The synthesized zeolites exhibit a high capacity for adsorbing metal ions from the used solution, with their concentrations being minimal even after the first hour of mixing, and remaining so after 24 hours of contact. This highlights their viability as a water remediation strategy with both high cost-efficiency and reduced environmental impact, coupling secondary resources with advanced materials for environmental remediation (in line with the circular economy principles).

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