Natural and eco-friendly material for the removal of metals from surface and wastewaters

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Activation technics

In this study, a natural zeolite (NZ) originated from Racosu de Jos, Romania, crushed and ground to a granulation of 0.5 – 1 mm was used. Before the activation treatment, the adsorbent material was washed with distilled water to remove the impurities and dried at room temperature.

Thermal activation (TAZ): NZ was kept at 150 °C in an oven (Memmert, Germany) for 24h.

Chemical activation (CAZ): NZ was mixed with 500 mL of 2M NaCl and kept under continuous stirring for 24h. The chemically activated zeolite (CAZ) was washed with distilled water until no significant differences were observed in the electrical conductivity and pH (350I Multiparameter, WTW, USA) of two sequential washing steps. Finally, the CAZ was collected by centrifugation (Universal 320, Hettich, Germany) and dried at room temperature.

Thermo-chemical activation (TCAZ): TCAZ was activated in two stages. Firstly, the NZ was thermally activated at 150 °C for 24h and then, chemically activated, by keeping under stirring the TAZ with 2M NaCl for 24h. Finally, the thermo-chemically activated zeolite was washed and dried at the room temperature.

Material characterization

The crystalline phases of NZ, TAZ, CAZ and TCAZ were characterized using X-ray diffraction made of D8 Advance diffractometer (Bruker, Germany), operating at room temperature, 40 kV and 40 mA with CuKα radiation (λ = 1540.60 Å). The functional groups of natural and activated zeolite were characterized using Spectrum BX II FT-IR spectrometer (Perkin Elmer, USA) on KBr pellets containing 1% (w/w) sample.

Metal adsorption measurements

1 g of natural or activated zeolite was put in contact with 50 mL of highly polluted water samples. The mixture was shaken at 15 rpm for 24h and 72h in a shaker (Reax 20, Heidolph, Germany) to ensure equilibrium. The adsorbent was filtered and the concentration of metals (Mn, Fe, Ni, Cu) was analyzed by inductively coupled plasma mass-spectrometry (ICP-MS) after acidulation with 65% HNO_3 to a pH<2, using an ELAN DRC II spectrometer (Perkin Elmer, United States). The amount of metals remaining in the adsorbent phase q_e and the removal efficiency E were calculated using the following equations:

$$q_e = \frac{C_0 - C_e}{m} * \frac{V_s}{1000} \quad (1)$$

$$E = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where: q_e is the amount of metals adsorbed per gram of adsorbent, at equilibrium (mg/g), V_s is the volume (mL), m is the weight of the adsorbent (g), E is the removal efficiency (%), C_o and C_e are the initial and equilibrium concentrations of metals surface and wastewaters (mg/L).

The water samples:

- The surface waters sampled from Rosia Rivulet (***SW1***) and Valea Sesii Rivulet (***SW2***), tributaries of the Aries River, a severe polluted river in Romania due to the intensive historical and ongoing mining activities.
- A wastewater sampled from a local industrial unit (***WW1***). In order to test several levels of metal concentrations, ***WW1*** was chemically enhanced with Certified Multi-Element ICP Standard IV (Merck, Germany)(***WW2***).

RESULT and DISCUSSIONS

Zeolite characterization

The XRD pattern

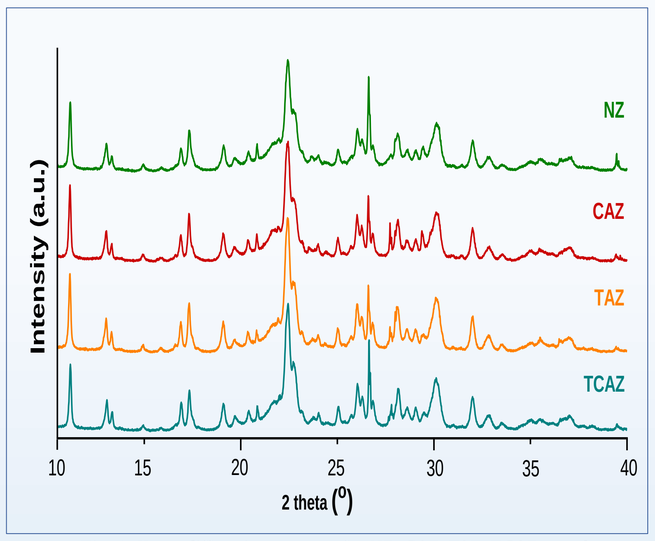

Fig. 1. X-ray diffraction patterns for NZ, CAZ, TAZ, TCAZ samples.

- Display the characteristic peaks of clinoptilolite as the major crystalline phase, accompanied by quartz, muscovite and albite.
- The used slight thermal (TAZ), chemical (CAZ) and thermo-chemical (TCAZ) treatments result in minor to no structural changes detectable by XRD.
- For CAZ and TCAZ samples, the treatment with NaCl sharpened the diffraction peaks, resulting in a slight increase in the crystallinity of zeolites. The diffraction pattern of TCAZ sample specified the presence of crystalline NaCl post-exposure.

The FT-IR characterization

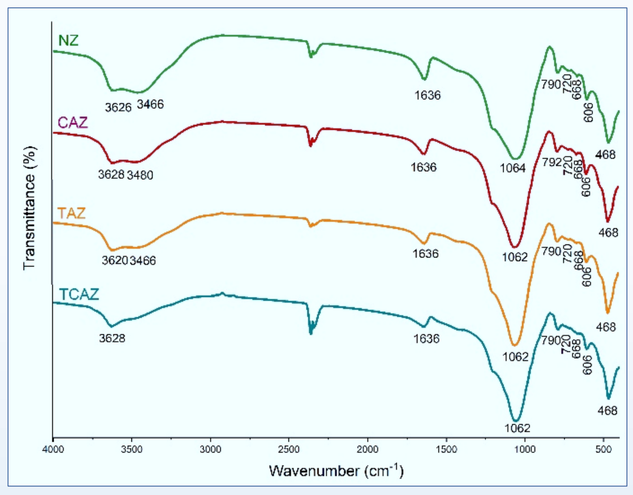

Fig. 2. Fourier transform infrared spectra for NZ, CAZ, TAZ, TCAZ samples.

- The vibration of T-O bonds (T=Si and Al) was identified around 1062 $cm^{-1}$and the vibration of Si-O-Si and O-T-O bonds at 790 and 606 cm^{-1}, respectively.
- The band at 468 cm^{-1} was attributed to vibrations of TO_4 tetrahedron, while the band at 1640 cm^{-1} to Si-O bond vibration.
- The band at 3480 cm^{-1} was attributed to the vibration of Si-OH groups fixed to network defects by hydrogen bonds and to the vibration of loosely bond water molecules on the network surface.
- The intensity of these bands decreased in case of TAZ, CAZ and TCAZ zeolites, due to the loss of adsorbed water during the thermal treatment.

Metal adsorption capacity of the natural and activated zeolite

Surface water

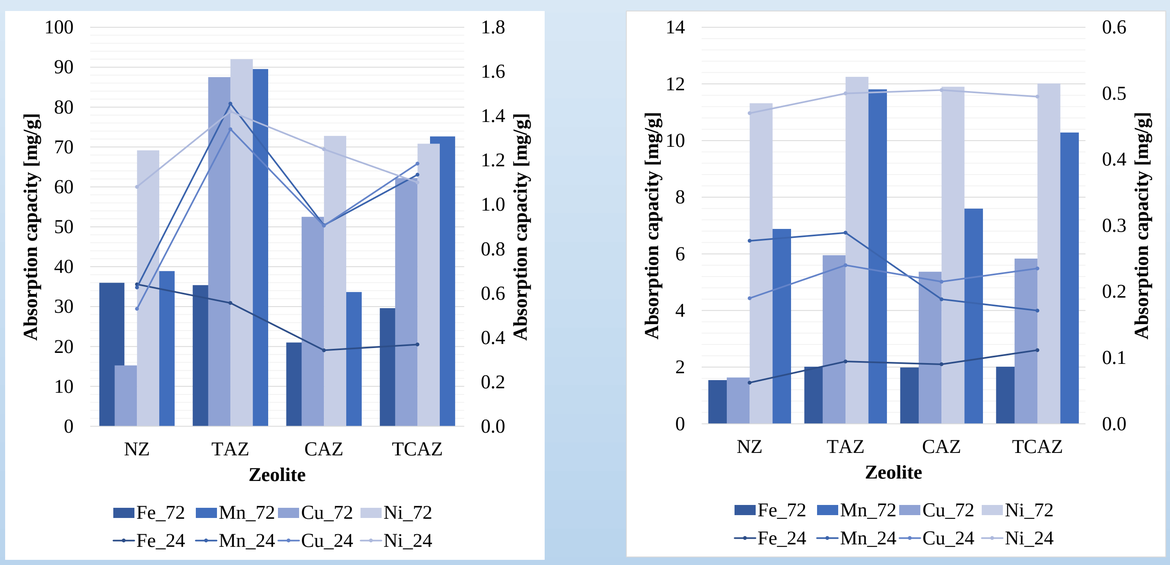

Fig. 3. The absorption capacity of the natural and modified zeolite of Mn, Fe, Ni and Cu from SW1 and SW2 samples

Wastewater

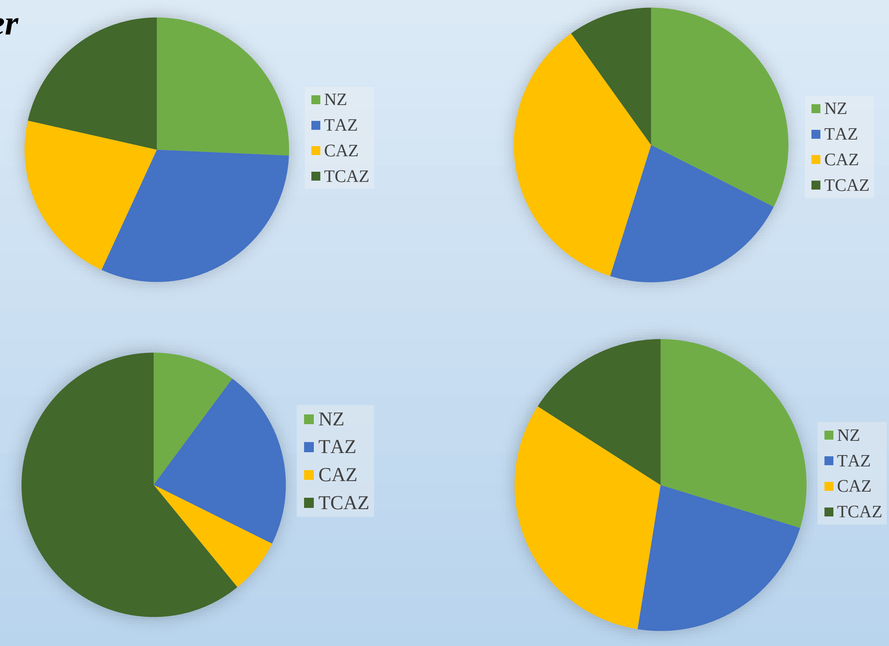

Fig. 4. The absorption capacity (qe) of NZ, TAZ, CAZ and TCAZ of Mn, Fe, Ni and Cu removal from WW1 at 24h / 72h and from WW2 at 24h/ 72h

CONCLUSION

- In the present study, the metal adsorption capacity of a natural and modified zeolite was tested. The NZ was thermally activated at 150 °C for 24h (TAZ), chemically activated with 2M NaCl (CAZ) and thermo-chemically activated (TCAZ) by a combined method of the previous two activation techniques.
- The XRD pattern showed that clinoptilolite, quartz, muscovite and albite were the main mineral constituents of the natural zeolite. The XRD and FT-IR analysis showed that no major changes occurred in the structural and molecular characterization of the NZ after the activation treatments.
- The results of the adsorption experiments suggested that activation processes of zeolites enhanced their ability to adsorb Mn, Fe, Ni and Cu.
- Among the tested adsorbent materials, the results of the investigation indicated that TAZ could be considered the most suitable material for removing Mn, Fe, Ni and Cu and similar chemical compounds from surface and wastewaters.

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