

Pharmaceuticals removal from Contaminated water by using natural materials as adsorbents

M. BRIENZA ^{(A)*}, F. LELARIO ^(A), S. A. BUFO ^(A,B), LEE-ANN MODLEY ^(B), L. SCRANO ^(C)

^(a) Department of Sciences, University of Basilicata, Via dell'Ateneo Lucano 10, Potenza, 85100, Italy

^(b) Department of Geography, Environmental Management and Energy Studies, University of Johannesburg, Johannesburg, 2092, South Africa

^(c) Department of European Cultures, University of Basilicata, Matera, 75100, Italy

* monica.brienza@unibas.it

BACKGROUND AND AIM

Pharmaceuticals, fundamental in the therapy and prevention of known pathologies, are responsible for environmental pollution. These substances, called "emerging contaminants", are harmful to human health because they enter the environment in quantities exceeding the natural self-capacity purification of the ecosystems. The wastewater treatment plants (WWTPs) cannot remove these substances, which can undergo chemical/biological transformations in the environment, forming thus by-products that are sometimes more toxic than the parent molecules; successively, they move into rivers and drinking water supplies. All these phenomena represent a severe public health problem. In this study, the volcanic ashes collected on Monte Vulture (PZ, Italy) were tested for the removal of sulfamethoxazole (SMX) and trimethoprim (TMP), two associated drugs active in urinary infections. The persistence of these compounds in the environment is very concerning because their trace levels can be responsible for the formation of antibacterial resistance genes (Yang et al., 2017).

RESULTS AND DISCUSSION

Characterization. XPS analysis of samples showed different signals, including the Si 2s (153.6 eV), which is attributable to a pyroxene and olivine structure, according to Seyama and Soma (1985). The signal Si 2p (103.6 eV) is attributable to pyroxene, according to Wagner et al. (1982). Noteworthy are also the signals of Al 2p (74.0 eV) that, according to Seyama and Soma (1985), are attributable to pyroxene and the signal of Fe 2p (710.6 eV) attributable to the presence of olivine [Seyama and Soma, 1987].

Catalytic oxidation in the adsorption processes

The natural presence of metals in the adsorbent allows the material to exhibit an excellent capacity for catalytic applications. During the adsorption processes, a known amount of PMS (800 μ M) was added into the reaction systems with 4mg L⁻¹ of sulfamethoxazole. Benefiting from the effective transfer of electrons on volcanic clay/PMS, the degradation rate of sulfamethoxazole (SMX) was significantly faster than its adsorption rate and oxidation by the Fenton processes. The blank test showed that 43% of the SMX was removed from water using only PMS or Fenton like process (PMS/Fe). The SMX degradation in the volcanic clay/PMS was efficient, and this substance was removed entirely within two h.

MATERIALS AND METHODS

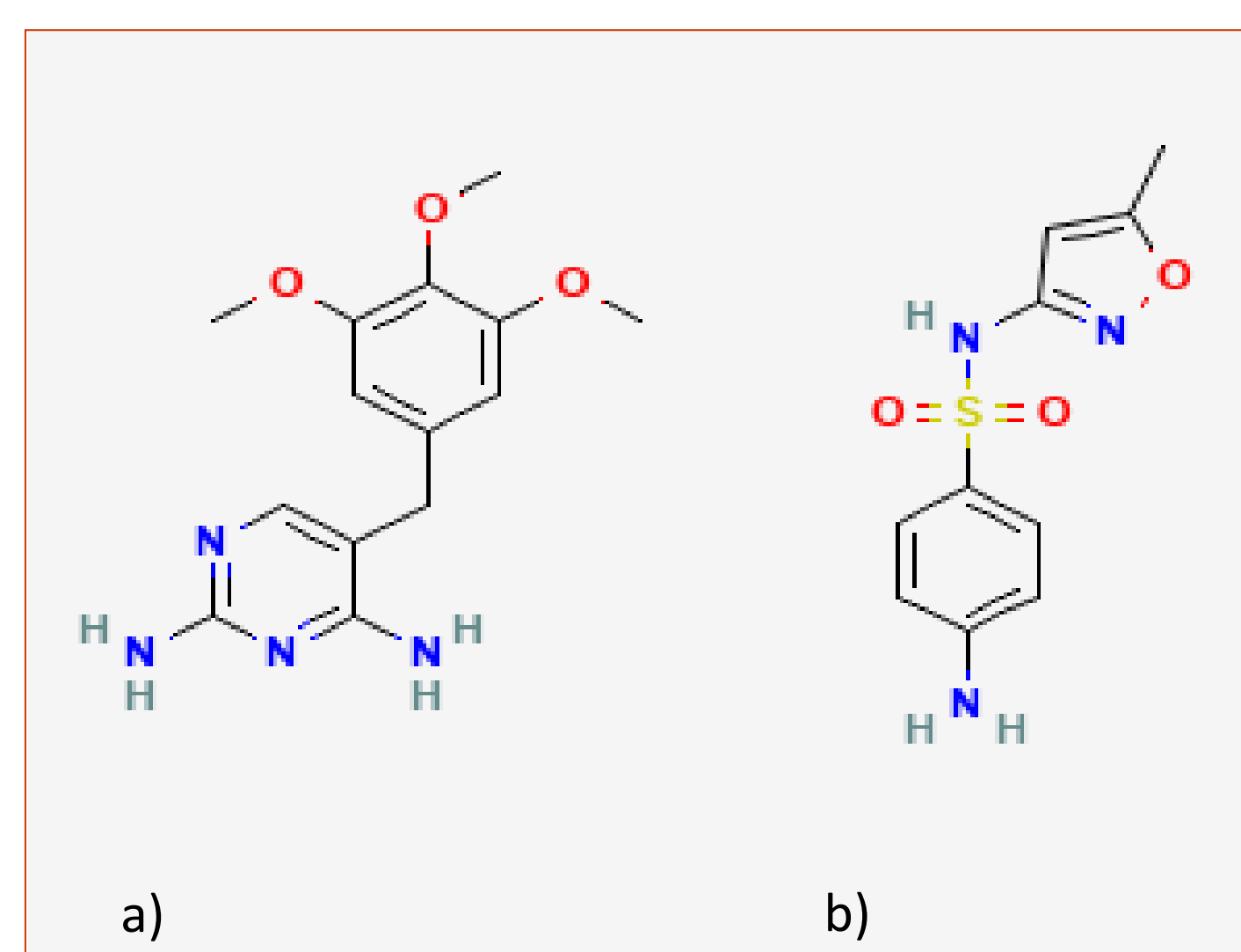
Analytical grade standards of trimethoprim (certified reference material), sulfamethoxazole (purity 98%) and potassium peroxydisulfate, with the commercial name of Oxone[®] (PMS, KHSO₅, 0.5 KHSO₄, 0.5 K₂SO₄), were purchased from Sigma Aldrich (St. Louis, USA).

Characterization of natural adsorbent was carried out by using:

- The X-ray photoelectron spectroscope (XPS) SPECS Phoibos 100- MCD5 spectrometer;

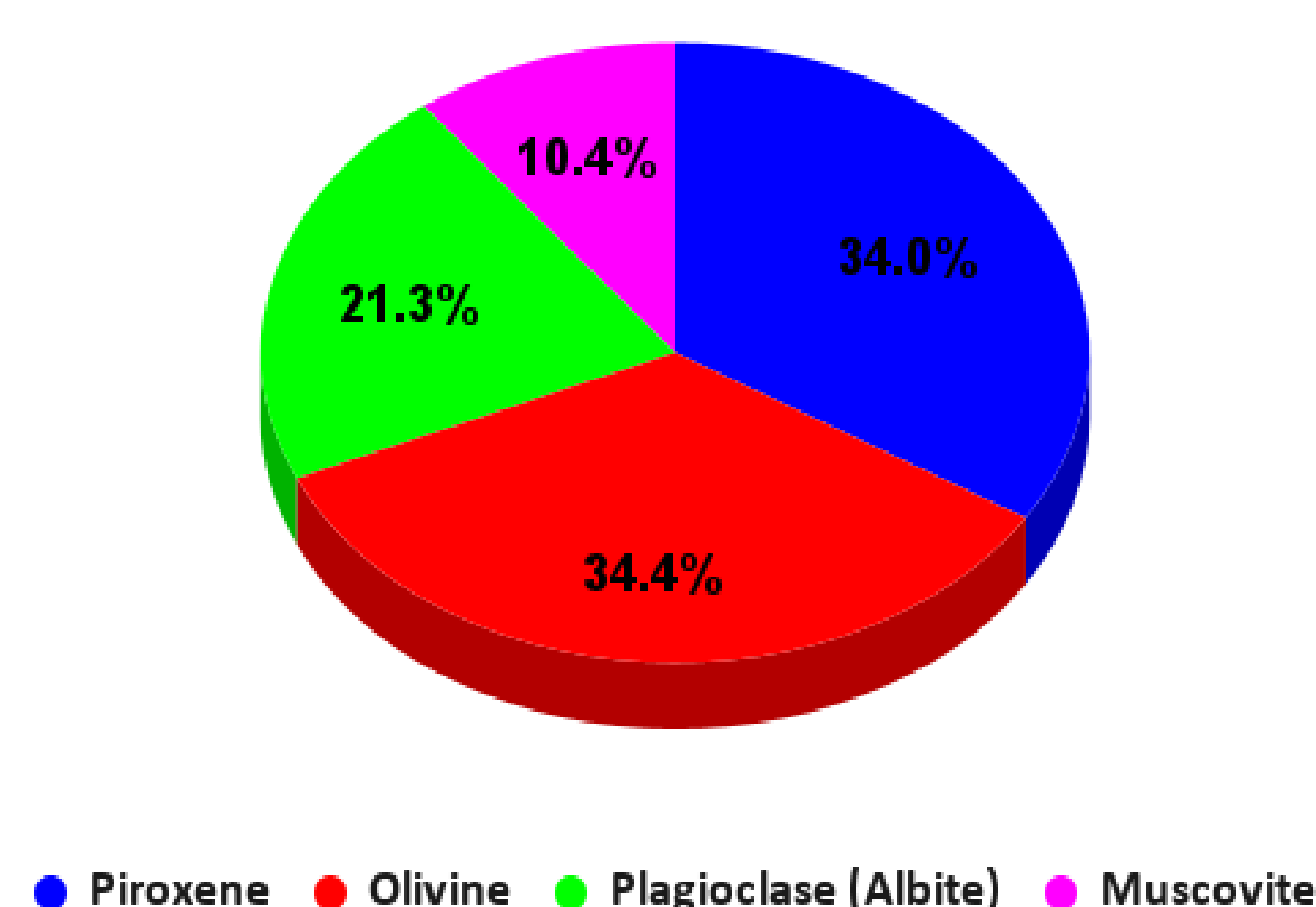
- The Scanning Electron Microscope coupled with elementary microanalysis (SEM / EDS);

The adsorption was batch performed in 250 mL Erlenmeyer flasks and the eluted solution was analyzed by the High-performance liquid chromatography (HPLC) system (Agilent Technologies 1200 series, USA) equipped with a Kinetex C18 100Å column (250 x 4.6 mm i.d., 5 μ m particle size) and a diode array detector (DAD), set at λ = 270 nm.



Batch filtration

a) Trimethoprim and b) Sulfamethoxazole



CONCLUSION

This study has highlighted and confirmed how the natural materials filtration process is adequate but not always wholly efficient. Preliminary tests revealed that this material was an excellent TMP adsorbent but not for SMX. The presence of metals like Fe and Al makes it capable of activating oxidizing agents such as sodium persulfate (PS). Indeed, experiments showed that the SMX was efficiently degraded under the test conditions. A systematic study must be performed to evaluate the influence of the most critical factors, such as initial antibiotic and PS concentrations, liquid-to-solid ratio, and reaction time, on the removal efficiency. Factor levels can be chosen to cover a range of values of practical interest. Statistical analysis can help to highlight the main effects and interactions between variables. Nonetheless, the results of this study suggest that the proposed approach could represent a valuable strategy for in-situ and ex-situ remediation of antibiotic-contaminated waters and soils.

Acknowledgements XPS data were provided by Dr. F. Langerame and Prof. A. M. Salvi at ESCA Laboratory, University of Basilicata.

REFERENCES

- Yang Y., Jiang J., Ma J., Liu G., Cao Y., Liu W., Li J., Pang S., Kong X., Luo C., 2017, Degradation of sulfamethoxazole by UV, UV/H₂O₂ and UV/persulfate (PDS): formation of oxidation products and effect of bicarbonate, *Water Research*, 118, 196-207.
- Seyama H., Soma M., 1985, *Journal of Chemical Society, Faraday Transaction 1: Physical Chemistry in Condensed Phase*, 81, 485-495.
- Wagner C.D., Passoja D.E., Hillery H.F., Kinisky T.G., Six H.A., Jansen W.T., Taylor J.A., 1982, *Journal of Vacuum Science and Technology*, 21, 933,
- Seyama H., Soma M., 1987, *Journal of Electron Spectroscopy and Related Phenomena*, 42, 1, 97-101.