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Natural Clay-Based Materials for the Removal of Antibiotics from Contaminated Water

Donatella Coviello[a], Janet B. García-Martinez[b], Roberto Buccione[c], Laura Scrano[d], Andres F. Barajas-Solano[b], Monica Brienza[c,*]

[a] Department of Engineering, Università Parthenope di Napoli, Napoli, Italy
[b] Department of Environmental Science, Universidad Francisco de Paula Santander, Cùcuta, Colombia
[c] Department of Science, Università degli Studi della Basilicata, Potenza, Italy
[d] Department of European and Mediterranean Cultures, Università degli Studi della Basilicata, Matera, Italy
monica.brienza@unibas.it

The release of antibiotics into the environment has increased remarkably due to the extensive use of these pharmaceuticals worldwide. Sulfamethoxazole (SMX) and trimethoprim (TMP), two antibiotics proposed in the 3rd Watch List (WL) under the Water Framework Directive (Directive 2000/60/EC) and often prescribed together, were selected as representative pollutants. This study investigates volcanic soil collected from Monte Vulture (PZ, Italy) as a material tested to remove SMX and TMP from wastewater. XRD showed that volcanic soil was composed of 33.95 % pyroxene, 34.41 % olivine, 21.25 % albite, and 10.39 % muscovite. Preliminary tests revealed that this material was an excellent adsorbent of TMP but not of SMX. The presence of metal like Fe and Al makes it capable of activating oxidizing agents such as potassium peroxymonosulfate (PMS). In fact, experiments showed that the SMX was efficiently degraded under the test conditions. Additionally, a systematic study was performed to evaluate the influence of the most critical factors, such as initial antibiotic concentrations, liquid-to-solid ratio, and reaction time on the removal efficiency. The range of levels evaluated for each factor was selected according to the level of information they can provide. A central composite design coupled with response surface methodology was used. From a statistical analysis of the results, the main effects and interactions between variables were estimated. A polynomial model was also developed and validated to provide a mathematical description of the removal process. Overall, 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.

1. Introduction

Environmental pollution by emerging contaminants is one of the hot spot problems. Many pollutants released into the environment are very easily found in aquatic compartments, both in drinking water (Benotti et al., 2009) and in wastewater (Pascale et al., 2020). Major pollutants include heavy metals, organic micropollutants, personal care products, and pharmaceuticals (Nielsen and Bandosz, 2016). Among the latter, two of the most detected compounds are trimethoprim and sulfamethoxazole (Figure 1). The first one is a synthetic antimicrobic molecule belonging to diaminopyrimidine class (Wróbel et al., 2020). The second one is an antimicrobic belonging to the sulphonamides family and acts as a competitive inhibitor of the enzyme dihydropteroate synthase (Gupta et al., 2013). The persistence of these hazardous compounds in the environment is very concerning because trace levels, such as μg/L (Nielsen and Bandosz, 2016), can promote the formation of antibacterial resistance genes (Yang et al., 2017). Considering their potential impacts on environment and health, additional treatments have to be applied to drastically reduce the load of such molecules in dis-charged effluents and best achieve non-detectable concentrations. Several technologies have already proven to be effective for this purpose. Among the most cited appear activated carbon adsorption as well as advanced oxidation processes. In the last decade, hybrid configurations (adsorption/oxidation) has been extensively studied for the degradation of organic compounds. Recently, a hybrid process of classical adsorption of

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pollutants on a fixed bed of activated carbon followed by batch wet catalytic oxidation at higher temperature and pressure on the same bed of activated carbon, which is then regenerated in situ, has been also evaluated for the remediation of phenols. The drawback of the mentioned technologies is the high cost and the low applicability at large scale. However, natural-based solutions can be a promising alternative. In this context, the present paper has two objectives related to the remediation of selected antibiotics: first, to characterize the natural soil from Mt Vulture volcano (Basilicata, Italy); second, test its capacity to adsorbed/oxidate contaminants.

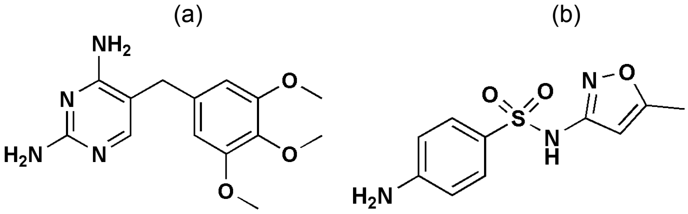

Figure 1: Chemical structure of a) trimethoprim and b) sulfamethoxazole

Experimental work on the oxidative process is still in progress and is focused on degradation by sulphate radicals activation to remove sulfamethoxazole. Laboratory batch experiments were (and are) performed in order to study adsorption kinetics.

2. Materials and methods

Analytical grade standards of trimethoprim, sulfamethoxazole (purity <=100 %) and potassium peroxymonosulfate, with the commercial name of Oxone ® (PMS, $KHSO_5$, 0.5 $KHSO_4$, 0.5 K_2SO_4), were purchased from Sigma Aldrich (St. Louis, USA). For chemical analysis acetonitrile and formic acid were HPLC grade from Honeywell (Wabash, Indiana, US). Water was ultrapure Milli-Q grade (18.2 MΩ cm^{-1} resistivity at 25 °C). Stock solutions 1,000 mg/L were prepared in methanol (LC-MS grade) provided by Carlo Erba reagents (Milano, Italy). The natural soil adsorbent used within this work is from Mt. Vulture volcano (Basilicata, Italy) was characterized by XRPD and XPS analysis.

2.1 XRPD analysis

X-ray powder diffraction (XRPD) analysis was carried out by diffractometer (X'Pert PW3040, Philips) with Cu-Kα radiation and a 40 kV, 30 mA, and 0.02 ° (2θ) step size setup. Prior to analysis, the sample was finely ground and, finally, placed on the slide for analysis.

2.2 XPS analysis

XPS analysis was carried out by spectrometer (Phoibos 100- MCD5, SPECS) operating at 10 kV and 10 mA, in medium area (Ø=2 mm) mode, using achromatic MgKα (1,253.6 eV) radiation and a pressure in the analysis chamber higher than 10^{-9} mbar. Wide spectra were collected in fixed analyser transmission (FAT) with a constant pass energy of 20 eV and channel widths of 1.0.

2.3 Reaction grade determination

The reaction grade determination analysis was carried out by measuring the pH of a suspension soil – water and soil – KCl solution. 10 g of soils were placed in a 50 mL Falcon tube and then 25 mL of distilled water or KCl 1 M solution were added. Falcon tubes were left under stirring for two hours and then the pH was measured.

2.4 HPLC-DAD analysis

The concentration of trimethoprim and sulfamethoxazole was monitored by a 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 µm particle size) and a diode array detector (DAD), set at λ = 270 nm. The mobile phase consisted of biphasic gradient using water acidified with 0.1 % formic acid (A) and acetonitrile (B), structured as follows: 0-2 min 100 % A, 2-3 min. from 100 % A to 60 % A, 3-8 min 60 % A, 8-9 min. from 60 % A to 0 % A, 9-12 min 0 % A, 12-15 min from 0 % A to 100 % A and finally, 15-18 min 100 % A.

2.5 Batch adsorption and catalytic degradation experiments

Batch adsorption experiments were carried out whit different solid-to-liquid ratio in flasks containing 100 mL of liquid solutions at different concentration of trimethoprim (TRM); they were continuously mixed with magnetic

stirrer. The initial and final concentrations of TRM were measured regularly for each experiment. The equilibrium experiments were performed by stirring 100 mL of TRM solution with initial concentration of 4 mg/L as optimum condition. The aqueous samples were taken at fixed times. After adsorption, the adsorbent samples were separated by filtration at 0.2 µm, and the supernatants were analysed for residual TRM by HPLC-UV.
Preliminary, batch oxidative processes were performed in 100 mL of solution containing SMX 5 mg/L and 800 µM of PMS as oxidant agent. The amount of adsorbent material was 28.2 g.

3. Results and discussion

3.1 Characteristics of volcanic soil

Mt. Vulture volcano is a large volcano of post-Calabrian age, located near the western edge of the Bradanica trench in Southern Apennine chain, Basilicata, Italy (Fiore et al., 1992). Inside the crater of a minor cone, there are the two natural lakes of Monticchio (Basilicata). Soil present in this area have different characteristics, many of them exhibiting andic properties and is the largest hydrocarbon reservoir in continental Europe (Gizzi et al., 2029). The XRPD analysis indicates that the volcanic soil contains pyroxene (34.0 %), olivine (34.4 %), plagioclase (21.3 %) and muscovite (10.4 %) and that chemical composition is mainly by SiO_2, Al_2O_3, Fe_2O_3 with lower presence of MgO and K_2O. This XRPD analysis also identified that pyroxene phase consists of Augite, while Olivine one of Forsterite and Fayalite. The two Olivine phases detected in the samples are not totally pure (they are very rare in nature) but they are intermediate phases between the two pure phases Forsterite Mg_2SiO_4 and Fayalite Fe_2SiO_4. 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) (Table 1). The signal Si 2p (103.6 eV), that according to Wagner et al. (1982), is attributable to pyroxene. 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).

Table 1: Results of XPS analysis

Element	eV	Reference	
Si 2s	153.6	Seyama H, 1985	olivine, piroxeno
Si 2p	103.6	Wagner C.D., 1982	piroxeno
Mg 2s	93.6		
Al 2s	128.6		
Al 2p	74.0	Seyama H, 1985	piroxeno
Fe2p	710.6	Seyama H., Soma M., 1987	olivina
Ca 2p	353.6		
K 2p	303.6		
O1s	553.6		
O2s	33.6		

3.3 Reaction grade determination

Evaluating the reaction grade parameter is critical because it can indicate the cation exchange capacity by conditioning the property of the soil to retain cations by adsorption. This method is very suitable for the characterization of andisols (Violante and Adamo, 2000), such as volcanic soil used in this work. The results obtained show that in water the pH is 8.1, which classifies the soil as moderately alkaline, while in KCl, a pH of 6.6 will be recorded. This lowering of pH is compatible with a high presence of ion exchange sites in the samples. Sulfamethoxazole is a very polar molecule in which we have a delocalized negative charge on the sulfonyl group and the presence of this group could explain why this molecule does not adsorb on the natural material.

3.4 Effect of contact time

The effect of contact time on the rate of removal of trimethoprim was investigated. In batch adsorption experiment, all of the parameters except contact time, including solid/liquid ratio (0.02 ÷ 0.04 g/mL), agitation speed (450 ÷ 750 rpm), initial contaminant concentration (4 ÷ 8 mg/mL), were kept constant. The effect of contact time on trimethoprim adsorption efficiency was showed in table 2. From the data shown in the table, it can be seen that the variation in contact time is closely related to molecule concentrations. Indeed, while at a concentration of TRM 4 mg/L, all other parameters being constant, the variation of contact time determines a variation of absorption ranging from 7 to 13.21 %, while at a concentration of 8 mg/L it is registered a variation ranging from 4.3 to 15.28 %. In a more evident way, it can be observed that at a concentration of 6 mg/L a variation of 30 min of adsorption time determines a variation of 36 % of adsorbed molecule.

Table 2: Effect of contact time on the rate of removal of trimethoprim

C_0 (mg/L)	v (rpm)	t (minutes)	Solid/Liquid (g/mL)	% of adsorption
4	450	20	0.02	51.66
4	450	50	0.02	62.17
4	750	20	0.02	56.52
4	750	50	0.02	69.73
4	450	20	0.04	64.26
4	450	50	0.04	72.95
4	750	20	0.04	65.08
4	750	5	0.04	72.08
6	600	5	0.03	34.87
6	600	35	0.03	70.81
6	600	65	0.03	75.75
8	450	20	0.02	44.08
8	450	50	0.02	59.15
8	750	20	0.02	52.44
8	750	50	0.02	56.74
8	450	20	0.04	56.58
8	450	50	0.04	69.94
8	750	20	0.04	57.86
8	750	50	0.04	73.14

3.5 Catalytic oxidation in the adsorption processes

The natural presence of metals into the natural adsorbent allows the material to exhibit excellent capacity to be used for catalytic applications. During the adsorption processes, a known amount of PMS (800 µM) was added into the reaction systems with 4 mg/L of sulfamethoxazole. Benefiting from the effective transfer of electrons on volcanic soil/PMS, the degradation rate of SMX was significantly faster than its adsorption rate and its oxidation by Fenton processes. The blank test showed that 43 % of the SMX was removed from water using only PMS or Fenton like process (PMS/Fe). It can be seen from Figure 2 that SMX degradation rate in the volcanic soil/PMS was efficient and could be completely removal within 2 h.

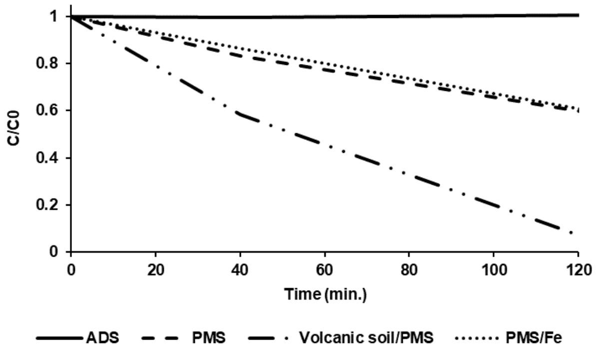

Figure 2: Sulfamethoxazole degradation profiles in the adsorption process using Fenton like oxidation based on PMS activation

4. Conclusion

The application of natural based material for the removal antibiotics from contaminated water was successfully investigated using abundant available low-cost adsorbents. Preliminary results shows that the tested volcanic soil is an effective adsorbent for the removal of trimethoprim from aqueous solutions. Batch adsorption experiments showed that volcanic soil was efficient to remove trimethoprim, but did not show any appreciable ability in taking out sulfamethoxazole. In contrast, its ability to activate oxidant agent such as peroxymonosulfate demonstrate to be very effective in oxidation of sulfamethoxazole.

The results of the tests carried out on this innovative material are very encouraging. Obviously, as these are preliminary studies, it is necessary to investigate variables such as treatable pollutants, interferences, conditions (pH, temperature, pollutant concentration, etc.), optimal dosages as well as the engineering solutions to be adopted in order to ensure its safe use in real-scale plants. Additionally, experiments are scheduled to test the natural activation of different oxidant agents; it would be interesting to extend the ability of this natural material as a potential disinfection treatment.

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