



# Analysis of sulfamethoxazole and trimethoprim adsorption on sewage sludge and fish waste derived adsorbents



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## ABSTRACT

Sewage sludge, fish waste, and mixtures of the two were pyrolyzed at 650 and 950 °C in order to convert them into stable adsorbents. To test their performance in the removal of pharmaceuticals from water, sulfamethoxazole (SMX) and trimethoprim (TMP) were chosen as model adsorbates. Adsorption isotherms were measured in batch adsorption tests at room temperature. The adsorbents prepared at 950 °C were more effective than those obtained at 650 °C. Even though both pharmaceuticals were adsorbed in the highest amount on the material composed of pyrolyzed fish waste, for TMP removal the composite obtained from 90% sewage sludge and 10% fish waste was equally effective. To elucidate the adsorption mechanism, detailed surface analyses by TA-MS, XRD and potentiometric titration were carried out. Favorable surface chemistry seems to be the factor governing the performance of these adsorbents as media for the pharmaceuticals' removal from an aqueous phase. The main adsorption mechanism is based on chelation, acid-base interactions and polar interactions with the inorganic phase.

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## 1. Introduction

Tandem with industrialization, a growing problem of environmental pollution has developed worldwide. Much of the contamination ultimately accumulates in aquatic systems, and has been detected in both drinking and wastewater [1,2]. These water sources require remediation from pollutants including heavy metals [3], dyes [4], personal care products [5], agricultural by-products such as pesticides [6], endocrine disrupting compounds [7] and pharmaceuticals [8]. Of the latter group, two of the most commonly detected pharmaceuticals in wastewater are sulfamethoxazole (SMX) and trimethoprim (TMP) [9–11]. Both are bacteriostatic antibiotics, which are often detected simultaneously, likely due to their administration in combination. The removal efficiency of these substances in wastewater treatment facilities varies greatly depending on the treatment processes employed (for a thorough review see Ref. [12]). The chronic exposure that results from low removal efficiency can lead to the development of antibiotic resistance, and therefore an improvement in removal technologies is a priority. The concentration of TMP in waste is reported to be between 0.66 and 0.71 µg/L and that of SMX can reach 2 µg/L

[13,14]. The removal efficiencies are reported to be between 24 and 36% for SMX and between 69 and 92.5% for TMP [10,15].

Current technologies for water remediation include: membrane filtration (including bioreactors, reverse osmosis and nanofiltration) [16], sand filtration [17], ozonation [18], and adsorption [19,20]. The most common method in the latter category is that based on activated carbons as adsorbents. They are effective due to their high surface area and porosity [21]. To produce carbonaceous and well-performing adsorbents for a pollutant removal many precursor materials have been used including coirpith [22], rice husk [23], rubber tires [24], olive pits and walnut shells [25], and PET [26]. Thus the raw materials from which adsorbents can be produced are numerous and diverse. Ultimately, what must be taken into account is the feasibility of producing such materials by considering the technological requirements for a production, local availability of the precursor materials, and very importantly, a cost effectiveness. Adsorbents produced from wastes have the double benefit of preventing the accumulation of an undesired material, and of introducing an economically feasible alternative of an environmental technology. To that end, the present study focuses on the repurposing of waste from the treatment of sewage at wastewater plants, as well as waste from a fish consumption market.

The sewage sludge that is formed as a by-product of the sewage treatment process can be carbonized and in this form used

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successfully as an adsorbent for the removal of pollutants such as H<sub>2</sub>S [27], dye [28], and phenol [29]. A combination of the organic and inorganic phases yields adsorbents with a unique surface chemistry. To further add diversity to the surface features, fish waste (originating from consumption) was used as a second component in our adsorbents. The fish bones are rich in calcium and phosphorus (mainly in the form of hydroxyapatite, Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>), which have proven to be effective pollutant adsorbents [30,31]. Moreover, our previous work has shown that the sewage and fish wastes may react synergistically to form an adsorbent with characteristics that are beneficial for the removal of carbamazepine from an aqueous phase [32].

While porosity and surface area are important factors governing the adsorption capacity of a material [33], the surface chemistry has been shown to play a more crucial role in the adsorption of carbamazepine on sewage and fish-waste based materials [32]. The adsorbent's surface groups can be modified applying various synthesis routes. A pyrolysis temperature impacts the oxygen-containing surface groups of the carbon phase, such as lactone, phenol, carboxyl, quinone, and carbonyl groups [34], which are known to control the acidity/basicity of the carbonaceous adsorbents [35]. These groups might be important for a reactive adsorption process. Besides affecting surface groups on the carbon phase, a pyrolysis temperature also determines the chemistry and microstructure of the inorganic phases of composite adsorbents [36].

Based on the above, the objective of this study is to investigate the effectiveness of the sewage sludge/fish waste mixture to remove sulfamethoxazole and trimethoprim from an aqueous phase (pure water), and to examine the role of the adsorbents' surface features in the removal process of these specific micro-pollutants. The concentrations of these pharmaceuticals in water in our experiments ranges from 1 to 100 mg/L and they do not undergo chemical reaction/photolysis in water solution under our experimental conditions. Applying these waste materials for the adsorbents' production might help to minimize municipal wastes and to solve environmental pollution problems. Their costs of production, estimated based on the energy consumption and large-scale production, is about USD 5/Kg, which is in the price range of general purpose activated carbons.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Adsorbent preparation

Sewage sludge (New York City Department of Environmental Protection) and fish waste (from a local fish market) adsorbents were prepared as reported previously [32]. In brief, materials were dried (120 °C), homogenized and carbonized individually, as well as in composites with ratios of sewage sludge to fish waste of 50:50, 75:25, or 90:10. The precursor materials and their mixtures were carbonized at two distinct temperatures, 650 °C and 950 °C, in a nitrogen atmosphere at a heating rate of 10 °C/min, with a holding time of 1 h. Materials were named so that the percentage of sewage sludge (S) is followed by the percentage of fish waste (F), and finally the pyrolysis temperature is indicated by I (for 650 °C) or II (for 950 °C). For example, a sample that contains 90% sewage sludge and 10% fish waste, and pyrolyzed at 650 °C is referred to as S90F10-I. The particle sizes of all samples were between 25 and 600 μm.

#### 2.1.2. Adsorbates

The sulfamethoxazole and trimethoprim (Fig. 1) (Chem-Impex International Inc. Wood Dale, IL) used in this study have a purity of >99%.

### 2.2. Methods

#### 2.2.1. Thermal analysis/mass spectroscopy

Thermal analysis was carried out on TA instrument thermal analyzer (SDT Q600). Before the analyses the samples were exposed to either deionized water (control), or an aqueous solution of pharmaceuticals, and then dried at 120 °C for 24 h. About 30 mg of each material was heated up to 1000 °C, at a rate of 10 °C/min in a helium atmosphere (flow 100 mL/min). Analyses were carried out up to the pyrolysis temperatures. The weight loss was recorded and from the TG curves the differential thermogravimetric (DTG) curves were obtained.

Simultaneously with the weight loss measurements, the off-gases from the samples were analyzed by a ThermoStar Gas Mass Spectrometer (GSD; Pfeiffer Vacuum), which was connected to the TA instrument. Thermal profiles of m/z detected in the off-gases were obtained.

#### 2.2.2. Potentiometric titration

A DMS Titrand 888 automatic titrator (Metrohm) was used for potentiometric titration experiments. The initial samples (0.05 g) were either in contact with deionized water (20 mL) to serve as a control for the spent samples (0.05 g), or exposed to a sulfamethoxazole or trimethoprim (20 mL) solution. The initial and spent samples were dried (120 °C), dispersed in 25 mL of 0.1 M NaNO<sub>3</sub>, and stirred under a N<sub>2</sub> atmosphere (to prevent interference of atmospheric CO<sub>2</sub>) until the pH stabilized. HCl (0.1 M) was used to titrate the samples from their initial basic pH until pH 3. The experimental data was transformed into proton binding curves (Q), which were deconvoluted into continuous pK<sub>a</sub> distributions of surface groups by using the SAEIUS method [37].

#### 2.2.3. X-ray diffraction

The powdered samples (~0.3 g) were analyzed on a Phillips X'Pert X-ray diffractometer with CuK<sub>α</sub> radiation (voltage –40 kV, current –40 mA). Crystallographic phase identification was completed with X'PERT Highscore Plus.

#### 2.2.4. DRIFT spectroscopy

Diffuse Reflectance Infrared Fourier Transform spectroscopic (DRIFTS) analyses were carried out on a Nicolet magna-IR 830 spectrometer. Adsorbent samples (5%) were mixed with spectroscopic grade KBr and finely ground in a mortar. The samples were measured against a KBr background. 32 scans at a resolution of 4 were collected. The reflectance spectra were expressed in Kubelka–Munk units.

#### 2.2.5. Evaluation of porosity

Nitrogen adsorption isotherms of the initial samples, and those used for adsorption of pharmaceuticals, were measured at –196 °C on ASAP 2020 (Micromeritics). Prior to measurements, the samples (about 0.15 g) were heated at 120 °C and out-gassed until 10<sup>–4</sup> Torr was reached. The BET surface area, total pore volumes, V<sub>t</sub> (from the last point of isotherm at relative pressure equal to 0.99), and micropore volume, V<sub>mic</sub> (from DR equation), were calculated from the isotherms.

#### 2.2.6. Adsorption of pharmaceuticals

Adsorption kinetics were determined by dispersing 0.1 g of adsorbent (particle size between 25 and 600 μm) in 20 mL of pharmaceutical solution (100 mg/L). The suspensions were placed in a shaker bath (100 rpm at 30 °C). Samples were filtered at time points 0–72 h, and the concentration of the remaining pharmaceutical in the filtrate was determined by high-performance liquid chromatography (Waters 2695) with a LiChroCART C18 column.

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