Exploring Sewage Sludge/Fish Waste-Based Materials As Adsorbents Of Pharmaceuticals From Water Phase

Lilja Nielsen
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EXPLORING SEWAGE SLUDGE/FISH WASTE-BASED MATERIALS AS ADSORBENTS OF PHARMACEUTICALS FROM WATER PHASE

By Lilja Nielsen

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY

From the program in EARTH AND ENVIRONMENTAL SCIENCES

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2016
This dissertation, entitled “Exploring sewage sludge/fish waste-based materials as adsorbents of pharmaceuticals from water phase”, presented by Lilja Nielsen has been read and accepted by the Graduate Faculty in Earth and Environmental Sciences to satisfy the dissertation requirement for the degree of Doctor of Philosophy.

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Abstract

EXPLORING SEWAGE SLUDGE/FISH WASTE-BASED MATERIALS AS ADSORBENTS OF PHARMACEUTICALS FROM WATER PHASE

By Lilja Nielsen

Adviser: Dr. Teresa J. Bandosz

In an effort to enable wastewater treatment that is more economical and environmentally friendly, alternative adsorbents composed of sewage sludge and fish waste were tested for the removal of pharmaceuticals from aqueous phase. Sewage sludge, fish waste and their homogenized mixtures (90:10, 75:25, 50:50) were carbonized at two temperatures (650 and 950 °C). The obtained materials were extensively characterized in terms of their chemistry and porosity. Adsorption isotherms were used to determine adsorption capacity for 3 model pharmaceuticals: carbamazepine, sulfamethoxazole, and trimethoprim. To simulate the complex environment in the wastewater treatment plant, the adsorption capacity for a multi-component solution, containing equal amounts of all 3 pharmaceuticals was also determined. To elucidate the surface changes during adsorption, analysis by TA-MS, XRD, FT-IR, XRD, SEM and potentiometric titration were conducted. The higher carbonization temperature led to the better performing material, and the composite materials demonstrated a synergistic effect. Amongst the 950 °C carbonized materials, adsorption performance varied by pharmaceutical, as the mechanism of adsorption depended on the characteristics of the pharmaceutical and its interaction with the specific surface chemistry. Although carbamazepine adsorbed in the highest quantity from both single and multi-component solutions, the amount adsorbed decreased for all pharmaceuticals from multi-component solution.
Acknowledgements

There are many to whom I owe a debt of gratitude during the course of my PhD process…

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I would also like to thank Dr. Urs Jans for his patience and guidance in the world of HPLC analysis, and his challenging comments that incented me to improve my work. And to Dr. Michal Kruk, who on multiple occasions took the long ride from Staten Island to City College without complaint. I thank heartily for his insights, especially with regard to my material characterization.

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8.16 Comparison of FTIR spectra for WVA, initial and after TMP adsorption

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<th>Description</th>
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</tr>
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</tr>
<tr>
<td>8.21</td>
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<td>8.22</td>
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</tr>
<tr>
<td>8.23</td>
<td>Total numbers of groups detected on the surface of the commercial carbons by potentiometric titration; initial, exposed to the single pharmaceuticals and to the multi-component solution</td>
</tr>
<tr>
<td>8.24</td>
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</tr>
<tr>
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</tr>
<tr>
<td>8.26</td>
<td>Reactions of amine groups with surface carboxylic acids</td>
</tr>
<tr>
<td>8.27</td>
<td>Reactions of carbonyl/quinone/phenol groups with amine moieties</td>
</tr>
</tbody>
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1. Introduction

1.1 Pharmaceuticals in the aquatic environment
Growing populations worldwide have put a strain on the delicate environmental balance, especially the limited supply of freshwater. The discharge of compounds produced by industrial, agricultural, household, and medical practices into aquatic systems has resulted in the dispersal and persistence of such compounds ecosystem-wide, without full recognition of the associated risks. Amongst the classes of compounds detected are anti-corrosives, deodorizers, fragrances, plasticizers, insecticides, detergents, fire retardants, cosmetics, solvents, and veterinary and human pharmaceuticals, which belong to the pharmaceutical and personal care products (PPCPs) group of micropollutants, that are being investigated for their potential ecological harm [1, 2]. However, of particular concern are the pharmaceuticals, which are a numerous and varied class, that are grouped by biological activity, chemical structure, or mode of action, and include: anti-inflammatory, anticonvulsants, antibiotics, antidepressants, statins, contraceptive hormones, β-blockers, lipid regulators, etc. [1, 3]. It is estimated that antibiotics alone are consumed at a worldwide level of up to 200,000 tons per year [4]. Not only are the parent compounds numerous, but their metabolites and other transformation products have also been detected, primarily in outflow from hospitals, residences, and veterinary practices [3]. The diversity of the compounds represents a challenge for the wastewater treatment plants (WWTP), and as such they have been singled out as the main point source of pharmaceutical transfer to the aquatic environment [3]. During water treatment, the large number of intermediate compounds that form can degrade differently depending on the wastewater regimen (See Fig. 1.1 for a general schema of wastewater treatment). Additionally, based on the analysis of water treatment plant influent, pharmaceuticals generally occur in mixtures [2], which further complicates the treatment process. Currently WWTP are not able to effectively remove such substances before the treated
water is released to the receiving waters, leading to the detection of residual pharmaceuticals in both WWTP effluent [5-8] and in drinking water [9-11]. The contaminated water can have adverse health effects despite the fact that many of residual pharmaceuticals are detected in the ng to μg/L concentration range [12]. The majority of studies conducted have been of an acute exposure [13], however there is also clear evidence that a low concentration chronic exposure can also negatively impact organismal health [14-16]. Even at the ng/L level some pharmaceuticals have been linked to reproductive impairment [17], and to alterations in endocrine and immune function [18-20]. With antibiotics, there is the additional concern of causing resistance in bacterial populations, rendering antibiotic compounds ineffective in the future [21].

Wastewater treatment generally involves a 3-step process. Preliminary treatment involves screen removal of large debris and grit removal that allows heavier particles to settle, followed by primary treatment in which sludge settles and less dense fats are skimmed from the top. Secondary treatment involves a biological phase in which water is passed over a bacterial film, and may involve a nitrification or nutrient removal step. Tertiary treatment does not exist in all plants, but can include treatments such as sand filtration, carbon adsorption, and disinfection.

Fig. 1.1. Schematic diagram of wastewater treatment plan (diagram generated based on information from: [6, 22, 23]).
1.1.1. Background on carbamazepine, sulfamethoxazole and trimethoprim

Only in the past two decades has technology enabled the detection of pharmaceuticals at the low ng/L environmental levels [1, 24]. Since then it has become apparent that certain pharmaceuticals are consistently detected in ground, surface and drinking water samples. Amongst the most frequently detected substances are carbamazepine (CBZ), sulfamethoxazole (SMX) and trimethoprim (TMP). SMX and TMP are commonly co-administered [25], thus their simultaneous detection is expected. Benotti et al. [11] analyzed samples from 19 US water utility plants for 51 compounds, and Kolpin et al. [1] for 95 compounds in 139 stream sites. Both studies consistently found that CBZ, SMX and TMP were amongst the most often present pharmaceuticals in the aqueous environment. This trend holds true on a global scale as well, as can be seen in the results collected in Tables 1 – 3, which show average detections of CBZ, SMX and TMP in the wastewater treatment plant (WWTP) at 92, 83 and 90%, respectively. The selection of these three pharmaceuticals as model adsorbates in the current study is therefore based on the ubiquitous presence of these species, and thus the urgent need to study and optimize their removal from wastewaters.

Fig. 1.2. shows the structure and properties of the three model adsorbates, CBZ, SMX, and TMP. CBZ is used for the treatment of epilepsy, seizures, and more recently for psychiatric treatments of schizophrenia and bipolar disorder [26]. Annual worldwide consumption of CBZ was estimated to be 1014 tons in 2008, and of the CBZ consumed 72% is absorbed and the other 28% is discharged unchanged in feces [27]. SMX and TMP are bacteriostatic antibiotics that are usually co-administered in a 5:1 ratio for a synergistic inhibition of folic acid synthesis [25], and used for the treatment of ear, venereal, urinary, respiratory, and gastrointestinal tract infections, and recently as prophylaxis for HIV patients [28]. Consumption quantities of SMX and TMP are
more scarce, however data from 1987 indicates their usage at 561 tons annually for USA, Japan, Germany, UK, Italy and Brazil combined [29]. Influent to the wastewater treatment plant contained TMP and SMX in their unmetabolized form at a frequency of 60 and 15 %, respectively [30].

![Fig. 1.2. Structure and properties of carbamazepine, sulfamethoxazole, and trimethoprim](image)

<table>
<thead>
<tr>
<th></th>
<th>Carbamazepine</th>
<th>Sulfamethoxazole</th>
<th>Trimethoprim</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>( C_{13}H_{12}N_2O )</td>
<td>( C_{10}H_{11}N_3S )</td>
<td>( C_{14}H_{12}N_4O_3 )</td>
</tr>
<tr>
<td>Therapeutic class</td>
<td>anticonvulsant</td>
<td>antibiotic</td>
<td>antibiotic</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>236.27 g</td>
<td>253.28 g</td>
<td>290.32 g</td>
</tr>
<tr>
<td>Melting point</td>
<td>190 °C</td>
<td>170-172 °C</td>
<td>197-200 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>411 °C</td>
<td>482 °C</td>
<td>526 °C</td>
</tr>
<tr>
<td>( pK_a )</td>
<td>13.9</td>
<td>1.6, 5.7</td>
<td>7.1</td>
</tr>
<tr>
<td>( \log K_{ow} )</td>
<td>2.45</td>
<td>0.89</td>
<td>0.91-1.26</td>
</tr>
</tbody>
</table>

1.1.2. Detection and removal of selected adsorbates

Tables 1.1 - 1.3 additionally indicate the concentrations of the target compounds detected in the influent and effluent from wastewater treatment plants, as well as the removal efficiency of the treatments. In some instances, a higher concentration of the substance can be detected in the effluent than in the influent. This is due to pharmaceuticals that are to some degree excreted as metabolites, and then during water treatment are transformed back to the original substance [30]. The efficiency of WWTPs to remove SMX and TMP is less than 50% on average (Tables 1.2 and 1.3) after conventional treatment with activated sludge (CAS), and for CBZ no significant removal was reported after CAS in any of the studies (Table 1.1). The low removal efficiency of CBZ can be linked to the somewhat hydrophilic nature of the compound (\( \log K_{ow} < 3 \)) and its
resistance to biodegradability [31]. WWTPs with advanced tertiary treatments demonstrated improved removal rates when technologies such as reverse osmosis, adsorption on activated carbon, and ozonation were employed. However, many plants worldwide lack this type of technology, and the necessary funds to implement these practices, despite the clear need to implement cost effective strategies for better contaminant removal.

Table 1.1. WWTP detection and removal efficiency of carbamazepine

<table>
<thead>
<tr>
<th>WWTP location</th>
<th>FOD (%)</th>
<th>Influent (ng/L)</th>
<th>Effluent (ng/L)</th>
<th>Removal Efficiency (%) with CAS</th>
<th>Additional removal % (treatment)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sweden</td>
<td>-</td>
<td>1680</td>
<td>1180</td>
<td>30 (P-R)</td>
<td></td>
<td>[32]</td>
</tr>
<tr>
<td>Germany</td>
<td>-</td>
<td>7</td>
<td>0</td>
<td>13 (MBR)</td>
<td></td>
<td>[33]</td>
</tr>
<tr>
<td>Spain</td>
<td>82</td>
<td>120 - 310</td>
<td>110 - 230</td>
<td>20 ± 15</td>
<td></td>
<td>[34]</td>
</tr>
<tr>
<td>Italy</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td>[5]</td>
</tr>
<tr>
<td>Austria</td>
<td>-</td>
<td>325 - 1850</td>
<td>465 - 1619</td>
<td>-43 to -3 (P-R)</td>
<td>-35 to 14 (MBR)</td>
<td>[35]</td>
</tr>
<tr>
<td>Spain</td>
<td>-</td>
<td>17 - 250*</td>
<td>12 - 180*</td>
<td>-200 to 77*</td>
<td></td>
<td>[36]</td>
</tr>
<tr>
<td>South Korea</td>
<td>86</td>
<td>42</td>
<td>226</td>
<td>-9 to -5 (MBR)</td>
<td></td>
<td>[37]</td>
</tr>
<tr>
<td>Austria</td>
<td>-</td>
<td>-</td>
<td>-9 to 35</td>
<td></td>
<td></td>
<td>[38]</td>
</tr>
<tr>
<td>Taiwan</td>
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<td>82 - 357</td>
<td>93 - 214</td>
<td>-26 (UV), 0 - 40 (Cl)</td>
<td></td>
<td>[39]</td>
</tr>
<tr>
<td>Switzerland</td>
<td>-</td>
<td>482 ± 586</td>
<td>461 ± 292</td>
<td>7.6 ±18 (P-R)</td>
<td>90 ± 9 (AC), 97 ± 4 (O3)</td>
<td>[40]</td>
</tr>
<tr>
<td>Japan</td>
<td>-</td>
<td>17 - 250*</td>
<td>12 - 180*</td>
<td>-200 to 77*</td>
<td></td>
<td>[31]</td>
</tr>
<tr>
<td>Japan</td>
<td>-</td>
<td>82</td>
<td>2 - 46</td>
<td>56 - 96 (SF), 60 - 98 (O3)</td>
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<td>[7]</td>
</tr>
<tr>
<td>South Korea</td>
<td>87 - 100</td>
<td>10 ± 10</td>
<td>5 ± 10</td>
<td>&lt;25</td>
<td>85 (SF + Cl)</td>
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<tr>
<td>EU</td>
<td>-</td>
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<td>100 - 1200</td>
<td>&lt;10 to 53</td>
<td>0 (P-R)</td>
<td>[42]</td>
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<td>-</td>
<td>225 - 275*</td>
<td>250 - 300*</td>
<td>&lt;10</td>
<td>&lt;10 (MBR)</td>
<td>[43]</td>
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<tr>
<td>France</td>
<td>-</td>
<td>640</td>
<td>&lt;30 (SF)</td>
<td>&gt;70 (RO, O3, AC)</td>
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<td>[44]</td>
</tr>
<tr>
<td>Germany</td>
<td>100</td>
<td>2247</td>
<td>2100</td>
<td>7 (P-R)</td>
<td></td>
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<tr>
<td>Germany</td>
<td>-</td>
<td>2000 ± 1300</td>
<td>2100 ± 700</td>
<td>0 (P-R)</td>
<td></td>
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<tr>
<td>Finland</td>
<td>-</td>
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<td>7 (SF), &gt;99 (SF + O3)</td>
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<tr>
<td>USA</td>
<td>92</td>
<td>191</td>
<td>186</td>
<td>85 (SF+AC+Cl)</td>
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<td>USA</td>
<td>-</td>
<td>189 - 199</td>
<td>161 - 281</td>
<td>16 (UF), 16 (AC), &gt;99 (MBR)</td>
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<td>N/A</td>
<td>N/A</td>
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<td>420</td>
<td>410</td>
<td>2</td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td>UK</td>
<td>100</td>
<td>104 - 3110</td>
<td>152 - 4596</td>
<td>-22 to 45*</td>
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Table 1.2. WWTP detection and removal efficiency of sulfamethoxazole

<table>
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<th>FOD (%)</th>
<th>Influent (ng/L)</th>
<th>Effluent (ng/L)</th>
<th>Removal Efficiency (%) with CAS</th>
<th>Additional removal % (treatment)</th>
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<td>20</td>
<td>70</td>
<td>-250 (P-R)</td>
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<td>310</td>
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<td>[51]</td>
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<tr>
<td>Spain</td>
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<td></td>
<td></td>
<td>99</td>
<td>[34]</td>
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</tr>
<tr>
<td>Spain</td>
<td>-</td>
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<td>250</td>
<td>60</td>
<td>[52]</td>
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<td>-</td>
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<td></td>
<td>24</td>
<td>[5]</td>
<td></td>
</tr>
<tr>
<td>Korea</td>
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<td>450</td>
<td></td>
<td>&gt;96</td>
<td>[53]</td>
<td></td>
</tr>
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<td>Austria</td>
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<td>24 - 145</td>
<td>18 - 91</td>
<td>-278 to 32 (P-R)</td>
<td>61 to 66 (MBR)</td>
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<tr>
<td>Switzerland</td>
<td>-</td>
<td>230 - 570</td>
<td></td>
<td>-138 to 60</td>
<td>70 to 90 (MBR)</td>
<td>[6]</td>
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<tr>
<td>Switzerland</td>
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<td>230 - 570</td>
<td>211 - 860</td>
<td>-274 to 63 (SF)*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Croatia</td>
<td>-</td>
<td>590</td>
<td>390</td>
<td>34*</td>
<td>[48]</td>
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<tr>
<td>USA</td>
<td>70</td>
<td>&lt;50 - 1250</td>
<td>&lt;50 - 370</td>
<td>18 to 100</td>
<td></td>
<td></td>
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<tr>
<td>UK</td>
<td>67 - 100</td>
<td>&lt;3 - 274</td>
<td>&lt;3 - 44</td>
<td>-20 to 73*</td>
<td></td>
<td></td>
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<tr>
<td>South Korea</td>
<td>57</td>
<td>194</td>
<td>136</td>
<td>64 - 70 (MBR), &gt;99 (RO)*</td>
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<td></td>
<td>33 to 91</td>
<td></td>
<td>[38]</td>
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<tr>
<td>Hong Kong</td>
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<td>147 - 356</td>
<td>15 - 47</td>
<td>68</td>
<td>96 (Cl)</td>
<td>[55]</td>
</tr>
<tr>
<td>Taiwan</td>
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<td>179 - 1760</td>
<td>47 - 964</td>
<td>26 to 56 (Cl), 88 (UV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sweden</td>
<td>-</td>
<td>&lt;80 - 674</td>
<td>&lt;80 - 304</td>
<td>42 (P-R)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Switzerland</td>
<td>-</td>
<td>340 ± 261</td>
<td>171 ± 127</td>
<td>38 ± 30 (P-R)</td>
<td>64 ± 25 (AC + UF), 93 ± 7 (O3)</td>
<td>[40]</td>
</tr>
<tr>
<td>France</td>
<td>-</td>
<td>180</td>
<td>&lt;30</td>
<td>&gt;70 (RO, O3, AC)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Japan</td>
<td>-</td>
<td>104</td>
<td>40</td>
<td>62</td>
<td>72 (SF), 96 (O3)</td>
<td></td>
</tr>
<tr>
<td>South Korea</td>
<td>60 - 100</td>
<td>8 ± 5</td>
<td>2 ± 2</td>
<td>3 - 27</td>
<td>73 (SF + Cl)</td>
<td>[41]</td>
</tr>
<tr>
<td>Luxembourg</td>
<td>-</td>
<td>13 - 155</td>
<td>4 - 39</td>
<td>75</td>
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<td>China</td>
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<td>5450 - 7910</td>
<td>&lt;100</td>
<td>&gt;98 (SF, Cl)</td>
<td></td>
<td>[58]</td>
</tr>
<tr>
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<td>-</td>
<td>210 - 800*</td>
<td>100 - 180*</td>
<td>56</td>
<td>61 (MBR)</td>
<td>[43]</td>
</tr>
<tr>
<td>Israel</td>
<td>-</td>
<td>298 ±93</td>
<td>N/A</td>
<td>29</td>
<td>60 (UF), 70 (MBR), 98 (RO)</td>
<td>[59]</td>
</tr>
<tr>
<td>USA</td>
<td>92</td>
<td>3</td>
<td>2</td>
<td>33</td>
<td>100 (SF+AC+Cl)</td>
<td>[46]</td>
</tr>
<tr>
<td>USA</td>
<td>-</td>
<td>426 - 1110</td>
<td>23 - 69</td>
<td>84 (AC), &gt;99 (MBR)</td>
<td></td>
<td>[47]</td>
</tr>
<tr>
<td>Germany</td>
<td>-</td>
<td>820 ± 230</td>
<td>620 ± 90</td>
<td>24 (P-R)</td>
<td></td>
<td>[22]</td>
</tr>
<tr>
<td>Australia</td>
<td>100</td>
<td>360</td>
<td>270</td>
<td>25</td>
<td></td>
<td>[8]</td>
</tr>
<tr>
<td>Australia</td>
<td>89</td>
<td>250</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>China</td>
<td>-</td>
<td>10 - 118</td>
<td>9 - 78</td>
<td>0 - 63 (UV/Cl)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>USA</td>
<td>-</td>
<td>1090</td>
<td>210</td>
<td>81 (Cl)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>China</td>
<td>-</td>
<td>72 - 284</td>
<td>N/A</td>
<td>51</td>
<td>76 (MBR)</td>
<td>[23]</td>
</tr>
<tr>
<td>Italy</td>
<td>-</td>
<td>246</td>
<td>46</td>
<td>81</td>
<td></td>
<td>[63]</td>
</tr>
</tbody>
</table>
Table 1.3. WWTP detection and removal efficiency of trimethoprim

<table>
<thead>
<tr>
<th>WWTP location</th>
<th>FOD (%)</th>
<th>Influent (ng/L)</th>
<th>Effluent (ng/L)</th>
<th>Removal Efficiency (%) with CAS</th>
<th>Additional removal % (treatment)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>-</td>
<td>210 - 7900</td>
<td>82 (Cl), 70 - 97 (SF, Cl), 77 (SF, UV)*</td>
<td>[64]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sweden</td>
<td>-</td>
<td>80</td>
<td>40 (Cl), 70 - 97 (SF, Cl), 77 (SF, UV)*</td>
<td>[32]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>USA</td>
<td>-</td>
<td>590</td>
<td>-40 to 20</td>
<td>15 to 74 (SF), 87 to 90 (MBR)</td>
<td>[6]</td>
<td></td>
</tr>
<tr>
<td>Switzerland</td>
<td>-</td>
<td>210 - 440</td>
<td>20 - 310</td>
<td>-48 to 95 (SF)*</td>
<td>[25]</td>
<td></td>
</tr>
<tr>
<td>Croatia</td>
<td>-</td>
<td>1172</td>
<td>290</td>
<td>15 to 74 (SF), 87 to 90 (MBR)</td>
<td>[48]</td>
<td></td>
</tr>
<tr>
<td>China</td>
<td>-</td>
<td>120 -320</td>
<td>120 - 230</td>
<td>-17 to 62</td>
<td>[65]</td>
<td></td>
</tr>
<tr>
<td>USA</td>
<td>-</td>
<td>140 - 1100</td>
<td>120 - 230</td>
<td>-11 (P-R)</td>
<td>[54]</td>
<td></td>
</tr>
<tr>
<td>UK</td>
<td>100</td>
<td>464 - 6769</td>
<td>385 - 3052</td>
<td>15 to 74 (SF, SF, UV)*</td>
<td>[49]</td>
<td></td>
</tr>
<tr>
<td>South Korea</td>
<td>71</td>
<td>21</td>
<td>58</td>
<td>40 to 68*</td>
<td>[37]</td>
<td></td>
</tr>
<tr>
<td>Hong Kong</td>
<td>-</td>
<td>129 - 161</td>
<td>49 (P-R)</td>
<td>93 (Cl)</td>
<td>[55]</td>
<td></td>
</tr>
<tr>
<td>Taiwan</td>
<td>-</td>
<td>259 - 949</td>
<td>203 - 415</td>
<td>35 (UV), 22 to 56 (Cl)</td>
<td>[39]</td>
<td></td>
</tr>
<tr>
<td>Sweden</td>
<td>-</td>
<td>99 - 1300</td>
<td>66 - 1340</td>
<td>3 (P-R)</td>
<td>[56]</td>
<td></td>
</tr>
<tr>
<td>Switzerland</td>
<td>-</td>
<td>235 ± 52</td>
<td>158 ± 73</td>
<td>94 ± 4 (AC + UF), 99 ± 2 (O3)</td>
<td>[40]</td>
<td></td>
</tr>
<tr>
<td>Japan</td>
<td>-</td>
<td>54</td>
<td>70</td>
<td>90 (SF, 99 (O3))</td>
<td>[7]</td>
<td></td>
</tr>
<tr>
<td>EU</td>
<td>-</td>
<td>N/A</td>
<td>&lt;10 to 40</td>
<td>0 (P-R)</td>
<td>[42]</td>
<td></td>
</tr>
<tr>
<td>UK</td>
<td>-</td>
<td>213 - 300</td>
<td>&lt;10 to 40</td>
<td>0 (P-R)</td>
<td>[66]</td>
<td></td>
</tr>
<tr>
<td>Israel</td>
<td>-</td>
<td>33 ± 27</td>
<td>55</td>
<td>66 (UF), 96 (MBR), 93 to 97 (RO)</td>
<td>[59]</td>
<td></td>
</tr>
<tr>
<td>USA</td>
<td>-</td>
<td>135 - 693</td>
<td>42 - 48</td>
<td>64 (AC), &gt;99 (MBR)</td>
<td>[47]</td>
<td></td>
</tr>
<tr>
<td>Germany</td>
<td>-</td>
<td>1100 ± 260</td>
<td>340 ± 80</td>
<td>69 (P-R)</td>
<td>[22]</td>
<td></td>
</tr>
<tr>
<td>Australia</td>
<td>100</td>
<td>340</td>
<td>50</td>
<td>85 (P-R)</td>
<td>[8]</td>
<td></td>
</tr>
<tr>
<td>Australia</td>
<td>100</td>
<td>430</td>
<td>10</td>
<td>98 (not specified)</td>
<td>[60]</td>
<td></td>
</tr>
<tr>
<td>China</td>
<td>-</td>
<td>N/A</td>
<td>N/A</td>
<td>19 (P-R)</td>
<td>[23]</td>
<td></td>
</tr>
</tbody>
</table>

Key to tables: conventional activated sludge treatment (CAS), phosphate reduction (P-R), disinfection with chlorine/sodium hypochlorite (Cl), adsorption on activated carbon (AC), sand filtration (SF), membrane bioreactor (MBR), MF (microfiltration), UF (ultrafiltration), reverse osmosis (RO), O₃ (ozonation). (*) indicates values calculated from figures.

1.1.3. Environmental risks of the selected adsorbates

Toxicity studies were conducted in order to understand the risk posed by environmental exposure to CBZ, SMX and TMP. The no observed effect concentration (NOEC), lowest observed effect concentration (LOEC), and half maximal effect concentration (EC₅₀) are included in Table 1.4, and serve to measure the risk to a variety of organisms after exposure to CBZ, SMX and TMP.
The duration of exposure is important, as it can be seen that chronic exposure generally resulted in higher toxicity than the acute exposure. This increase in toxicity can be seen in the water flea, *C. dubia*, as 50% mortality was provoked by 15.51 mg/L of SMX after 48 hours, but only 0.21 mg/L had the same result after 7 days of exposure. Inter-species sensitivity can also be noted, with a general trend of a diminished sensitivity in the larger organisms, such as fish. Using the LC50, it is possible to calculate a risk a quotient for each compound. To calculate the risk quotient first the predicted environmental concentration (PEC) must be determined as shown [67]:

$$\text{PEC}_w = \frac{A \times (100-R)}{365 \times P \times V \times D \times 100}$$

(1)

where A is the amount used (kg/year), R is the removal rate (%), P is the population of the considered area, V is the volume of wastewater per day per capita, and D is the dilution factor in the environment. The risk quotient is defined as the PEC divided by the predicted no effect concentration (PNEC). If the PEC equals or exceeds the PNEC, then ecological risk is suspected.

Depending on local consumption and WWTP technologies, the extent of exposure to individual pharmaceuticals can vary between locations [14, 68, 69], yet for CBZ, SMX and TMP, studies indicate that even a low level exposure in water can lead to adverse ecological consequences (Table 1.4). The ubiquitous detection of these three compounds in the aquatic environment, combined with their potential ecological repercussions, make it imperative to investigate their removal from the aqueous phase.
Table 1.4. NOEC, LOEC and EC₅₀ values [mg/L] of carbamazepine (CBZ), sulfamethoxazole (SMX) and trimethoprim (TMP) on various classes of organisms.

<table>
<thead>
<tr>
<th>Class</th>
<th>Organism</th>
<th>CBZ</th>
<th>SMX</th>
<th>TMP</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bacteria</td>
<td>V. fisheri</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LC₅₀ 5 min</td>
<td>52.5</td>
<td>74.2</td>
<td>165.1</td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td>LC₅₀ 15 min</td>
<td>52.5</td>
<td>78.1</td>
<td>176.7</td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td>LC₅₀ 30 min</td>
<td>23.3</td>
<td></td>
<td></td>
<td>[68]</td>
</tr>
<tr>
<td>Algae</td>
<td>P. subcapitata</td>
<td></td>
<td>0.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LC₅₀ 72 h</td>
<td></td>
<td></td>
<td></td>
<td>[68]</td>
</tr>
<tr>
<td></td>
<td>NOEC 96 h</td>
<td>&gt;100</td>
<td></td>
<td></td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>LOEC 96 h</td>
<td>&gt;100</td>
<td></td>
<td></td>
<td>[15]</td>
</tr>
<tr>
<td>Aquatic plant</td>
<td>L. minor</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LC₅₀ 7 days</td>
<td>25.5</td>
<td></td>
<td></td>
<td>[70]</td>
</tr>
<tr>
<td>Aquatic invertebrates</td>
<td>B. calyciflorus</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NOEC</td>
<td>0.377</td>
<td></td>
<td></td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>LOEC</td>
<td>0.754</td>
<td></td>
<td></td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>LC₅₀ 24 h</td>
<td></td>
<td>26.27</td>
<td></td>
<td>[68]</td>
</tr>
<tr>
<td></td>
<td>LC₅₀ 48 h</td>
<td></td>
<td>9.63</td>
<td></td>
<td>[68]</td>
</tr>
<tr>
<td>Aquatic invertebrates</td>
<td>C. dubia</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NOEC</td>
<td>0.025</td>
<td></td>
<td></td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>LOEC</td>
<td>0.100</td>
<td></td>
<td></td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>LC₅₀ 48 h</td>
<td></td>
<td>77.7</td>
<td></td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>LC₅₀ 48 h</td>
<td></td>
<td>15.51</td>
<td></td>
<td>[68]</td>
</tr>
<tr>
<td></td>
<td>LC₅₀ 7 days</td>
<td></td>
<td>0.21</td>
<td></td>
<td>[68]</td>
</tr>
<tr>
<td>Aquatic invertebrates</td>
<td>D. magna</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LC₅₀ 24 h</td>
<td></td>
<td>25.2</td>
<td></td>
<td>[68]</td>
</tr>
<tr>
<td></td>
<td>LC₅₀ 48 h</td>
<td></td>
<td>&gt;100</td>
<td></td>
<td>[70]</td>
</tr>
<tr>
<td></td>
<td>LC₅₀ 48 h</td>
<td></td>
<td>&gt;100</td>
<td>189.2</td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td>LC₅₀ 48 h</td>
<td></td>
<td>13.8</td>
<td></td>
<td>[15]</td>
</tr>
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<td></td>
<td>76.3</td>
<td>177.3</td>
<td>120.7</td>
</tr>
<tr>
<td>Crustacean</td>
<td>T. platyurus</td>
<td></td>
<td>36.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LC₅₀ 24 h</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fish</td>
<td>O. latipes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LC₅₀ 48 h</td>
<td>35.4</td>
<td>&gt;750</td>
<td>&gt;100</td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td>LC₅₀ 96 h</td>
<td>35.4</td>
<td>562.5</td>
<td>&gt;100</td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td>D. rerio</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LC₅₀ 96 h</td>
<td></td>
<td>≥1000</td>
<td></td>
<td>[68]</td>
</tr>
<tr>
<td></td>
<td>NOEC 10 days</td>
<td>25</td>
<td></td>
<td></td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>LOEC 10 days</td>
<td>50</td>
<td></td>
<td></td>
<td>[15]</td>
</tr>
</tbody>
</table>
1.2. Water remediation technologies

Since it can be seen from the removal efficiencies presented in Tables 1.1 – 1.3 that pharmaceuticals are not effectively removed after treatment with conventional activated sludge, the need exists for more advanced strategies to be applied. Amongst the currently employed technologies that have shown promise in the removal of pharmaceutical contaminants are: filtration (ultra, nano) and reverse osmosis, membrane bioreactors/integrated fixed-film activated sludge, advanced oxidative processes (including UV and ozonation), and adsorption on activated carbons.

1.2.1. Filtration and reverse osmosis

Filtration uses a membrane with a particular pore size to separate a component that is suspended in a liquid. Filters are classified by the size of the pores such that nano-, ultra-, and micro-filters have pores ranging from 1-10 nm, 5-100 nm, and 50-5000 nm, respectively [70]. Although microfilters have pore sizes too large to be effective for pharmaceutical removal, they can be used as a pre-treatment for other filtration methods [71]. Polymeric RO membranes have pores as small as 0.1 nm, and use high pressure (as high as 200 bar [72]) for transport through the membrane. Electrodialysis reversal, which is akin to RO except that the separation across the membrane is driven by an electrochemical gradient, has also been used with the purpose of purifying wastewater from pharmaceutical contaminants [47, 73]. In particular, RO has been effective in removing SMX and TMP at rates >95% [8, 37], however the success of a filtration technology is limited by scaling and fouling (deposition of particles on the membrane surface) [74]. In the case of RO, energy consumption is also a concern, as it requires about 4 kW electricity to produce one cubic meter of treated water [75].
1.2.2. Membrane bioreactors

Membrane bioreactors (MBR) and integrated fixed-film activated sludge incorporate a combination of activated sludge treatment with a solid-liquid separation by a micro- or ultra-filtration membrane [76]. MBR are often used as a pre-treatment before RO or nanofiltration [47], and offer the advantages of more compact WWTPs and a complete retention of suspended solids [35]. Success of the pharmaceutical removal by MBR is strongly linked to the sludge retention time (SRT). For example, TMP removal was 30% after a SRT of 33 days, yet increased to 87% with 60-80 days of retention time [6]. However, high operation costs as well as membrane fouling (and reduced flux due to microbial extracellular substances) are disadvantages of this approach to waste water remediation [76]. Additionally, the removal effectiveness of MBR depend on the molecular structure of the pollutant. A previous study found that MBR were incapable of removing several pharmaceuticals, including CBZ [37]. Ultimately, MBR tend to be less effective against molecules that contain chlorine or a certain number of aromatic rings [77].

1.2.3. Advanced oxidative processes

Advanced oxidative processes (AOP) include: O₃, UV, H₂O₂ (as well as combinations thereof, such as O₃/UV, UV/H₂O₂, etc.), Fenton, or photo-Fenton technologies, amongst others [78]. AOP treatments can eliminate pollutants by oxidation with a hydroxyl until mineralization is reached, yielding CO₂ and water as end-products [79]. AOP have proven effective for the removal of a wide spectrum of recalcitrant compounds that were not treatable by conventional techniques due to their high chemical stability [80]. O₃ has been shown to be successful in the removal of CBZ, SMX and TMP from effluent [81], however there are some drawbacks to AOP technology as it is energy intensive, and requires the use of expensive reactants (O₃, H₂O₂) [78]. The operating cost for oxidizing water with ozone is around $6.25 – 8.75/m³ [82]. Additionally,
treatment with O$_3$ has been found to produce carcinogenic bromate ions as a by-product [83]. The treatments with UV and photo-Fenton technologies are limited to wastewaters without turbidity in order for the radiation to penetrate the water [84].

1.2.4. Adsorption

Among the possible techniques for wastewater treatments, the adsorption process is seen as one of the most efficient and economical methods for the removal of pollutants from waste water [84]. All adsorbents function by causing pollutants from a liquid phase to adhere a solid surface [85] therefore, the surface area is an important characteristic of an adsorbent [86]. The attraction to the surface is due to a combination of physical (physisorption) and chemical (chemisorption) processes. Physisorption is driven by van der Waals forces, while chemisorption involves chemical reactions, including redox processes [87]. Additional differences can be noted in Table 1.5. The treatment of wastewater with varied adsorbents has shown effective in reducing a wide range of organic pollutants, such as pharmaceuticals [88]. Cost can vary depending on the source material of the adsorbent, from $0.02/kg for peat moss to $15.43/kg for chitosan [86]. The possibility of regeneration [89] of some adsorbents can lower the cost, as well as the environmental burden.

Table 1.5. Comparison of physisorption and chemisorption (based on [87]).

<table>
<thead>
<tr>
<th></th>
<th>Physisorption</th>
<th>Chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attractive force</td>
<td>van der Waals</td>
<td>Electron sharing or transfer</td>
</tr>
<tr>
<td>Reversibility</td>
<td>Fully reversible</td>
<td>Irreversible</td>
</tr>
<tr>
<td>Site specificity</td>
<td>Not site specific</td>
<td>Site specific</td>
</tr>
<tr>
<td>Heat of Adsorption</td>
<td>Low (20 – 40 KJ/mol)</td>
<td>High (&gt;80 KJ/mol)</td>
</tr>
<tr>
<td>Layers of adsorbate</td>
<td>Multilayer</td>
<td>Unilayer</td>
</tr>
<tr>
<td>on adsorbent</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1.3. Fundamentals of adsorption on carbon

Activated carbons are the most popular and widely used adsorbents for the treatment of waste water worldwide [86]. Carbon-based adsorbents are produced by the high temperature pyrolyzation of a carbonaceous material in an inert atmosphere [86]. A further development of the carbon surface can be accomplished with a subsequent activation step. Ultimately adsorption results from attractive intermolecular interactions. This is a spontaneous and exothermic process [90]. Forces, such as electrostatic and dispersive, between the adsorbent and adsorbate molecules enable physisorption to occur.

1.3.1. Intermolecular Attraction

1.3.1.1. Dipole interactions

The attraction of electrostatic forces is the result of the presence of dipoles. When there is a non-uniform distribution of the positive and negative charges in a molecule, a dipole results. The dipole can be permanent, instantaneous, or induced. The electron rich and electron poor areas of adjacent molecules have an electrostatic attraction, and which can lead to an attraction to the adsorbent surface (Fig. 1.3). The main intermolecular attraction for physisorption are van der Waals forces, which can be subdivided into Debye, Keesom, and London dispersion forces [91]. When the interaction occurs between permanently polarized molecules, it is referred to as a Keesom (or dipole-dipole) reaction. A special kind of Keesom interaction can occur when hydrogen atoms are present. The hydrogen represents a polarized region that is attracted to an electronegative atom (such as nitrogen, oxygen, or fluorine), and forms a relatively strong Keesom interaction called a hydrogen bond [92]. However, when an induced dipole (a dipole that occurs in an otherwise non-polar molecule) interacts with a permanently polar molecule, it is
called a Debye interaction [91]. Finally when there is an instantaneous interaction between two nonpolar molecules that both have induced dipoles, it is referred to as London dispersion forces. An attraction between the partial charge of a dipole (induced or permanent) and an ion is also possible [92].

![Diagram of dipole interactions](image)

Fig. 1.3. Polar interactions of adsorbates and adsorbents. Note: adsorbent surface charge will be a function of pH.

**1.3.1.2. Aromatic interactions**

Although aromatic rings do have dipole moments, they have quadrupole (alignment of two dipoles) moments. In a quadrupole moment, the positively charged carbon ring has clouds of π-electrons above and below (see Fig. 1.4). Quadrupole-quadrupole interactions occur between quadrupolar molecules that are oriented such that the positively-charged (σ-bond) ring of one molecule is electrostatically attracted to the delocalized π-electrons of the other, and stabilized by
London dispersion forces [93]. These are referred to as \( \pi-\pi \) stacking interactions, and they play a major role in adsorption of aromatic compounds, and also interactions such as intercalation [94]. The quadrupole moment of an aromatic compound can also be involved in electrostatic reactions with a cation, called a cation-\( \pi \) reaction [95].

![Quadrupole Charge Distribution](image)

Fig. 1.4. The quadrupole charge distribution in an aromatic ring.

### 1.3.1.3. Coordination Complexation

In adsorbents that contain metal species, the formation of a coordination complex may play an important role in contaminant removal [96]. Complexation occurs between the metal ion, which acts like a Lewis acid, and coordinate ly bonds to the ligand, which acts like a Lewis base [97]. This can occur as an innersphere or outersphere coordination, wherein the ligand may be directly coordinated to the metal or via the water surrounding the cation, respectively [97].

### 1.3.2. Factors affecting adsorption

Regardless of whether adsorption proceeds as a function of chemi- or physi-sorption, certain characteristics and conditions will determine whether it is thermodynamically favorable for
adsorption to occur. The nature of the adsorbent, the adsorbate, as well as additional factors such as pH, temperature, and the presence of competing adsorbates are factors that will impact the removal efficiency of a target adsorbate.

1.3.2.1. Nature of the adsorbent

Surface area and pore structure

Extended surface area and highly developed porosity contribute to the successful application of carbons as adsorbents [90]. The specific surface area of carbon adsorbents is usually in the range of 800-1500 m$^2$/g, and is due to the choice of the precursor material, preparation temperature and any activation steps [90]. Micropores represent a major portion of the surface area [87]. As can be seen in Fig. 1.5, pores widths are classified as macro-, meso-, and micro-pores, possessing diameters of >50 nm, 2 to 50 nm, and <2 nm, respectively [98]. The pores form a capillary system where larger pores serve as conduits to smaller pores. Upon contact between an adsorbate and adsorbent, the pores of the latter are filled with the adsorbate until the surface tension reaches a state of thermodynamic equilibrium. Amongst the classes of pores, micropores have been shown to have a particularly important role in adsorption. Generally, as pore size decreases, adsorption increases (assuming no size exclusion of the adsorbate), due to increased contact points between the adsorbate and the adsorbent surface area, and also due to overlaps in the potential between pore walls [99]. The most common method for determining the material’s surface area is by Brauner, Emmett, Teller (BET) nitrogen adsorption, which determines the volume of a monolayer [87]. The pore size and pore size distribution are based on the analysis of the nitrogen adsorption isotherms.
Fig. 1.5. Adsorbate (gray circles) in the pore structure of a carbon adsorbent. Based on [98].

**Particle size**

The particle size of an adsorbent may have a bearing upon adsorption. Powdered activated carbon has particles of about 44 μm, while granular activated carbon is mainly in the range of 0.6 to 4.0 mm [90]. Ordinarily surface area increases with particle size however, in the case of adsorbents a high surface area is the result of porosity (see Fig. 1.6), therefore a particle of small size may still achieve a high surface area [87].
Fig. 1.6. SEM image of adsorbent from sewage sludge waste.

**Ash content**

The ash content of a carbon adsorbent is an important physical characteristic. It refers to the non-carbon portion of the adsorbent that remains from the pyrolysis of a precursor material. Most commercial carbons have an ash content in the range of 2 – 5 wt % [100]. An elevated ash content could correlate negatively with the adsorption capacity due to the occurrence of undesired side reactions [100], however in some cases it has a beneficial impact by promoting catalytic activity [101], depending on the nature of the adsorbent and the adsorbate.

**Surface chemistry**

Surface chemistry has a great impact on the physicochemical properties of the carbon adsorbents. These adsorbents consist primarily of layers of fused aromatic rings, which are stabilized by van der Waals forces. It can be seen from Fig. 1.7 that the edges of the carbon contain active sites that chemisorb heteroatoms (oxygen, hydrogen, nitrogen, sulfur, etc), which determine the
adsorptive properties of a particular carbon [102]. The concentration, type and distribution of the chemical species adsorbed on the carbon surface can vary greatly, and they result from the composition of the initial material and the preparation method [90]. The most important heteroatom found on the carbon surface is oxygen, representing a content of 1 – 25 %, depending on the preparation process (oxygen content decreases with an increased heat treatment) [87]. The formation of certain oxygen-containing functionalities increases the acidity of the surface (due to carboxyl, anhydride, hydroxyl, phenol, lactone and lactol groups), while others contribute to increased basicity (from chromene, pyrone and quinone groups) [90, 102]. (Although some oxygen-containing groups may slightly increase the basicity of the surface, the main contribution comes from the delocalized π-electrons of the polyaromatic sheets [103]). Nitrogen is another heteroatom that can be detected among the surface groups as a result of the choice of precursor material or treatment process. The presence of nitrogen-containing functionalities can modify the surface to be more acidic (due to the formation of lactams, imides, and amines), or more basic (due to formation of pyridines and pyrroles) [102]. The polarity of an adsorbent also increases as a result of nitrogen incorporation [99]. Hydrogen is another heteroatom that is commonly present on the carbon surface, and can be found in functionalities such as carboxylic acids, phenolic groups, amines [102]. In addition, heteroatoms of sulfur, phosphorus and halogens (fluorine, chlorine, bromine, iodine) may be associated with the carbon surface. Ultimately the resulting chemical species found on the surface reflect the starting material and preparation treatments (incomplete carbonization, activation steps, etc). Due to the fact that these functional groups form along the edges of the carbon sheets, which constitute the main adsorbing surface, they therefore determine the behavior of the carbon during adsorption/reactive adsorption [90]. Determination of the acidic and basic species (but not neutral species such as ketones, aldehydes,
esters, ethers, etc) of the carbon surface is generally achieved with Boehm or potentiometric titrations.

![Functional groups on the carbon surface](image)

Fig. 1.7. Functional groups on the carbon surface. Based on [102].

### 1.3.2.2. Nature of the adsorbate

**Solubility**

One of the most significant properties affecting the adsorptive capacity is the solubility of the adsorbate. Adsorption strength is inversely proportional to solubility. High solubility indicates a strong solute-solvent affinity, and in order for adsorption to occur, it would be necessary to overcome the solute-solvent interactions [87]. An adsorbate with high hydrophobicity would therefore adsorb more favorably on a hydrophobic carbon adsorbent.

**Molecular size and weight**

The capacities of an adsorbent for contaminant removal are affected by the size and weight of the adsorbate. It has also been shown that molecules of low molecular weight are preferentially adsorbed [104]. Molecules of smaller diameter are less restricted when diffusing through
micropores during adsorption [105]. A size exclusion of an adsorbate can occur if the contaminant size and shape is too large to enter the pores. It has been determined that this exclusion occurs when the pore width is less than 1.7 times the second largest dimension of the adsorbate [99]. For CBZ and SMX, this means adsorbent pores must have a minimum width of 15 Å for exclusion to not occur (molecule dimensions from [106]). For larger adsorbates, adsorption is improved by increased mesopore volume as the mesopores reduce the diffusion path length [105].

**Polarity**

The polarity of an adsorbate is another factor that greatly impacts adsorption. The surface of a carbon adsorbent is mainly nonpolar and hydrophobic. Water undergoes hydrophobic interactions with the nonpolar regions of the carbon and the nonpolar moieties of the adsorbents. An association occurs between the latter two, and therefore carbons are more effective in the removal of nonpolar adsorbates than polar ones [87]. However, the presence of functional groups on the adsorbate molecule can impart polar characteristics [87]. As the polarity of an adsorbate increases, so does the solubility, and therefore adsorption decreases. The factors of polarity and solubility on adsorption are interrelated such that as adsorbate molecules increase in size, if the functionalities decrease solubility and polarity, adsorption could still increase despite the larger molecular size [87].

**1.3.2.3. Characteristics of the solution**

Factors such as pH, temperature, and the presence of competing adsorbates can also impact the removal efficiency of a target adsorbate.
The adsorption from the liquid phase on carbons can be profoundly affected by the pH of the solution. The pH determines the surface charge of the carbon adsorbent. The pH\textsubscript{PZC} (point of zero charge) is defined as when the electrical charge density on the adsorbent surface is zero [107]. If the pH of the solution is greater than the pH\textsubscript{PZC}, there will be a negative average surface charge, as surface oxygen complexes of acidic character (such as carboxyl or phenolic functionalities) dissociate from the surface [107]. However, if the pH is lower than the pH\textsubscript{PZC}, the average surface charge will be positive. This could result from nitrogen functionalities, or oxygen complexes that are basic in nature (such as pyrones or chromenes), or electron-rich regions that act like Lewis bases [107].

The pH of the solution also impacts the adsorption of electrolyte adsorbates. Most pharmaceuticals are weak acids or bases, which means they can dissociate, the degree to which is indicated by their dissociation constant (pK\textsubscript{a}) [108]. The pK\textsubscript{a} reveals the pH at which the protonated and deprotonated fractions are equal. By varying the pH of the solution, and thus the availability of protons, the equilibrium can be shifted. If the pH is higher than the pK\textsubscript{a}, the compound exists mainly in a deprotonated form, while the protonated form is more common when the pH is lower than the pK\textsubscript{a} (see Fig. 1.8). Although both protonated and deprotonated forms of a compound can be adsorbed, the quantity adsorbed on carbon is greater amongst the undissociated forms. The undissociated compounds are less soluble, and therefore adsorb readily on the nonpolar carbon [108]. The dissociated adsorbate is more soluble and undergoes dipolar interactions with water, and therefore adsorption (due to electrostatic interactions) occurs to a lesser extent [109]. For an adsorbate with a high pK\textsubscript{a}, as the alkalinity of the solution increases, the fraction of undissociated species increases, thereby improving the adsorption capacity [110].
Meanwhile, an adsorbate with a low pKa would be nearly entirely dissociated at a high pH, which combined with the increased negative charge of the carbon surface at high pH, would result in a low adsorption capacity [110]. Ultimately, the optimum adsorption of a compound is found when the pH of the solution is most similar to the compound’s pK_a [87].

(a) carbamazepine

(b) sulfamethoxazole

(c) trimethoprim

Fig. 1.8. Protonation/deprotonation of (a) carbamazepine, (b) sulfamethoxazole and (c) trimethoprim

Temperature

Temperature of the system is another factor that impacts adsorption. Adsorption is a spontaneous and exothermic process, and as such, a decrease in the temperature usually results in an increased physical adsorption capacity [87]. The decreased temperature may result in slower reaction
kinetics, despite the overall increased adsorption capacity [108]. On the other hand, as the temperature increases, the physical adsorption capacity usually decreases due to undissipated heat that increases the vibrations of the lattice and prevents adsorption [111]. Chemisorption is generally endothermic, and thus an increase in temperature will increase the adsorption capacity [108]. As the solute goes from a dissolved to an adsorbed state, the enthalpy changes, and the magnitude of that change can, to a certain extent, be used to classify physi- and chemi-sorption [87]. Temperature affects other factors, such as solubility, which would generally increase with an increased temperature, but the extent to which this would affect an adsorption capacity would depend on the particular solute and system in question [112]. The concentration of the adsorbate is also a factor, as low initial concentrations showed more pronounced effects in response to temperature changes [113]. In fact, it has been shown that WWTP effluent contains higher amounts of pollutants (especially hydrophobic molecules) in winter than summer because the removal efficiency decreases in lower temperatures [41].

Concentration and exposure duration

Dosage and time are additional factors to be considered when determining an adsorption efficiency. The removal of an adsorbate from a solution generally proceeds quickly initially, but then reaches a plateau when equilibrium is reached [114]. In fact, in one study, extension of the contact time did not prove to significantly increase adsorption, even when temperature was decreased from ambient to 5 °C [109]. Increasing the solute concentration does not affect the removal efficiency as the number of adsorption sites remains constant [115]. However, increasing the adsorbent concentration can impact adsorption. Generally, the greater the adsorbent amount, the greater the opportunity is for contaminants to attach to the adsorbent surface (due to the increased availability of adsorption sites). The removal of SMX improved
13% with an increase in the activated carbon dose from 5 to 10 mg/L [109]. Nearly all instances show an increased removal with an increase in the adsorbent dose, however one study showed that although the total removal of adsorbate increased with an increased adsorbent dose, the removal efficiency decreased due to the aggregation of the adsorbent particles [116].

*Competing adsorbates*

The presence of additional adsorbates can influence the adsorption capacity of the target compound. The source of those could be ions from minerals (Ca2+, Mg2+) [87], or natural organic matter (such as humic, fulvic and tannic acids) that are naturally present in the water source. When such substances are present they can block the pores in the carbon adsorbent, and compete for binding sites with the target pollutants, which decreases the removal of the pollutants [109].

Competition can also occur between pollutants, as they generally co-exist in the environment, therefore it is important to understand how the interactions of these pollutants impact the adsorption efficiency. These additional ions could occupy the available sorption sites in a competitive or complementary (noncompetitive) manner [117]. The factors and characteristics mentioned earlier, such as the pH of the system and concentration of the solute/adsorbent, can create adsorption conditions that are more advantageous for one contaminant than the other [118]. For example, Chang et al [117] found that the adsorption affinity of various pharmaceuticals on a carbon adsorbent increased with increased $K_{OW}$. Ultimately, the degree of competition for adsorption sites is determined by the similarity in the molecular structure and physicochemical properties of the adsorbates [119]. If contaminants do not share similar characteristics, and sorption occurs on diverse sites, then complementary adsorption can be expected. For example, complementary adsorption occurs between CBZ and phenanthrene, as
the presence of the latter did not diminish the adsorption capacity of CBZ [119]. However, the adsorption capacity of SMX was greatly reduced when competing with diclofenac for adsorption sites [117].

1.3.3. Equilibrium isotherm models

When an adsorbent surface is initially exposed to molecules of solute, the rate of adsorption is rapid as there are many active sites available. However, as these sites become occupied, the adsorption rate declines. The molecules will continue to adsorb until reaching a chemical equilibrium with their fraction in the aqueous phase. A dynamic equilibrium is established in which molecules are desorbed from the surface, while simultaneously the same amount of molecules are adsorbed on the surface. Therefore, adsorption equilibrium is defined as equal rates of adsorption and desorption. The relationship between the concentration of molecules at the solid-liquid interface (adsorbed) and those in the bulk solution are referred to as an adsorption isotherm [90]. The adsorption isotherm is characteristic of each solute-adsorbent-adsorbate system. The shape of a particular adsorption isotherm can also provide information about the types of adsorption phenomena. There are several isotherm relationships commonly used in adsorption from an aqueous phase (see Fig. 1.9).
Fig. 1.9. Typical adsorption isotherms in aqueous phase, based on [85].

Of the several types of adsorption isotherms from aqueous phase, any with a downward curvature are favorable, while an upward curvature is unfavorable. Unfavorable means that the adsorbent is not very effective at capturing small amounts of solute from a dilute solution [85]. The linear isotherm rarely occurs. The Langmuir equation is one of the oldest and most frequently used fitting equations. It operates on certain assumptions: 1) coverage is monolayer, 2) the surface is homogenously energetic, and 3) there is no lateral interaction between adsorbed molecules (because the heat of adsorption is constant). The formula is given by [120]:

\[ q = \frac{q_m K_L C_e}{1 + K_L C_e} \] (2)

where \( q \) is the adsorbed amount, \( q_m \) is the maximum adsorbed amount, \( K_L \) is the Langmuir adsorption equilibrium constant, and \( C_e \) is the equilibrium concentration.
Although the Langmuir equation describes monolayer physisorption and also chemisorption well, when the adsorbate size is large, the calculated surface area may appear smaller than it actually is as the monolayer will accommodate fewer adsorbate molecules [121]. Because the requirements of homogenous energy between sites and monolayer coverage aren’t always satisfied, the Freundlich equation is used to fit adsorbents with heterogeneous energy sites. It was noticed that the heat of adsorption decreased with increased adsorption, leading to the conclusion that adsorption sites are distributed exponentially with respect to the adsorption energy [122]. The Freundlich equation reflects the variation in the heat of adsorption with coverage, and is frequently used to describe the adsorption of organic compounds on the heterogeneous surface of carbons [122]. The formula is given by [120]:

\[ q = K_F C_e^{1/n} \]  

(3)

where \( q \) is the adsorbed amount, \( K_F \) is the Freundlich constant that indicates relative capacity, \( n \) is the constant related to the adsorbent material heterogeneity, and \( C_e \) is the equilibrium concentration.

The Freundlich equation is of great significance for chemisorption, although some physical adsorption has been explained with this equation [90]. The Freundlich isotherm is an empirical equation, and the \( K_F \) and \( n \) can change with temperature. A limitation of the Freundlich equation is that it does not reach saturation when the concentration in a solution is increased [123]. To overcome this inadequacy and still describe adsorption on a heterogeneous surface, the Langmuir and Freundlich equations can be combined to form the Langmuir-Freundlich isotherm model. The formula is given by [120]:

\[ q = \frac{q_m K_{LF} C_e^{1/n}}{1 + K_{LF} C_e^{1/n}} \]  

(4)
where \( q \) is the adsorbed amount, \( q_m \) is the maximum adsorbed amount, \( K_{LF} \) is the Langmuir-Freundlich equilibrium constant, \( n \) is the constant related to the adsorbent material heterogeneity, and \( C_e \) is the equilibrium concentration.

A number of adsorption isotherm models have been developed over time: Dubinin-Radushkevich, Temkin, Toth, Koble-Corrigan, Hill, Flory-Huggins, etc (see [124] for a review). While they provide invaluable insight to the adsorption mechanisms, surface properties, and degree of affinity of the adsorbents, it is well beyond the scope of this project to consider them all.

1.4. Alternative adsorbent materials

Although commercial activated carbons are prized for their ease of use and pollutant removal effectiveness, the cost can be seen as a draw-back to its implementation in water treatment. Fortunately, many precursor materials can be pyrolized to form a well-functioning adsorbent. A wide assortment of agricultural and industrial by-products show potential as adsorbents for water treatment, such as: almond shells [125], rice husk [126], orange peel [127], olive pits [128], coirpith [129], lignin [130], tires [131], PET [132], fly ash [133], biodiesel solids [134], etc. (see Table 1.6 for additional precursor materials, and for a thorough review see [135]).
Table 1.6. Alternative precursor materials for the production of carbon adsorbents [135].

<table>
<thead>
<tr>
<th>Material</th>
<th>Source</th>
<th>Adsorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bagasse</td>
<td>Kelp and seaweed</td>
<td>Sugar-beet sludge</td>
</tr>
<tr>
<td>Lampblack</td>
<td>Blood</td>
<td>Leather waste</td>
</tr>
<tr>
<td>Bones</td>
<td>Lignin</td>
<td>Spent Fuller’s earth</td>
</tr>
<tr>
<td>Lignite</td>
<td>Cereals</td>
<td>Molasses</td>
</tr>
<tr>
<td>Coal</td>
<td>Nut shells</td>
<td>Oil shale</td>
</tr>
<tr>
<td>Coffee beans</td>
<td>Peat</td>
<td>Corn cobs</td>
</tr>
<tr>
<td>Petroleum acid sludge</td>
<td>Cottonseed hulls</td>
<td>Petroleum coke</td>
</tr>
<tr>
<td>Distillery waste</td>
<td>Potassium ferrocyanide waste</td>
<td>Fish</td>
</tr>
<tr>
<td>Pulp-mill waste</td>
<td>Rice hulls</td>
<td>Fruit pits</td>
</tr>
<tr>
<td>Rubber waste</td>
<td>Municipal waste</td>
<td>Newspaper</td>
</tr>
<tr>
<td>Palm tree cobs</td>
<td>Jute stick</td>
<td>Wheat straw</td>
</tr>
<tr>
<td>Coconut coir</td>
<td>Sunflower seeds</td>
<td>Refinery wastes</td>
</tr>
</tbody>
</table>

There are various factors that can contribute to the cost of producing an adsorbent: the source of the precursor, preparation treatment, recycling and lifetime issues. Overall it appears that waste-based adsorbents are meeting the objective of providing a cost effective alternative to commercially activated carbons. As can be seen in the cost comparison in Fig. 1.10, while commercial activated carbon requires an investment of around $21/Kg, most waste-based adsorbents have associated costs of less than $2/Kg. However, to be a competitive alternative to commercial carbons, the waste-based adsorbents must also be able to effectively remove pollutants from waste water. Redding et al [136] found that lignin-based carbons not only removed the same quantity of pollutants as commercial carbons, but also had a bed life 3-4 times that of the commercial carbon. The perks from using locally-available waste materials are the costs of producing an adsorbent are kept low, production is low-tech and manageable even in developing areas, and the re-purposing of wastes prevents build-up and costly disposal.
Fig. 1.10. Cost of adsorbents ($/Kg) from various precursor material. Brackets refer to reference numbers as follows: a[137], b[138], c[138], d[139], e[140], f[141], g[142], h[86], i[125], j[130].

1.4.1. Sewage sludge and fish waste

Another waste material that has been investigated as a potential adsorbent precursor is sewage sludge. Sewage sludge is a by-product of the digestion of biomass from the sewage treatment process, and consists of organic and inorganic (such as sand and metal oxides) components [143]. Sludge contains organic components, and thus it is a good candidate for conversion into an adsorbent material. Plus, its use would not only provide an inexpensive precursor, but also aid a waste accumulation issue. Figure 1.11 shows the amount of dry sludge produced annually by selected countries. The US produces over 6.5 million metric tons per year, which creates a huge and costly disposal issue, with roughly 30% of the dry sludge going directly into the landfill [144]. The pyrolysis of sewage sludge results in an adsorbent with a surface area of up to nearly 200 m$^2$/g, depending on preparation method [145]. Despite the relatively low surface area (as compared to commercial carbon adsorbents), sewage sludge-based materials have demonstrated
adsorption capacities comparable to those of commercial carbons [145, 146]. Sewage sludge has been used as an adsorbent in previous studies to effectively remove pollutants such as $\text{H}_2\text{S}$ [145-147], dyes [148-150], phenol [151, 152], carbon tetrachloride [153], pesticides [154] and heavy metals [155-157]. Note that many of these studies were published within the last two years, indicating a growing interest in the repurposing of sewage sludge. This focus could ultimately lead to a WWTP operation of nearly zero waste production.

![Fig. 1.11. Annual sewage sludge production in select countries, based on data from [144].](image)

Another precursor material of interest for the production of adsorbent is fish waste (from consumption). Fish waste is comprised of bones, shells and scales, and thus contains 70 % (by weight) of inorganic compounds (mainly hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), and the remaining 30 % is organic compounds (such as keratin) [158]. More than 148 million tons of fish are caught annually worldwide [159], and of that, 40-60 % is discarded during the deheading,
descaling and filleting process [160]. Repurposing of this raw material not only eases a disposal problem, but generates an adsorbent that has already been successfully used for the removal of heavy metals [161] and dyes [162]. The success of fish waste as an adsorbent is likely due to its hydroxyapatite component and the ability of the calcium ions to remove positively charged pollutants by ion exchange [162].

By mixing the sewage sludge and fish waste, it is possible to create an adsorbent with unique properties. The combination of carbonaceous and polar phases could have a beneficial synergistic effect for the removal of a diverse array of pharmaceuticals. The objective of the current research is to test whether these waste-based adsorbents’ unique features can offer benefits not found in commercial carbons for waste water treatment. The precursor composition of the waste-based adsorbents can be altered to maximize reactivity between the adsorbents and particular pollutants. The ultimate goal is to generate a material capable of handling the treatment challenge presented by the multi-component contamination in WWTPs, and to do so by the economical repurposing of waste materials.
2. Objectives and Research approach

Based on the environmental issues presented in Chapter 1, the objective of this thesis is to produce adsorbents from the repurposing of sewage sludge and fish waste for the removal of pharmaceuticals from the aqueous phase, with a special focus on understanding the mechanism of adsorption. The adsorption capacity of the waste-based adsorbents is compared to two model commercially available activated carbons to assess whether the waste-based adsorbents are a viable economical alternative. For the removal of pharmaceuticals from waste water, the ability to tailor the adsorbents to optimally remove compounds of certain characteristics will depend on understanding the mechanisms of adsorption.

The specific goals of the project can be outlined as follows:

- To develop an adsorbent from waste that’s of comparable effectiveness to what is currently available on the commercial adsorbent market.

- To apply the waste-derived adsorbent to the adsorption of pharmaceuticals.

- To evaluate whether varying proportions of sewage sludge and fish waste will alter the chemistry of the materials so as to improve adsorbent performance.

- To understand the competitiveness of adsorption process in complex systems (mixtures of pharmaceuticals).

- To test the effects of preparatory aspects, such carbonization temperature, on the adsorbent characteristics and to propose the adsorption mechanism.

The findings obtained in this research are presented in the following chapters. Chapter 3 summarizes the materials and instrumentation used, as well as the techniques and analyses
applied. Chapter 4 presents the characterization of the materials, including their specific surface area, pore volume, inorganic composition, surface chemistry and structure. Chapter 5 briefly shares the results of adsorption of pharmaceuticals on the materials prepared at 650 °C. Chapter 6 discusses the adsorption on waste-based materials prepared at 950 °C. Both the adsorption from single-component and multi-component pharmaceutical solutions will be addressed. Chapter 7 gives a comparison of the performance of the waste-based materials prepared at the two distinct pyrolysis temperatures. Chapter 8 offers information of the adsorption of the same pharmaceuticals on commercial adsorbents, to understand the adsorption mechanisms, and for the sake of the performance comparison with the waste-based adsorbents. Chapter 9 draws conclusions over the project, and Chapter 10 offers perspectives on future research in this field.
3. Materials and methods

3.1 Materials

3.1.1. Pharmaceuticals

All chemicals used in this study were reagent grade. Carbamazepine (Sigma-Aldrich, St. Louis, MO) has a purity of >98%. Sulfamethoxazole and trimethoprim (Chem-Impex International Inc. Wood Dale, IL) have a purity of > 99%. Chemical structures and characteristics can be seen in Fig. 1.2. Single component solutions were prepared for each pharmaceutical at the concentrations of: 1, 3, 5, 10, 30, 50, 80, and 100 mg/L in deionized water. Multi-component solution was prepared by mixing equal amounts (by mass) of carbamazepine, sulfamethoxazole, and trimethoprim at 8 concentrations (1, 3, 5, 10, 30, 50, 80, 100 mg/L).

3.1.2. Adsorbent materials

Anaerobically digested and dewatered sewage sludge (New York City Department of Environmental Protection) and fish waste (local fish market) were dried (120 °C) and then homogenized in a grinder. As the precursors are water unstable materials and are unsuitable for aqueous phase treatment in their raw form, a heat treatment was applied to stabilize them. Samples were carbonized individually, as well as in composites with ratios of sewage sludge to fish waste of 90:10, 75:25, and 50:50. Carbonization was conducted at two distinct temperatures, 650 °C and 950 °C, in a nitrogen atmosphere at a heating rate of 10 C/min, and a holding time of 1 h. The pyrolized adsorbents were then ground to a particle size < 600 μm. The naming of materials reflects the composition such that the percentage of sewage sludge (S) is followed by the percent fish waste (F), and then the preparation temperature is indicated by I for 650 °C, and II for 950 °C. See Table 3.1 for clarification.
Table 3.1 Composition and preparation temperature of the waste-based adsorbents and the corresponding sample names.

<table>
<thead>
<tr>
<th>650°C-carbonized adsorbents</th>
<th>Composition</th>
<th>950°C-carbonized adsorbents</th>
</tr>
</thead>
<tbody>
<tr>
<td>S100-I</td>
<td>100% sewage sludge</td>
<td>S100-II</td>
</tr>
<tr>
<td>S90F10-I</td>
<td>90% sewage sludge 10% fish waste</td>
<td>S90F10-II</td>
</tr>
<tr>
<td>S75F25-I</td>
<td>75% sewage sludge 25% fish waste</td>
<td>S75F25-II</td>
</tr>
<tr>
<td>S50F50-I</td>
<td>50% sewage sludge 50% fish waste</td>
<td>S50F50-II</td>
</tr>
<tr>
<td>F100-I</td>
<td>100% fish waste</td>
<td>F100-II</td>
</tr>
</tbody>
</table>

The final yield of the adsorbents after pyrolysis ranged from 21.4 to 39.8 % (Table 3.2). A previous study [163], using similar adsorbent materials that were activated with CO₂, showed a decrease in the content of the beneficial carbon phase that may be important in the removal of organic contaminants. As such, the current study was undertaken without any activation step.

Table 3.2. Percentage yield of waste-based adsorbents post pyrolysis

<table>
<thead>
<tr>
<th>Adsorbent Samples</th>
<th>Post-pyrolysis Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S100-II</td>
<td>39.8</td>
</tr>
<tr>
<td>S90F10-II</td>
<td>37.2</td>
</tr>
<tr>
<td>S75F25-II</td>
<td>35.3</td>
</tr>
<tr>
<td>S50F50-II</td>
<td>32.8</td>
</tr>
<tr>
<td>F100-II</td>
<td>21.4</td>
</tr>
</tbody>
</table>

For the performance comparison, two commercial activated carbons were chosen. WVA-1100 is a wood-based carbon, chemically activated with phosphoric acid (Mead-Westvaco). S208C is made of coconut shells, and activated physically with steam (Calgon Carbon). For brevity, they are referred to as WVA and S208.
3.2 Methods

3.2.1. Adsorbent characterization

3.2.1.1. Elemental analysis

The initial waste-based adsorbents were oxidized in a furnace at 950 °C, and the ash was fluxed with 1 g Li$_2$B$_4$O$_7$ in a platinum crucible at 950 °C, then diluted to 200 mL with 5 % HCl. Ash elements were determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) on a Varian Vista-MPX ICP-OES, and the percentage of detected oxides were calculated. This work was carried out by Asbury Carbons Inc (Asbury, NJ).

3.2.1.2. Determination of porosity

Nitrogen adsorption isotherms were measured to determine the porosity and surface area of the materials. The initial samples, and those exposed to pharmaceuticals, were measured at -196 ºC on ASAP 2020 (Micromeritics). Prior to measurements, samples (about 0.15 g) were out-gassed at 120 ºC until 10$^{-4}$ Torr was reached. The isotherms were used to calculate the surface area ($S_{BET}$), total pore volume ($V_t$; calculated from the volume of nitrogen adsorbed at P/P0 = 0.99), and micropore volume ($V_{mic}$; calculated using Dubinin-Astakhov equation) [164]. The BJH method [165] was used to calculate the pore size distributions.

3.2.1.3. Thermal analysis/mass spectroscopy

Thermal analysis was conducted on a TA instrument thermal analyzer (SDT Q600) under a helium atmosphere (flow: 100 mL/min). Prior to analysis, the samples were exposed to either deionized water (control), single-component or the multi-component pharmaceutical solution. Since the exhausted samples had been exposed to the aqueous phase, in order to prevent
Chapter 3

differences due to treatment, the initial samples were exposed to an identical quantity of water as a control. After, the samples were dried at 120 °C for 24 hours. Approximately ~ 30 mg of adsorbent was heated to a max of 1000 °C at a rate of 10 °C/min. Analyses were carried out up to the pyrolysis temperatures of the adsorbents. From the recorded weight loss, the thermogravimetric and the differential thermogravimetric curves were obtained.

Simultaneously with the thermal analysis, the gasified products desorbed from the surface of the adsorbents were collected, and analyzed by a ThermoStar Gas Mass Spectrometer (GSD; Pfeiffer Vacuum), which was connected to the TA instrument. The GSD contains a secondary electron multiplier detector and a Faraday detector for scanning the off-gas. The thermal profiles of the mass to charge ratio (m/z) in a range of 1-100 were identified.

3.2.1.4. Potentiometric titration

Potentiometric titration can indicate the strength and number of acidic groups present on the surface of the adsorbent materials. Measurements were performed on a DMS Titrando 888 automatic titrator (Metrohm). After exposure to either deionized water (control) or a pharmaceutical solution, the dried adsorbent (0.05 g) was dispersed in 25 mL of 0.1 M NaNO₃, and stirred under a N₂ atmosphere (to prevent interference of atmospheric CO₂) until the pH stabilized. While continuously stirring, waste-based samples were titrated with HCl (0.1 M) from their initial pH until pH 3. Commercial carbons, however, were adjusted to a pH 3 with HCl, and then titrated with NaOH (0.1 M) to pH 11. The experimental data was transformed into proton binding curves (Q), representing the total amount of protonated sites. The SAEIUS deconvolution [166] was applied to calculate the continuous pKₐ distributions of the acidic surface species.
3.2.1.5. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR studies were carried out in a Nicolet magna-IR 830 spectrometer. Two analysis methods were used: total attenuated total reflectance (ATR) and Diffuse Reflectance (DRIFTS). ATR results were obtained without KBr addition. For DRIFTS analyses the adsorbent samples (5%) were mixed with dried spectroscopic grade KBr and finely ground in a mortar. For both analyses spectra were collected 32 times and corrected for the background noise. The reflectance spectra were expressed in Kubelka-Munk units.

3.2.1.6. X-ray diffraction spectroscopy (XRD)

XRD spectroscopy was conducted by loading powdered samples (~ 0.3 g) into the recessed well of the aluminum sample holder. Analysis was conducted on a PANalytical X’Pert Powder X-ray diffractometer with CuKα radiation (voltage 40 kV, current 40 mA). The crystallographic phase identification was completed with X’PERT Highscore Plus.

3.2.1.7. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX)

SEM images were collected for selected samples (S100-I, S90F10-I, F100-I, S100-II, S90F10-II, F100-II). Imaging was completed on a Zeiss Supra 55 VP with an accelerating voltage of 5.00 kV. The EDX analysis of the surface composition was performed with an accelerating voltage of 15.00 keV.

3.2.1.8. X-ray scanning photoelectron spectroscopy (XPS)

For the commercial carbons, initial and samples exposed to CBZ and SMX were sent for XPS analysis by the research group of Mark Biggs at the University of Adelaide, Australia. Their procedure was as follows: Analyses of the carbons were conducted using a Kratos Axis-Ultra
spectrometer, using a monochromatic Al Kα source (1487 eV) operating at 15 kV and 14 mA, $10^{-8}$ Pa vacuum in the analyser chamber and an analysis spot size of 300×700 μm. Spectrometer pass energy of 40 eV was used for all elemental spectral regions, whilst 160 eV pass energy was used for the survey spectra used for surface atomic concentration calculation. The binding energy scale of spectrometer was calibrated using the metallic Cu 2p$_{3/2}$ and Cu 3p$_{3/2}$ lines and Au Fermi Edge of the respective reference metals. All measurements were performed at a take-off angle of 90°. The CasaXPS (version 2.3.5) and Multipack software was used to fit photoelectron spectra. Many organic materials, and their surfaces, contain species that are sensitive to prolonged X-ray exposure, particularly under ultra-high vacuum conditions. In all analyses presented in this study, the sample stage temperature was reduced to less than -120 °C using a liquid nitrogen cooling system. This has been shown to preserve the chemical environment of matrix and adsorbed elements for periods far longer than data collection times [167], even with X-ray intensities experienced on synchrotron sources [168].

### 3.2.2. Adsorption of pharmaceuticals

#### 3.2.2.1. Adsorption kinetics

Adsorption kinetics were determined by placing 0.1 g of a waste-based adsorbent in a 50 mL Erlenmeyer flask and adding 20 mL of pharmaceutical solution (100 mg/L). Flasks were sealed with parafilm and placed in a shaker bath (100 rpm at 30 °C). For the commercial carbons, due to their high adsorption capacity, it was necessary to use 0.05 g of adsorbent with 100 mL of pharmaceutical solution (100 mg/L) in a 200 mL flask. Samples were filtered at time points ranging from 0 to 72 hours. The concentration of pharmaceuticals remaining in the filtrate was determined as specified in the HPLC methodology in section 3.2.2.4. Equilibrium for waste-based adsorbents was reached in 5 hours, and for commercial carbons, in 72 hours.
3.2.2.2. Single-solute adsorption isotherms

Batch adsorption tests were conducted to determine equilibrium isotherms. 0.1 g of a waste-based adsorbent was dispersed in 20 mL of pharmaceutical solutions at 8 concentrations (1 – 100 mg/L), and placed in the shaker bath (100 rpm, 30 °C) for 5 hours. For commercial carbons, 0.05g of carbon was dispersed in 100 mL of a pharmaceutical solution at 8 concentrations (1-100 mg/L) and placed in the shaker bath (100 rpm, 30 °C) for 72 hours. After the determined equilibrium time points, samples were filtered and the filtrate was analysed for the remaining pharmaceutical content by the HPLC method outlined in section 3.2.2.4. The equilibrium adsorption capacity was calculated and fitted to the Langmuir-Freundlich (L-F) equation (equation 4 of section 1.3.3). Trials of fitting the experimental data to either the Langmuir or the Freundlich equations were conducted, however the L-F equation gave a better goodness of fit for this data.

The pH of the pharmaceutical suspensions were not controlled using a buffer. Buffer ions could compete for adsorption sites with the target adsorbates’ molecules, complicating the analysis of the reactive adsorption mechanisms. However, the pH values of the system during adsorption were monitored by recording the initial and final pH values of the suspensions (Sartorius PB-11).

3.2.2.3. Multi-component adsorption isotherms

The adsorption isotherms measured from the multicomponent solutions were conducted in batch adsorption experiments. 0.1 g of waste-based adsorbent was dispersed in 20 mL of the multi-component (CBZ/SMX/TMP) pharmaceutical solution, or 0.05 g of commercial carbon in 100 mL of the multi-component pharmaceutical solution. In the multi-component solution all three pharmaceuticals were present in equal amounts (by mass) and prepared at 8 concentrations (1, 3, 5, 10, 30, 50, 80, 100 mg/L). Samples were placed in a shaker bath (100 rpm, 30 °C) for 5 hours
for waste-based adsorbents or 72 hours for commercial adsorbents. After equilibrium was reached, samples were filtered and the filtrate analyzed for the remaining pharmaceutical concentration by HPLC, as described below. The equilibrium adsorption capacity was calculated from fitting to the L-F equation (equation 4 of section 1.3.3).

As mentioned above, a buffer was not used to control the pH of the multi-component trials, in order to prevent competition between the pharmaceuticals and the buffer ions for adsorption sites.

3.2.2.4. Pharmaceutical analysis

The filtrates from the adsorption studies were analyzed for the remaining pharmaceutical concentration by high performance liquid chromatography (HPLC) with a Waters 2695, fitted with a LiChroCART® C18 column. For the single-solute pharmaceutical analysis, isocratic methods were used. For CBZ analysis the mobile phase consisted of 65% methanol and 35% Milli-Q water with trifluoroacetic acid (0.1%). For SMX analysis the mobile phase was 35% methanol and 65% Milli-Q water with trifluoroacetic acid (0.1%). And for TMP analysis, the mobile phase consisted of 45% methanol and 55% Milli-Q water with 0.1% trifluoroacetic acid. For all analyses the total flow was 1 mL/min and the injection volume 10 μL. Calibration curves were prepared with each pharmaceutical in the concentration range of 0.01 to 100 mg/L.

For the analysis of the multicomponent solution a gradient mobile phase was used that adjusted from 25% methanol and 75% water with 0.1% trifluoroacetic acid to 65% methanol and 35% water with 0.1% trifluoroacetic acid, and then back to the initial concentrations over the course of 20 minutes at a flow rate of 1 mL/min. The retention times for CBZ, SMX and TMP were 18.6, 5.4, and 9.1 minutes, respectively, with an injection volume of 10 μL. The equilibrium adsorption capacity was calculated and fitted to the L-F equation (equation 4 of section 1.3.3).
4. Material characterization

4.1 Elemental composition

The carbon content of the sewage sludge/fish-waste adsorbents ranges between 26-45% (Fig. 4.1). Due to burn-off, the materials prepared at the higher pyrolysis temperature have lower percentages of carbon, with 29% carbon on average in the samples obtained at 950 °C, as compared to 38% on average in the 650 °C-pyrolyzed samples. Samples prepared from the pure fish waste have the highest percentage of carbon within each pyrolysis class, with 45% in the samples obtained at 650 °C, and 36% in the samples obtained at 950 °C.

![Bar chart showing carbon content in adsorbents](image)

Fig. 4.1. Carbon content [%] in the waste-based adsorbents.

The remaining inorganic matter contains aluminum, iron, silicon, and calcium oxides (Table 4.1). The former three oxides originate from sewage sludge, while calcium oxide is mainly from the bones and shells found in the fish waste. The composite adsorbents reflect their source
materials in their inorganic make-up. Thus it can be seen that F100 samples (both pyrolysis
temperatures) have calcium oxide representing on average 92% of their inorganic composition,
while S50F50, S75F25 and S90F10, have 39%, 25 %, and 18% of calcium oxide on average,
respectively. The percentage of calcium corresponds to the amount of the fish waste in the
composite, while the amounts of the other inorganic components, mainly of silica, are directly
linked to the percentage of sewage sludge. It can be seen that the inorganic content is unaffected
by the carbonation temperature. The composition of the waste-based adsorbents is an important
factor that should be taken into account when analyzing the surface interactions/reactions that
occur during adsorption.

Table 4.1 Most represented oxides [wt. %] determined from the elemental analysis of waste-
based initial adsorbents during ICP analysis.

<table>
<thead>
<tr>
<th>Sample:</th>
<th>Oxides [wt. %]</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>S100-I</td>
<td></td>
<td>12.6</td>
<td>13.8</td>
<td>14.8</td>
<td>46.0</td>
</tr>
<tr>
<td>S90F10-I</td>
<td></td>
<td>11.7</td>
<td>18.3</td>
<td>14.0</td>
<td>43.1</td>
</tr>
<tr>
<td>S75F25-I</td>
<td></td>
<td>10.8</td>
<td>23.6</td>
<td>12.7</td>
<td>40.3</td>
</tr>
<tr>
<td>S50F50-I</td>
<td></td>
<td>8.4</td>
<td>38.0</td>
<td>10.0</td>
<td>30.9</td>
</tr>
<tr>
<td>F100-I</td>
<td></td>
<td>0.3</td>
<td>89.7</td>
<td>0.3</td>
<td>2.3</td>
</tr>
<tr>
<td>S100-II</td>
<td></td>
<td>11.9</td>
<td>14.2</td>
<td>15.5</td>
<td>49.0</td>
</tr>
<tr>
<td>S90F10-II</td>
<td></td>
<td>11.8</td>
<td>18.1</td>
<td>14.0</td>
<td>43.4</td>
</tr>
<tr>
<td>S75F25-II</td>
<td></td>
<td>10.6</td>
<td>25.9</td>
<td>12.6</td>
<td>38.6</td>
</tr>
<tr>
<td>S50F50-II</td>
<td></td>
<td>7.9</td>
<td>40.8</td>
<td>9.8</td>
<td>29.9</td>
</tr>
<tr>
<td>F100-II</td>
<td></td>
<td>0.1</td>
<td>94.1</td>
<td>0.3</td>
<td>1.1</td>
</tr>
</tbody>
</table>
4.2. Surface area and porosity

Nitrogen adsorption isotherms are shown in Fig. 4.2. Both materials carbonized at 650 °C and 950 °C demonstrate an isotherm type IV [169]. The isotherms level off at high pressure and are indicative of mesoporous structure. A hysteresis loop indicates the presence of bottle neck pores. From the adsorption isotherms the parameters of porous structure and size distribution were calculated.

![Nitrogen adsorption isotherms of waste-based adsorbents](image)

Analysis shows that the higher pyrolysis temperature increases the surface area for all samples except for F100-II (Table 4.2). The samples prepared at 650 °C had an average surface area of 64 ±6 m²/g, while the 950 °C prepared samples had an average surface area of 88 ±8 m²/g, with the exception of F100-II which had a surface area of 34 m²/g. As surface area is governed by the micropore volume, it is worth noting the alterations in the microporosity with an increase in the pyrolysis temperature. The samples prepared at 650 °C demonstrated an average pore volume of 0.099 ± 0.019 cm³/g, while those prepared at 950 °C had a $V_t$ of 0.125 ± 0.015 cm³/g, and
therefore it can be concluded that the increased carbonization temperature resulted in a more
developed microporosity. This phenomenon has been noted previously [170, 171], and attributed
to the release of thermal decomposition products which act as pore formers [170]. A decrease in
the volume of micropores with an increase in the treatment temperature for the fish-derived
adsorbents can be explained by an increase in the aromatization level of the carbon phase, the
formation of the more condensed structure, and the content of the inorganic phase. The latter
results in the limited release of pore formers.

Table 4.2. Parameters of the porous structure calculated from the nitrogen adsorption isotherms
for the initial waste-based adsorbents.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) [m(^2)/g]</th>
<th>( V_{\text{mic}} ) [cm(^3)/g]</th>
<th>( V_{\text{meso}} ) [cm(^3)/g]</th>
<th>( V_t ) [cm(^3)/g]</th>
<th>( V_{\text{mic}}/V_t )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S100-I</td>
<td>63</td>
<td>0.030</td>
<td>0.044</td>
<td>0.074</td>
<td>0.40</td>
</tr>
<tr>
<td>S90F10-I</td>
<td>74</td>
<td>0.039</td>
<td>0.057</td>
<td>0.096</td>
<td>0.41</td>
</tr>
<tr>
<td>S75F25-I</td>
<td>58</td>
<td>0.031</td>
<td>0.056</td>
<td>0.087</td>
<td>0.36</td>
</tr>
<tr>
<td>S50F50-I</td>
<td>67</td>
<td>0.031</td>
<td>0.074</td>
<td>0.105</td>
<td>0.29</td>
</tr>
<tr>
<td>F100-I</td>
<td>56</td>
<td>0.029</td>
<td>0.103</td>
<td>0.132</td>
<td>0.22</td>
</tr>
<tr>
<td>S100-II</td>
<td>101</td>
<td>0.044</td>
<td>0.101</td>
<td>0.145</td>
<td>0.30</td>
</tr>
<tr>
<td>S90F10-II</td>
<td>77</td>
<td>0.035</td>
<td>0.090</td>
<td>0.125</td>
<td>0.28</td>
</tr>
<tr>
<td>S75F25-II</td>
<td>86</td>
<td>0.038</td>
<td>0.095</td>
<td>0.133</td>
<td>0.29</td>
</tr>
<tr>
<td>S50F50-II</td>
<td>87</td>
<td>0.038</td>
<td>0.088</td>
<td>0.126</td>
<td>0.30</td>
</tr>
<tr>
<td>F100-II</td>
<td>34</td>
<td>0.019</td>
<td>0.079</td>
<td>0.098</td>
<td>0.19</td>
</tr>
</tbody>
</table>

With an increase in the amount of sewage sludge in the samples, the degree of mesoporosity
\((V_{\text{meso}}/V_t)\) increases. For sample S50F50-II, the mesoporosity constitutes 16% of the total
porosity, while for S100-II it reaches 56%. On average, the degree of mesoporosity increases
after heat treatment at 950 °C. This does not match the findings conducted on other waste-based
adsorbents, wherein the volume of mesopores generally shows little change in response to the
pyrolysis temperature of the carbonaceous materials [170, 171]. An increase in this parameter
for the current study can be linked to an enlargement of the micropores as a result of the removal of carbon, and the partial decomposition of the inorganic species [172].

The pore size distributions (Fig. 4.3) were calculated using the Barret-Joyner-Halenda method from the adsorption branches of the isotherms. It can be seen that the majority of the pore volume is found in mesopores larger than 30 Å. The results demonstrate the heterogeneity of the pore sizes in the samples and indicate higher textural heterogeneity in the samples carbonized at 650 °C than those at 950 °C. Due to the impact that surface area and porosity can have upon the adsorption capacity, they are important factors to take into consideration in the analysis of the adsorption process.

Fig. 4.3. Pore size distribution for the waste-based adsorbents, carbonized at (A) 650 °C and (B) 950 °C, calculated using the BJH method.

4.3 Thermal analysis/mass spectrometry

The DTG curves are shown in Fig. 4.4. The peaks represent weight loss as a result of the decomposition of materials upon heat treatment. Analysis was conducted up to the carbonization
temperature. The samples prepared at 650 °C (Fig. 4.4A) have peaks at 100, 350, 470 (only for F100-I), and 650 °C. The peak at 100 °C corresponds to the removal of adsorbed water from the pores of the materials. Since the waste-based adsorbents have a high content of the inorganic phase, it is expected that the only noticeable weight loss will be attributed to the hydroxylation/hydration reactions of the inorganic compounds when exposed to water and to the decomposition of inorganic salts, and not to the carbon removal. The small peak at 350 °C can be attributed to the decomposition of the inorganic phases consisting of calcium, magnesium, iron, and aluminum present in the pyrolyzed materials[173], and also to the decomposition of the oxygen groups of the carbon phase [174]. For sample F100-I, a small peak on the DTG curves at 470 °C represents the dehydroxylation of calcium hydroxide [175], present in large quantity in this sample (Table 4.1). Calcium hydroxide can contribute to the porosity development in this sample via burn-off in the carbon phase [176]. The peak at about 650 °C becomes more intense as the fish content increases. It is likely that it reflects the decomposition of carbonates, particularly calcium carbonate [177], which is a component of the fish waste.

In the case of the samples carbonized at 950 °C (Fig. 4.4B) the first peak on the DTG curves at 100 °C represents the removal of adsorbed water. The higher temperature shoulder is linked to the dehydroxylation of iron hydroxide [178]. This peak diminishes in its intensity with an increasing fish content owing to the fact that the sewage sludge is the main source of this iron-containing inorganic phase. With the addition of the fish waste, a broad hump with the maxima at 450 and 600 °C appears. Interestingly, the gradual increase in the fish-based phase results in an increase in the amount of the species decomposing at 650 °C. We link them to the decomposition of calcium [179] and magnesium carbonates [180]. The weight loss between 300 and 600 °C
might represent the dehydroxylation of magnesium hydroxide [181] and decomposition of iron [182] or aluminum salts such as sulfates [183].

Fig. 4.4. DTG curves for the initial waste-based adsorbents carbonized at 650 °C (A), and 950 °C (B).

Further information on the surface composition can be inferred from the fragmentation of the gases released from the surfaces of the adsorbents during thermal treatment (Fig. 4.5). The mass to charge ratio (m/z) detected (and the fragments attributed) for the initial samples (and for comparison to the exposed samples in chapter 6) were m/z 12 (C), 15 (NH), 17 (OH, NH₃), 18 (H₂O, NH₄⁺), 30 (NO), and 44 (CO₂). The profiles are similar for the samples of the same composition, regardless of preparation temperature. The thermal profiles of m/z 17 and 18 for all samples show peaks at 100 °C (representing the removal of physically adsorbed water). For the samples composed of pure fish waste, a second peak in these profiles appears at 370 °C, which represents the removal of water formed during the dehydroxylation of the calcium hydroxide. On the profiles of m/z 12 and 44, peaks at 580 and 850 °C are visible (representing the reaction of the oxygen groups with the carbonaceous phase to produce CO₂). The peak at 580 °C on m/z 44
increases in intensity with an increasing amount of fish waste in the adsorbent composition. This is due to the higher carbon content of the fish waste, as compared to the sewage sludge. The profile of $m/z$ 44 has more pronounced peaks for the samples prepared at 650 °C, due to lower burn-off resulting in more carbon content remaining available to react with the surface oxygen groups. The profiles of $m/z$ 15 and 30 do not show any peaks on the initial materials, but are included for comparison with the exhausted materials that are presented in chapter 6.
Fig. 4.5. \(m/z\) thermal profiles of initial waste-based adsorbents (multiplication factors: MW-12 x 1000, MW-15 x 500, MW-17 x 25, MW-18 x 10, MW-30 x 100, MW-44 x 200).
4.4 Potentiometric titration

Further differences in the surface chemical properties of the samples can be revealed by the analysis of the proton binding curves (Fig. 4.6). Their shapes (no sharp inflection points related to chemical reactions) exclude the extensive effects of an inorganic phase dissolution. All samples exhibit the basic nature of the surface species. The pH values of the point zero charge (pH_{PZC}) in all cases are between 9 and 10 and demonstrate a slight increase for the high temperature pyrolyzed samples. The samples also demonstrate an increase in the proton uptake with an increase in the content of the fish-derived phase in the composite. We link these basic properties to the presence of the calcium-containing mineral phases that are present in this waste (Table 4.1). Increasing the carbonization temperature decreases the number of basic species detected on the surface. This effect is likely caused by the decomposition of inorganic species and formation of more mineral phases [184].

Fig. 4.6. Proton uptake curves for the sewage sludge/fish waste-based adsorbents carbonized at 650 °C (A) and 950 °C (B).
The detailed changes are seen on the pKₐ distributions (Fig. 4.7). The materials prepared at the higher temperature generally have more groups present (with the exception of S100). When the content of carbonized fish waste increases, the contribution of functional groups from the carbon phase increases.

Fig. 4.7. The comparison of the pKₐ distributions for the sewage sludge/fish waste-based adsorbents carbonized at 650 °C (A) and 950 °C (B).

The peak positions and number of groups with particular pKₐ are shown in Table 4.3. The species detected between pKₐ 5-6, 6-7 and 7-8 represent bridging and terminal groups of silica [185] with the latter being less acidic [186].
Table 4.3. Peak positions and numbers of groups (in parentheses; [mmol/g]) for initial sewage sludge/fish waste adsorbents.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>pKₐ 4-5</th>
<th>pKₐ 5-6</th>
<th>pKₐ 6-7</th>
<th>pKₐ 7-8</th>
<th>pKₐ 8-9</th>
<th>All</th>
</tr>
</thead>
<tbody>
<tr>
<td>S100-I</td>
<td>9.56</td>
<td>5.82</td>
<td>(0.019)</td>
<td></td>
<td>7.45</td>
<td>(0.027)</td>
<td>0.046</td>
</tr>
<tr>
<td>S90F10-I</td>
<td>9.74</td>
<td>5.44</td>
<td>(0.048)</td>
<td>6.45</td>
<td>(0.013)</td>
<td>7.20</td>
<td>(0.023)</td>
</tr>
<tr>
<td>S75F25-I</td>
<td>9.54</td>
<td>5.27</td>
<td>(1.128)</td>
<td>6.48</td>
<td>(0.034)</td>
<td>7.56</td>
<td>(0.027)</td>
</tr>
<tr>
<td>S50F50-I</td>
<td>9.59</td>
<td>5.30</td>
<td>(0.202)</td>
<td>6.33</td>
<td>(0.101)</td>
<td>7.76</td>
<td>(0.057)</td>
</tr>
<tr>
<td>F100-I</td>
<td>9.84</td>
<td>5.11</td>
<td>(0.434)</td>
<td>6.30</td>
<td>(0.160)</td>
<td>7.88</td>
<td>(0.048)</td>
</tr>
<tr>
<td>S100-II</td>
<td>8.84</td>
<td>5.41</td>
<td>(0.053)</td>
<td></td>
<td>7.24</td>
<td>(0.025)</td>
<td></td>
</tr>
<tr>
<td>S90F10-II</td>
<td>9.83</td>
<td>5.39</td>
<td>(0.052)</td>
<td>6.30</td>
<td>(0.021)</td>
<td>7.57</td>
<td>(0.025)</td>
</tr>
<tr>
<td>S75F25-II</td>
<td>9.99</td>
<td>5.34</td>
<td>(0.066)</td>
<td>6.21</td>
<td>(0.045)</td>
<td>7.73</td>
<td>(0.035)</td>
</tr>
<tr>
<td>S50F50-II</td>
<td>10.3</td>
<td>5.40</td>
<td>(0.164)</td>
<td>6.67</td>
<td>(0.042)</td>
<td>7.94</td>
<td>(0.041)</td>
</tr>
<tr>
<td>F100-II</td>
<td>10.3</td>
<td>4.75</td>
<td>(0.385)</td>
<td>5.76</td>
<td>(0.028)</td>
<td>6.90</td>
<td>(0.037)</td>
</tr>
</tbody>
</table>

4.5. Fourier Transform Infrared spectroscopy

The ATR spectra data (Fig. 4.8) did not reveal much information due to the absorption of much of the IR spectra by the carbon phase of the materials. The spectra for the samples prepared at 650 °C showed bands at 1410 and 1000, which represent the stretch in C=O and C-O, respectively [187]. For the samples prepared at 950 °C, the bands at 2300 and 1020 correspond to CO₂ and C-O, respectively [188]. The spectra did not demonstrate discernable differences between materials of varying waste content.
The DRIFTs data is presented in section 5.1.3 for the sake of comparison with the exhausted samples.

Fig. 4.8. FT-IR spectra for the initial waste-based materials.

4.6. X-ray diffraction spectroscopy

X-Ray diffraction patterns for the initial and exhausted adsorbents are collected in Fig. 4.9. The main crystallographic phases for the sewage sludge-containing adsorbents are quartz (SiO₂), barringerite (Fe₂P), and anorthite (CaAl₂Si₂O₈). In the adsorbents containing fish waste, apatites (chloroapatite, hydroxyapatite) and calcium hydroxide represent the main crystallographic phases. The profiles of the composite samples show the crystallographic phases seen in both precursor materials, with the prevalence of specific phases depending on the percentage of the precursor in the composite. The samples pyrolized at 950 °C show a higher crystallization level of the mineral phases in comparison with those pyrolized at 650 °C.
Fig. 4.9. X-ray diffraction patterns for the waste-based adsorbents, carbonized at 650 °C (A) and 950 °C (B). ▲ SiO₂; ○ Fe₃P; ★ Ca₁₀(PO₄)₆(Cl, OH)₂; □ CaAl₂Si₂O₈; ○ AlPO₄; ◇ CaOH₂;
∇ (NH₄)₂CaSO₄·H₂O; □ Ca₁₀(PO₄)₆CO₃.

4.7. Scanning electron microscopy/energy dispersive X-ray

The SEM images (Fig. 4.10) show the differences in the samples’ morphology linked to their composition. The large pores between the particles of the inorganic phase in the sewage-derived samples are clearly visible (S100-I, S100-II). Based on EDX analyzes (Fig. 4.11) the surface contains phases of SiO₂ and carbon, with deposited particles (width 40-120 nm) composed of...
Fe\textsubscript{2}P. In the fish-derived samples, the carbon phase is visible, with the calcium-containing inorganic phases embedded in it. There are differences between the textures of the same origin samples that were carbonized at two different temperatures. Samples S100-I and S100-II have similar granular structures, however in the latter, the presence of the crystalline particles of Fe\textsubscript{2}P is more pronounced. This is due to the higher inorganic phase content in S100-II, and a more complete thermal transformation/crystallization of this phase [178] as a result of the high temperature applied.

Fig. 4.10. SEM images of S100-I, S100-II, S90F10-I, S90F10-II, F100-I, F100-II.
Fig. 4.11. EDX mapping of most represented elements in samples S100-I and II, S90F10-I and II, and F100-I and II.
In sample F100-I two different kinds of particles can be distinguished: granules, which contain phases of calcium and phosphorus and needle-like particles, on the surface of the carbon phase. The surface of F100-II, carbonized at 950 °C, shows particles of a rugous structure, yielding a surface of fissures. The large pores are less visible, and there is a higher dispersion of inorganic particles in comparison to sample F100-I. Adsorbent S90F10-I and II are shown as an example of a composite material. This composite greatly resembles the sewage sludge owing to its predominate content in the precursor. The large pores are visible, with the inorganic phases distributed on the surface. EDX analysis demonstrated a greater dispersion of the inorganic phase at the higher carbonization temperature. The carbonization temperature impacted the formation of pores, resulting in a looser structure of the sample obtained at 950 °C.
5. Adsorption on the waste-based adsorbents prepared at 650 °C

Of the waste-based materials, adsorption trials were first conducted with the adsorbents prepared at 650 °C.

5.1 Adsorption from a single-component solution

Adsorption trials from single component solution were conducted with three pharmaceuticals: carbamazepine, sulfamethoxazole and trimethoprim.

5.1.1. Carbamazepine

5.1.1.1. Adsorption isotherms of CBZ on the waste-based adsorbents carbonized at 650 °C.

The adsorption isotherms (fitted to the L-F equation) of CBZ on the waste-based adsorbents prepared at 650 °C are presented in Fig. 5.1. The fitting parameters and SEE errors are presented in Table 5.1. For all materials the correlation coefficient is greater than 0.99. Samples S50F50-I and F100-I demonstrate superior performances over samples S75F25-I, S100-I, and S90F10-I. At an arbitrary equilibrium concentration of 0.2 mmol/L the adsorption capacity of the S50F50-I is 23% greater than that on S100-I and S75F25-I, and 44% greater than that on S90F10-I.

Table 5.1. Fitting parameter to L-F equation of CBZ adsorption isotherms on waste-based adsorbents carbonized at 650 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>qm (mmol/g)</th>
<th>K (L/mmol)</th>
<th>n</th>
<th>R²</th>
<th>SEE</th>
</tr>
</thead>
<tbody>
<tr>
<td>S100-I</td>
<td>0.079</td>
<td>0.582</td>
<td>0.62</td>
<td>0.9956</td>
<td>5.55x10⁻⁵</td>
</tr>
<tr>
<td>S90F10-I</td>
<td>0.043</td>
<td>10.39</td>
<td>1.62</td>
<td>0.9985</td>
<td>3.81x10⁻⁶</td>
</tr>
<tr>
<td>S75F25-I</td>
<td>0.091</td>
<td>0.376</td>
<td>0.59</td>
<td>0.9958</td>
<td>3.89x10⁻⁶</td>
</tr>
<tr>
<td>S50F50-I</td>
<td>0.095</td>
<td>0.358</td>
<td>0.52</td>
<td>0.9995</td>
<td>1.23x10⁻⁶</td>
</tr>
<tr>
<td>F100-I</td>
<td>0.085</td>
<td>0.485</td>
<td>0.58</td>
<td>0.9966</td>
<td>1.48x10⁻⁵</td>
</tr>
</tbody>
</table>
Fig. 5.1 Adsorption isotherm of carbamazepine on the sewage sludge/fish waste-based adsorbents carbonized at 650 °C. Solid lines represent the fitting to the L-F equation.

A comparison of the measured (based on L-F fitting) and hypothetical (based on L-F fitting for the sludge and fish waste based adsorbent and assuming their physical mixtures) adsorption values is presented in Fig. 5.2. For every composite, with the exception of sample S90F10-I, the measured CBZ adsorption exceeded the predicted adsorption by 15-20 %. These results suggest that there is a synergistic effect of the composite formation affecting the adsorption mechanism.
Fig. 5.2. Comparison of measured (based on fitting to L-F equation) and hypothetical $q_m$ values (with percent difference between them) of adsorption capacity for CBZ. The hypothetical values were calculated assuming a physical mixture of the components and taking into account their % contributions in the composites.

5.1.1.2. Thermal analysis of CBZ on the 650 °C carbonized waste-based adsorbents

Analysis of the DTG curves of the initial and CBZ exhausted samples was conducted (Fig. 5.3). Samples were analyzed up to the carbonization temperature of the adsorbents, however no clear differences were observed due to the small amount of CBZ adsorbed (about 1%).
Fig. 5.3. DTG curves in helium for the 650 °C carbonized adsorbents, initial (dotted line) and spent with carbamazepine (solid line).

### 5.1.1.3. Potentiometric titration of 650 °C carbonized waste-based adsorbents exposed to CBZ

After CBZ adsorption, the changes in surface acidity can be seen in the proton binding curves (Fig. 5.4). Even though the adsorption capacities of the 650 °C materials are small, the changes observed indicate chemical interactions on the surface. The complexation of CBZ on metal cations might be the predominant mechanism of reactive adsorption on these materials.
Fig. 5.4. Proton uptake curves for the sewage sludge/fish waste-based adsorbents carbonized at 650 °C, initial and spent with carbamazepine.

The pKa distributions for materials before and exposure to CBZ are shown in Fig. 5.5. The samples that contain primarily sewage sludge, have fewer groups after exposure to CBZ by 13 to 35 %, as the basic species are consumed during adsorption. S50F50-I maintains the same number of surface groups before and after exposure. And F100-I has 23 % more groups after CBZ exhaustion, due to the appearance of new basic groups after adsorption. This is likely due to the high content of the carbon phase, on which dispersive interactions of the aromatic rings of CBZ are predominant, and the exposed amine groups from CBZ contribute to surface basicity.
Fig. 5.5. The comparison of the pK\textsubscript{a} distributions for the waste-based adsorbents carbonized at 650 °C, initial and after carbamazepine adsorption

### 5.1.1.4. XRD of CBZ on 650 °C carbonized waste-based adsorbents

X-Ray diffraction patterns for the initial and exhausted adsorbents are collected in Fig. 5.6 (for a detailed analysis of the initial materials see section 4.6). Subtle differences can be noted after exposure to CBZ. In samples S90F10-I, S75F25-I and S50F50-I the peaks representing anorthite (CaAl\textsubscript{2}Si\textsubscript{2}O\textsubscript{8}) increase in their intensity after carbamazepine adsorption. This might be related to an increase in the average level of crystallization/chemical homogeneity as a result of the removal of water soluble salts from the sludge. The XRD results for F100-I show a typical pattern for calcium phosphate carbonate (Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}CO\textsubscript{3}), however this species is not detected in the sample exposed to CBZ.
Fig. 5.6. X-Ray diffraction patterns for the sewage sludge/fish waste-based adsorbents, carbonized at 650 °C, initial and exposed to CBZ. ▲ SiO$_2$; ● Fe$_2$P; ★ Ca$_{10}$ (PO$_4$)$_6$(Cl, OH)$_2$; ■ CaAl$_2$Si$_2$O$_8$; ○ AlPO$_4$; ⊖ CaOH$_2$; ▽ (NH$_4$)$_2$CaSO$_4$·H$_2$O; □ Ca$_{10}$ (PO$_4$)$_6$CO$_3$. 
5.1.1.5. Summary of CBZ adsorption on the waste-based adsorbents carbonized 650 °C.

The attraction of CBZ for polar sites plays an important role, although taking into consideration the low porosity of the materials, physical adsorption does not appear to be the predominant mechanism of adsorption. This is evidenced by the fact that S90F10-I has the greatest surface area and volume of micropores, yet it demonstrated the lowest CBZ adsorption capacity of all the 650 °C prepared samples. In terms of the composition, the content of the carbon phase in the samples correlates well with the adsorption capacity for CBZ. The samples with the highest carbon content demonstrated superior adsorption capabilities, indicating the role of the π-π interactions between the aromatic rings of the adsorbent and CBZ. A synergistic effect was observed in the composite adsorbents composed of both waste precursors. This effect was clear for sample S50F50-I, where a higher quantity of CBZ was adsorbed than that on the materials prepared from sewage sludge or fish waste alone.

5.1.2. Sulfamethoxazole

5.1.2.1. Adsorption isotherms of SMX on 650 °C carbonized waste-based adsorbents

Fig. 5.7 shows the adsorption isotherms of SMX on the sewage sludge/fish waste derived adsorbents. The experimental data was fitted to Langmuir-Freundlich equation (R² and SSE values can be found in Table 5.2). Of the materials pyrolyzed at 650 °C, S100-I has the highest SMX adsorption capacity, and F100-I has the lowest. The materials with a high silica content demonstrate the highest SMX adsorption capacity. The high content of silica can be linked to the interactions of SMX with hydroxyl groups [189].
Fig. 5.7. Adsorption isotherm of SMX on waste-based adsorbents carbonized at 650 °C. Solid lines represent the fitting to the L-F equation.

Table 5.2. Fitting parameter to L-F equation of SMX adsorption isotherms on waste-based adsorbents carbonized at 650 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>qm (mmol/g)</th>
<th>K (L/mmol)</th>
<th>n</th>
<th>R^2</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>S100-I</td>
<td>0.017</td>
<td>0.678</td>
<td>0.56</td>
<td>0.9913</td>
<td>2.42x10^{-7}</td>
</tr>
<tr>
<td>S90F10-I</td>
<td>0.010</td>
<td>2.225</td>
<td>0.61</td>
<td>0.9738</td>
<td>6.53x10^{-7}</td>
</tr>
<tr>
<td>S75F25-I</td>
<td>0.007</td>
<td>1.512</td>
<td>0.65</td>
<td>0.9389</td>
<td>4.83x10^{-7}</td>
</tr>
<tr>
<td>S50F50-I</td>
<td>0.006</td>
<td>4.062</td>
<td>0.72</td>
<td>0.9784</td>
<td>2.48x10^{-7}</td>
</tr>
<tr>
<td>F100-I</td>
<td>0.001</td>
<td>12.667</td>
<td>1.05</td>
<td>0.9633</td>
<td>2.04x10^{-7}</td>
</tr>
</tbody>
</table>

Fig. 5.8 summarizes the impact on adsorption capacity of synthesized composite adsorbents, as opposed to the single-source materials. The numbers express the differences between the measured capacity and the hypothetical one, calculated assuming the physical mixture of the components. It can be seen that for SMX adsorption the single component materials generally perform better than the composite ones, although it should be recognized that the adsorption amounts on all the materials were low.
Fig. 5.8. Comparison of measured (based L-F fittings at a $C_{eq}$ of 0.1 mmol/L) and hypothetical $q_e$ values (with percent difference between them) of adsorption capacity for SMX. The hypothetical values were calculated assuming a physical mixture of the components and taking into account their % contributions in the composites.

In order to elucidate the impact of the various chemical and textural features of the adsorbents on the adsorption capacity of the target pharmaceuticals, the effects of the surface features on the adsorption capacity (at an arbitrarily chosen $C_{eq}$ of 0.1 mmol/g) were investigated. Increased surface area (Fig. 5.9.A) has a slight positive impact on the SMX adsorption capacity of the adsorbents. The adsorption capacity increases with the mesopore volume decrease (Fig. 5.9.B). The adsorption capacity decreases with an increasing fish content (and a decreasing sewage sludge content) (Fig. 5.9.C, $R^2 = 0.83$). The trend in Fig. 5.9.D is similar to Fig. 5.9.C, highlighting the fact that the fish waste is the primary source of the adsorbents’ calcium, while iron, alumina and silica originate from the sewage sludge.
Fig. 5.9. Dependence of adsorption capacity of SMX [mmol/g] on surface area [m$^2$/g] (A), volume of mesopores [cm$^3$/g] (B), percentage sewage sludge or fish waste (C), and percentage calcium or iron/aluminum/silica in the adsorbent (D).

5.1.2.2. Thermal analysis of SMX on 650 °C carbonized waste-based adsorbents

DTG curves (Fig. 5.10) were analyzed to gain further insight into the interactions between the adsorbates and the adsorbent surfaces. However, the samples prepared at 650 °C and exhausted with SMX demonstrate little difference in the thermal profiles of the initial and spent samples, which is linked to their low adsorption capacity.
Fig. 5.10. DTG curves in helium for the 650 °C carbonized adsorbents, initial (dotted line) and spent with sulfamethoxazole (solid line).

5.1.2.3. Potentiometric titration of 650 °C carbonized waste-based adsorbents exposed to SMX

There was an increased proton uptake on all the 650 °C carbonized materials after SMX adsorption (Fig. 5.11). The $\text{pH}_{\text{PZC}}$ values were more basic after exposure to SMX, and shifted from about pH 9 prior to SMX exposure, to pH 10 after. The $\text{pH}_{\text{PZC}}$ likely increases due to the reactivity of the amine group of SMX with the SiO$_2$ content of the adsorbents, which decreased the acidic surface groups.
Fig. 5.11. Proton uptake curves for sewage sludge/fish waste-based adsorbents carbonized at 650 °C, initial and spent with SMX.

From the pK$_a$ distributions (Fig. 5.12) it can be seen that the amount of groups increases 11 to 22 fold after adsorption with SMX. The increase was greatest for the samples where sewage sludge was the predominant component. Most of the increase in the number of total groups is due to the presence of a large amount of the strongly acidic groups of low pK$_a$ values. This indicates the acidification of the surfaces due to pharmaceutical adsorption.
Fig. 5.12. The comparison of the pKₐ distributions for the waste-based adsorbents carbonized at 650 °C, initial and after SMX adsorption.

5.1.2.4. X-ray Diffraction of SMX on 650 °C carbonized waste-based adsorbents

The X-ray diffraction patterns for the initial and spent samples pyrolyzed at 650 °C were analyzed (Fig. 5.13), however no major differences can be seen, likely owing to the small amount of SMX adsorbed.
Fig. 5.13. X-Ray diffraction patterns for the sewage sludge/fish waste-based adsorbents, carbonized at 650 °C, initial and exposed to SMX.

\[ \text{SiO}_2; \text{Fe}_2\text{P}; 3\text{Ca}_{10}(\text{PO}_4)_6(\text{Cl, OH})_2; \text{CaAl}_2\text{Si}_2\text{O}_8; \text{AlPO}_4; \text{Ca(OH)}_2; \nabla (\text{NH}_4)_2\text{CaSO}_4; \Box \text{Ca}_{10}(\text{PO}_4)_6\text{CO}_3 \]
5.1.2.5. Summary of SMX adsorption on 650 °C carbonized waste-based adsorbents

The waste-derived materials pyrolyzed at 650 °C have a low surface area and pore volume, compared to commercial adsorbents. However, this will have minimal impact on the removal capacities of these materials, as physical adsorption is not the predominant mechanism for removal of SMX from aqueous phase. For the removal of SMX, the inorganic content, and in particular SiO₂, would play an important role in acid-base interactions with the amine group. The sample with the highest quantity of SiO₂ content, S100-I, likely had the highest adsorption capacity for SMX for this reason.

5.1.3. Trimethoprim

5.1.3.1. Adsorption isotherms of TMP on 650 °C carbonized waste-based adsorbents

Fig. 5.14 shows the adsorption isotherms of TMP on the sewage sludge/fish waste derived adsorbents. The experimental data was fitted to L-F equation (R² and SSE values can be found in Table 5.3). Sample S90F10-I displayed the highest TMP adsorption capacity of the 650 °C pyrolyzed materials (at a Cₑq of 0.1), and S100-I, the lowest, with a 42 % lower quantity of adsorbate removed by the latter material.

Table 5.3. Fitting parameter to L-F equation of TMP adsorption isotherms on waste-based adsorbents carbonized at 650 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>qm (mmol/g)</th>
<th>K (L/mmol)</th>
<th>n</th>
<th>R²</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>S100-I</td>
<td>0.104</td>
<td>0.005</td>
<td>0.30</td>
<td>0.9289</td>
<td>1.05x10⁻⁵</td>
</tr>
<tr>
<td>S90F10-I</td>
<td>0.074</td>
<td>0.162</td>
<td>0.30</td>
<td>0.9839</td>
<td>8.73x10⁻⁶</td>
</tr>
<tr>
<td>S75F25-I</td>
<td>0.063</td>
<td>0.585</td>
<td>0.40</td>
<td>0.9917</td>
<td>2.28x10⁻⁶</td>
</tr>
<tr>
<td>S50F50-I</td>
<td>0.073</td>
<td>0.164</td>
<td>0.37</td>
<td>0.9965</td>
<td>1.12x10⁻⁶</td>
</tr>
<tr>
<td>F100-I</td>
<td>0.063</td>
<td>0.572</td>
<td>0.43</td>
<td>0.9873</td>
<td>4.31x10⁻⁶</td>
</tr>
</tbody>
</table>
Fig. 5.14. Adsorption isotherm of TMP on waste-based adsorbents carbonized at 650 °C. Solid lines represent the fitting to the L-F equation.

Fig. 5.15 summarizes the impact on adsorption capacity of synthesized composite adsorbents, as opposed to the single-source materials. The numbers express the differences between the measured capacity and the hypothetical one calculated assuming the physical mixture of the components. For the adsorption of TMP the benefit of using composite materials is clear. The best performing of the 650 °C pyrolyzed samples, S90F10-II had a higher adsorption capacity than the materials obtained solely from the single precursors, outperforming the hypothetical physical mixture of its components by 39%.
Fig. 5.15. Comparison of measured (based L-F fittings at a \( C_{eq} \) of 0.1 mmol/L) and hypothetical \( q_e \) values (with percent difference between them) of adsorption capacity for TMP. The hypothetical values were calculated assuming a physical mixture of the components and taking into account their % contributions in the composites.

5.1.3.2. Thermal analysis of TMP on 650 °C carbonized waste-based adsorbents

Analysis of the DTG curves of the samples pyrolyzed at 650 °C and exhausted with TMP demonstrated little difference from the thermal profiles of the initial samples (Fig. 5.16). The lack of differences is linked to their low adsorption capacity.
Fig. 5.16. DTG curves in helium for the adsorbents, initial (dotted line) and spent with trimethoprim (solid line).

5.1.3.3. Potentiometric titration of 650 °C carbonized waste-based adsorbents exposed to TMP

After TMP exposure, the Q value on the proton binding curves increases, indicating an increased proton uptake for all the samples (Fig. 5.17). The pH_{PZC} of the TMP exposed samples was more basic, nearly reaching pH 10 (after starting at pH 9) for all samples except F100-I, where it remained around pH 9.
Fig. 5.17. Proton uptake curves for sewage sludge/fish waste-based adsorbents carbonized at 650 °C, initial and spent with TMP.

From the pK\textsubscript{a} distributions (Fig. 5.18) it can be seen that the amount of groups increases 6 to 23 fold after adsorption with TMP. The increase was greatest for the samples where sewage sludge was the predominant component. Most of the increase in the number of total groups is due to the presence of a large amount of the strongly acidic groups of low pK\textsubscript{a} values. Therefore acidification of the surface is occurring as a result of pharmaceutical adsorption.
5.1.3.4. X-Ray Diffraction of TMP on 650 °C carbonized waste-based adsorbents

Examination of the XRD profiles (Fig. 5.19) for the initial and TMP exhausted samples pyrolyzed at 650 °C did not identify crystallographic structures pertaining to TMP. This could be due to the low quantity of TMP adsorbed on the materials, or the fact that TMP did not deposit on the surface in crystal form. For sample F100-I after TMP exposure, the calcium-containing species at 15 and 52 2θ decrease in content.
Fig. 5.19. X-Ray diffraction patterns for the sewage sludge/fish waste-based adsorbents, carbonized at 650 °C, initial and exposed to TMP.

▲ SiO₂; ● Fe₂P; 3Ca₁₀(PO₄)₆(Cl, OH)₂; ■ CaAl₂Si₂O₈; ○ AlPO₄; ♦ Ca(OH)₂; ∇ (NH₄)₂CaSO₄; □ Ca₁₀(PO₄)₆CO₃
5.1.3.5. Summary of TMP adsorption on 650 °C carbonized waste-based adsorbents

If physical adsorption governed the adsorption of TMP onto the waste-based materials, the porosity and the sizes of adsorbate would have been important factors. However, it was found that TMP adsorbed in greater quantity than SMX, despite TMP having a larger molecular size (and therefore the most pore diffusion constraint), thereby indicating the importance of chemical adsorption in the removal of TMP from aqueous phase. Likely the fact that TMP has two aromatic rings to facilitate π-π interactions with the carbon layers of the adsorbent contributed to adsorption at higher quantities than SMX, despite the larger molecular size. Another factor facilitating adsorption would be the chelation that could occur between the amines of TMP and the metals of the adsorbent. This highlights the importance of the inorganic phase. The best adsorption was on the adsorbents of composition S90F10 and F100. The performance of the fish waste materials is due to the high calcium content that enables chelation to occur. Although the SiO$_2$-rich sewage sludge did not provide opportunities for chelation, when 10 % fish waste was added, a synergistic effect was noted.

5.2 Adsorption from multi-component solution

To simulate the environment within water treatment plants where the inflow contains a mixture of a variety of pharmaceutical compounds, the 650 °C carbonized adsorbents were exposed to a solution containing carbamazepine, sulfamethoxazole and trimethoprim. The materials’ adsorption capacity for the multi-component solution was measured, and compared to both the adsorption from single solute solution for these materials.
5.2.1. Adsorption isotherms of multi-component pharmaceutical solution on waste-based adsorbents carbonized at 650 °C

Fig. 5.20 shows the adsorption isotherms of CBZ, SMX, and TMP from the multi-component solution on the sewage sludge/fish waste derived adsorbents prepared at 650 °C. Both CBZ and TMP adsorb in higher quantities than SMX from the multi-component solution. This is likely due to the pH values of the 650 °C adsorbent/adsorbate suspensions which created unfavorable conditions for SMX removal. SMX would be deprotonated at the experimental pH, resulting in increased hydrophobicity and low adsorption quantities.

Fig. 5.20. Adsorption isotherms of waste-based adsorbents carbonized at 650° C from multi-component pharmaceutical solution, containing CBZ, SMX, and TMP. Lines represent the fitting to the L–F equation.
In Fig. 5.21 it can be seen that with the application of multi-component solution, the quantity adsorbed of each pharmaceutical is reduced as compared to adsorption from single solute solution, due to competition for adsorption sites. In general, adsorption capacity decreased by 22 to 73%, with the exception of CBZ adsorption on S90F10-I, in which the amount adsorbed remained unchanged between the single and multi-component adsorption trials. Sample S90F10-I demonstrated the highest total amount of multi-pharmaceutical solution adsorbed, likely due to the contribution of TMP, which showed a high affinity for this material in the single solute adsorption trials. SMX remained adsorbed in the lowest quantities in both the single and multi-component trials. The best adsorption for SMX was achieved on S100-I, from both single and multi-component solution. This could be due to the higher content of SiO₂ in the S100-I material as compared to the other waste-derived adsorbents. SiO₂ could adsorb SMX in greater quantity than the other inorganic content because it could undergo acid-base interactions with the amine group of the SMX.
5.2.2. Thermal analysis of multi-component solution on waste-based adsorbents carbonized at 650 °C

The thermal decomposition patterns of the samples exposed to multi-component solution were analyzed and compared to those of the single-component and initial samples in order to gain further insight into the interactions between the adsorbates and the adsorbent surfaces. The DTG curves are shown in Fig. 5.22, and were analyzed up to the pyrolysis temperature of the materials. A subtle peak at 350 °C on the DTG curves, which corresponds to the decomposition temperatures of the pharmaceuticals (see Figs. 6.5, 6.14, 6.24), increases slightly in intensity after exposure to the multi-component solution. The results were not more pronounced due to the low amount of pharmaceutical adsorbed.
Fig. 5.22. DTG curves in helium for the waste-derived adsorbents; initial, used for the adsorption from single component solution and in the multi-component solution.

No further characterizations of the exhausted materials carbonized at 650 °C were conducted due to the low amount of pharmaceuticals adsorbed. It was anticipated that there would be a lack of significant differences between the initial and exposed materials.
6. Adsorption on the waste adsorbents prepared at 950 °C.

Due to the low adsorption on the 650 °C materials, adsorbents were prepared by carbonization at 950 °C. The higher preparation temperature could lead to increased surface area and pore volume resulting from greater burn-off. The carbon phase would also be expected to undergo a higher degree of aromatization. Both changes could have a beneficial impact on adsorption of the pharmaceuticals.

6.1. Adsorption from a single-component solution

Adsorption from a single-solute solution on the 950°C-carbonized waste-based adsorbents was conducted with three pharmaceuticals: carbamazepine, sulfamethoxazole, and trimethoprim.

Prior to the equilibrium adsorption measurements, kinetics studies were carried out to determine the time needed to reach equilibrium. The CBZ concentration decay curve (Fig. 6.1) shows a plateau after 5 contact hours with the waste-based adsorbent, indicating that the equilibrium was reached, and this time was then used in measurements of the adsorption isotherms.

![Kinetics curves for adsorption of CBZ, SMX and TMP on the surface of F100-II.](image-url)
Although the experimental pH was not controlled by the addition of a buffer, it was monitored throughout the adsorption experiments (Table 6.1). A buffer was not used as the buffer ions could compete for adsorption sites with the target adsorbates, and thus obscure analysis of the adsorption mechanism.

Table 6.1. pH values of adsorbate solutions and adsorbent/adsorbate suspensions at equilibrium.

<table>
<thead>
<tr>
<th>Suspension/solution</th>
<th>$\text{pH}_{\text{qe}}$ CBZ</th>
<th>$\text{pH}_{\text{qe}}$ SMX</th>
<th>$\text{pH}_{\text{qe}}$ TMP</th>
<th>$\text{pH}_{\text{qe}}$ CBZ/SMX/TMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbate solution</td>
<td>5.41</td>
<td>4.72</td>
<td>7.87</td>
<td>6.33</td>
</tr>
<tr>
<td>S100-II</td>
<td>9.83</td>
<td>7.86</td>
<td>8.99</td>
<td>9.39</td>
</tr>
<tr>
<td>S90F10-II</td>
<td>9.77</td>
<td>8.15</td>
<td>9.52</td>
<td>8.63</td>
</tr>
<tr>
<td>S75F25-II</td>
<td>8.87</td>
<td>9.44</td>
<td>10.10</td>
<td>10.04</td>
</tr>
<tr>
<td>S50F50-II</td>
<td>9.82</td>
<td>9.57</td>
<td>10.11</td>
<td>11.03</td>
</tr>
<tr>
<td>F100-II</td>
<td>10.26</td>
<td>11.24</td>
<td>11.46</td>
<td>11.82</td>
</tr>
</tbody>
</table>

6.1.1. Carbamazepine

6.1.1.1. Adsorption isotherms of CBZ on 950 °C carbonized waste-based adsorbents

Fig. 6.2 shows the adsorption isotherms fitted to the Langmuir-Freundlich equation (for equation details see section 1.3.3). The fitting parameters and the SEE errors are presented in Table 6.2 of the appendix, and for all materials the correlation coefficient ($R^2$) is greater than 0.99. Sample S90F10-II demonstrated nearly twice the adsorption capacity of the other adsorbents with 0.488 mmol/g of CBZ adsorbed. The lowest adsorption capacity was observed on S100-II. Due to the predominant mechanism of CBZ adsorption removal occurring by $\pi-\pi$ interactions, the low quantity of CBZ adsorption on S100-II is likely the result of this material containing the least content of the carbon phase of all the 950 °C prepared materials.
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Fig. 6.2. Adsorption isotherm of CBZ on waste-based adsorbents carbonized at 950 °C. Solid lines represent the fitting to the L-F equation.

Table 6.2. Fitting parameter to L-F equation of CBZ adsorption isotherms on waste-based adsorbents carbonized at 950 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>qm (mmol/g)</th>
<th>K (L/mmol)</th>
<th>n</th>
<th>R²</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>S100-II</td>
<td>0.231</td>
<td>0.455</td>
<td>0.37</td>
<td>0.9956</td>
<td>5.40x10⁻⁵</td>
</tr>
<tr>
<td>S90F10-II</td>
<td>0.488</td>
<td>0.453</td>
<td>0.38</td>
<td>0.9985</td>
<td>1.76x10⁻⁴</td>
</tr>
<tr>
<td>S75F25-II</td>
<td>0.262</td>
<td>1.088</td>
<td>0.38</td>
<td>0.9958</td>
<td>1.89x10⁻⁵</td>
</tr>
<tr>
<td>S50F50-II</td>
<td>0.262</td>
<td>1.001</td>
<td>0.42</td>
<td>0.9995</td>
<td>2.42x10⁻⁵</td>
</tr>
<tr>
<td>F100-II</td>
<td>0.289</td>
<td>1.012</td>
<td>0.38</td>
<td>0.9966</td>
<td>1.66x10⁻⁵</td>
</tr>
</tbody>
</table>

A comparison of the measured (based on L-F fitting) and hypothetical (based on L-F fitting for the sludge and fish waste based adsorbent, assuming their physical mixtures) is presented in Fig. 6.3. For every composite, the measured CBZ adsorption exceeded the predicted adsorption by 10-96 %. These results imply that there is a synergistic effect of the composite formation affecting the adsorption mechanism. This effect is most pronounced for sample S90F10-II, where hypothetical adsorption for the physical mixture would be 0.08 mmol/g, and the measured one
reached 0.16 mmol/g. In order to understand which features govern the adsorbents’ performance, the surfaces of the initial and exhausted samples were extensively characterized.

![Comparison of measured (based on fitting to L-F equation) and hypothetical q_m values (with percent difference between them) of adsorption capacity for CBZ. The hypothetical values were calculated assuming a physical mixture of the components and taking into account their % contributions in the composites.](image)

A comparison can be made of the surface area and pore volumes of the initial samples (Table 4.2) and the samples after CBZ adsorption (Table 6.3). Although little change was noted in the surface area and microporosity for most of the samples, S100-II and S90F10-II showed some decrease in their surface area. For these samples, it can be seen that the microporosity decreases while the mesoporosity increases, indicating that likely the micropores are collapsing to form mesopores. The loss of microporosity results in the decreased surface area.
Table 6.3. The parameters of porous structure for the adsorbents exhausted with CBZ, calculated from nitrogen adsorption isotherms.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ [m$^2$/g]</th>
<th>$V_{mic}$ [cm$^3$/g]</th>
<th>$V_{meso}$ [cm$^3$/g]</th>
<th>$V_t$ [cm$^3$/g]</th>
<th>$V_{mic}/V_t$ [cm$^3$/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S100-II + CBZ</td>
<td>49</td>
<td>0.024</td>
<td>0.123</td>
<td>0.147</td>
<td>0.16</td>
</tr>
<tr>
<td>S90F10-II + CBZ</td>
<td>50</td>
<td>0.024</td>
<td>0.087</td>
<td>0.111</td>
<td>0.22</td>
</tr>
<tr>
<td>S75F25-II + CBZ</td>
<td>66</td>
<td>0.030</td>
<td>0.107</td>
<td>0.137</td>
<td>0.22</td>
</tr>
<tr>
<td>S50F50-II + CBZ</td>
<td>65</td>
<td>0.032</td>
<td>0.091</td>
<td>0.123</td>
<td>0.26</td>
</tr>
<tr>
<td>F100-II + CBZ</td>
<td>56</td>
<td>0.027</td>
<td>0.091</td>
<td>0.118</td>
<td>0.23</td>
</tr>
</tbody>
</table>

6.1.1.2. Thermal analysis of CBZ on the waste-based adsorbents carbonized at 950 °C

The DTG curves are collected in Fig. 6.4. The peaks represent the weight loss as a result of the decomposition of materials and removal of adsorbed species upon heat treatment (for detailed DTG analysis of the initial samples, see section 4.3). After exposure to CBZ, the weight loss between 300 and 650 °C decreased, which might be linked to the complexation of CBZ with metal cations, changing their coordination and thus stability. Support for this hypothesis is the fact that the difference in the weight loss at this temperature range is greatest for the best performing sample, S90F10-II. The DTG curve for pure carbamazepine (Fig. 6.5) reveals a double peak between 200 and 400 °C related to the decomposition of amine groups (190 °C) and the aromatic moiety (411 °C) [190].
Fig. 6.4. DTG curves in helium for the adsorbents, initial (dotted line) and spent with CBZ (solid line).

Fig. 6.5. DTG curve of pure carbamazepine in N₂.
6.1.1.3. Potentiometric titration of 950 °C carbonized waste-based adsorbents exposed to CBZ

The proton binding curves for the samples after CBZ adsorption, and for comparison, the initial materials, are presented in Fig. 6.6. For some of the samples there was a decrease in the number of surface groups, while for some there was an increase, or little change in the number of groups. The lack of a clear trend suggests that acid-base interactions are not the predominant adsorption forces on these samples, and rather that chemical coordination with specific groups on the carbon is playing an important role. The availability and chemical nature of these groups likely controls the adsorption of CBZ on the materials.

Fig. 6.6. Proton uptake curves for the waste-based adsorbents carbonized at 950 °C, initial and spent after CBZ exposure.

The detailed changes are seen on the pKₐ distributions (Fig. 6.7). The peak positions and number of groups with particular pKₐ are included in Table 6.4. The new acidic species (conjugated acids
to amine groups of CBZ) are seen only for S90F10-II and F100-II as a new peak at pK$_a$ of about 6.3. On these samples the highest adsorption capacities were measured.

Fig. 6.7. The comparison of the pK$_a$ distributions for the waste-based adsorbents carbonized at 950 °C, initial and after CBZ adsorption.

Table 6.4. Peak positions and numbers of groups (in parentheses; [mmol/g]) for 950°C carbonized waste adsorbents exhausted with CBZ.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>pK$_a$ 4-5</th>
<th>pK$_a$ 5-6</th>
<th>pK$_a$ 6-7</th>
<th>pK$_a$ 7-8</th>
<th>pK$_a$ 8-9</th>
<th>All</th>
</tr>
</thead>
<tbody>
<tr>
<td>S100-II + CBZ</td>
<td>9.66</td>
<td>5.42 (0.037)</td>
<td>6.26 (0.011)</td>
<td>7.40 (0.022)</td>
<td>0.070</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S90F10-II + CBZ</td>
<td>9.34</td>
<td>5.55 (0.041)</td>
<td>6.66 (0.009)</td>
<td>7.44 (0.025)</td>
<td>8.80 (0.004)</td>
<td>0.078</td>
<td></td>
</tr>
<tr>
<td>S75F25-II + CBZ</td>
<td>10.0</td>
<td>5.34 (0.083)</td>
<td>6.35 (0.033)</td>
<td>7.70 (0.025)</td>
<td>0.140</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S50F50-II + CBZ</td>
<td>10.3</td>
<td>5.30 (0.160)</td>
<td>6.45 (0.054)</td>
<td>7.89 (0.041)</td>
<td>0.254</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F100-II + CBZ</td>
<td>10.2</td>
<td>4.68 (0.500)</td>
<td>6.74 (0.052)</td>
<td>7.89 (0.063)</td>
<td>0.614</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.1.1.4. XRD of CBZ on 950 °C carbonized waste-based adsorbents

X-Ray diffraction patterns for the initial and exhausted adsorbents are collected in Fig. 6.8 (for detailed analysis of the initial materials see section 4.6). The ammonium calcium sulfate phosphate \((\text{NH}_4)_2\text{CaSO}_4\cdot\text{H}_2\text{O}\) identified in the S50F50-II initial sample decreases in content after CBZ adsorption. This might be caused by the dissolution of some of these species during the adsorption process. The results also indicate a decrease in the calcium hydroxide content in the F100-II sample exposed to CBZ in water.

No crystallographic structure of CBZ is identified (Fig. 6.9) in the exhausted samples indicating that CBZ is not deposited as a crystal on the surface of the adsorbents or the amounts adsorbed are too small to be detected using the XRD method. Since similar crystallographic phases exist in all samples pyrolyzed at 950 °C, the exceptional behavior of S90F10-II as a CBZ adsorbent, including the strongest synergistic effect despite its low porosity, must be linked to the chemistry of the noncrystalline phases, or a favorable combination of all factors affecting the adsorption process.
Fig. 6.8. X-Ray diffraction patterns for the sewage sludge/fish waste-based adsorbents, carbonized at 950 °C, initial and exposed to CBZ. ▲ SiO$_2$; ● Fe$_2$P; ★ Ca$_{10}$(PO$_4$)$_6$(Cl, OH)$_2$;

■ CaAl$_2$Si$_2$O$_8$; ○ AlPO$_4$; ◇ CaOH$_2$; ◇ (NH$_4$)$_2$CaSO$_4$·H$_2$O; □ Ca$_{10}$(PO$_4$)$_6$CO$_3$. 

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Fig. 6.9. X-Ray diffraction patterns for pure carbamazepine.

6.1.1.5. Summary of CBZ adsorption on the waste-based adsorbents carbonized at 950 °C

Taking into account the chemical formula of CBZ, it should exhibit affinities to both polar and hydrophobic surface sites. The content of the polar mineral phase in the waste-based adsorbents is very high. The relatively high content of the carbon phase would impose some surface hydrophobicity, and should affect the porosity development and the chemistry of the surface in small pores. These pores would be the most active for CBZ physical adsorption, if this kind of an adsorption process is a predominant separation mechanism. However, taking into account the analyses of the adsorbents after CBZ adsorption, the amounts adsorbed do not appear to be dependent on the surface area or porosity. In fact, sample F100-II showed a higher adsorption capacity than that of S100-II, despite the latter having the larger surface area and porosity. Since F100-II has a higher content of the carbonaceous phase than that in S100-II, and more calcium oxide is able to participate in complexation reactions, it is likely that surface chemistry governs the adsorption of CBZ on the sewage sludge/fish waste adsorbents. In analyzing the adsorption
mechanism it is important to take into account that the adsorption takes place from the aqueous phase, and the high polarity of water will favor its adsorption on the polar centers. Here, the high dispersion of the hydrophobic carbon phase might decrease the competition between water and CBZ for the adsorption centers, giving the latter more chances to occupy the most energetically favorable positions. Creating a composite by the addition of the fish waste to the sewage sludge proved beneficial to the adsorbent performance. The fish waste apparently provided more carbonaceous phase. That carbon phase and the high temperature treatment promoted a favorable dispersion of the inorganic phase in mesopores, where complexation of CBZ on metal oxides could contribute to reactive adsorption.

6.1.2. Sulfamethoxazole

6.1.2.1. Adsorption isotherms of SMX on the waste-based adsorbents carbonized at 950 °C.

The adsorption isotherms of SMX on the waste-based adsorbents can be seen in Fig. 6.10. The experimental data was fitted to Langmuir-Freundlich equation (R² and SSE values can be found in Table 6.5). SMX was adsorbed in the range of 0.042 – 0.100 mmol/g, with S100-II representing the lower end of that spectrum, and F100-II, the upper. The preparation of the materials at 950 °C decreases the number of surface groups, including the hydroxyl groups. Previous studies have shown a link between adsorption on materials of high silica content and the presence of the surface hydroxyl groups [189]. Therefore it’s likely that the adsorption performance of SMX on the silica-rich S100-II was negatively impacted by the pyrolysis temperature and the resultant surface chemistry, whereas the preparation temperature effect did not negatively affect the surface chemistry of F100-II for SMX adsorption.
Fig. 6.10. Adsorption isotherm of SMX on the waste-based adsorbents carbonized at 950 °C.

Solid lines represent the fitting to the L-F equation.

Table 6.5. Fitting parameter to L-F equation of SMX adsorption isotherms on waste-based adsorbents carbonized at 950 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>qm (mmol/g)</th>
<th>K (L/mmol)</th>
<th>n</th>
<th>R²</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>S100-II</td>
<td>0.042</td>
<td>1.251</td>
<td>0.55</td>
<td>0.9925</td>
<td>1.84x10⁻⁶</td>
</tr>
<tr>
<td>S90F10-II</td>
<td>0.050</td>
<td>1.687</td>
<td>0.49</td>
<td>0.9946</td>
<td>2.42x10⁻⁶</td>
</tr>
<tr>
<td>S75F25-II</td>
<td>0.049</td>
<td>0.855</td>
<td>0.48</td>
<td>0.9892</td>
<td>2.64x10⁻⁶</td>
</tr>
<tr>
<td>S50F50-II</td>
<td>0.067</td>
<td>0.681</td>
<td>0.50</td>
<td>0.9942</td>
<td>2.57x10⁻⁶</td>
</tr>
<tr>
<td>F100-II</td>
<td>0.100</td>
<td>0.260</td>
<td>0.40</td>
<td>0.9967</td>
<td>2.00x10⁻⁶</td>
</tr>
</tbody>
</table>

Fig. 6.11 summarizes the impact of using the synthesized composite adsorbents, as opposed to the single-source materials, on the adsorption capacity. The numbers express the differences in % between the measured capacity and the hypothetical one calculated assuming the physical mixture of the components. It appears that in the process of SMX adsorption the single component materials generally perform better than the composite ones. Composite sample S90F10-II is of interest since it not only out-performs the other composite samples, but it also
demonstrates a 25% better performance than it hypothetically would have assuming the physical mixture of its components.

Fig. 6.11. Comparison of measured (based L-F fittings at a $C_{eq}$ of 0.1 mmol/L) and hypothetical $q_e$ values (with percent difference between them) of adsorption capacity for SMX. The hypothetical values were calculated assuming a physical mixture of the components and taking into account their % contributions in the composites.

A comparison can be made of the surface area and pore volumes of the initial samples (Table 4.2) and those after SMX adsorption (Table 6.6). For all composites a decrease in the porosity is found after the adsorption process. Interestingly, it is only for the fish-derived adsorbent which this trend is not followed. The only plausible explanation at this stage is the leaching of some soluble components, which are not stabilized by the sludge phase during pyrolysis, and thus might increase the surface area.
Table 6.6. The parameters of porous structure for the adsorbents exhausted with SMX, calculated from nitrogen adsorption isotherms.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ [m$^2$/g]</th>
<th>$V_{mic}$ [cm$^3$/g]</th>
<th>$V_{meso}$ [cm$^3$/g]</th>
<th>$V_t$ [cm$^3$/g]</th>
<th>$V_{mic}/V_t$ [cm$^3$/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S100-II + SMX</td>
<td>21</td>
<td>0.012</td>
<td>0.051</td>
<td>0.063</td>
<td>0.19</td>
</tr>
<tr>
<td>S90F10-II + SMX</td>
<td>66</td>
<td>0.033</td>
<td>0.097</td>
<td>0.130</td>
<td>0.25</td>
</tr>
<tr>
<td>S75F25-II + SMX</td>
<td>67</td>
<td>0.031</td>
<td>0.92</td>
<td>0.123</td>
<td>0.25</td>
</tr>
<tr>
<td>S50F50-II + SMX</td>
<td>82</td>
<td>0.038</td>
<td>0.083</td>
<td>0.121</td>
<td>0.31</td>
</tr>
<tr>
<td>F100-II + SMX</td>
<td>61</td>
<td>0.030</td>
<td>0.111</td>
<td>0.141</td>
<td>0.21</td>
</tr>
</tbody>
</table>

In order to elucidate the impact of the various chemical and textural features of the adsorbents on the adsorption capacity of the target pharmaceuticals, the effects of the surface features on the adsorption capacity (at an arbitrarily chosen $C_{eq}$ of 0.1mmol/g) were investigated. The results are presented in Figs. 6.12. Increased surface area (Fig. 6.12.A) has a negative impact ($R^2 = 0.90$) on the performance of the adsorbents. The amount adsorbed also decreases with an increase in the volume of micro and mesopores (Fig. 6.12.B, $R^2 = 0.91$). Since, generally, an increased surface area and porosity are beneficial for the adsorption capacity [191], this observed negative trend indicates that for this group of adsorbents the specific chemical features must be more important than their textural characteristics. The adsorption capacity increases with an increasing fish content (and a decreasing sewage sludge content) (Fig. 6.12.C, $R^2 = 0.73$). Since F100-II has a low porosity and surface area, it is reasonable to assume that the high temperature heating imposes surface chemistry changes that are favorable for attracting SMX. The trend in Fig. 6.12.D is similar to Fig. 6.12.C, highlighting the fact that the fish waste is the primary source of the adsorbents’ calcium, while iron, alumina and silica originate from the sewage sludge.
Fig. 6.12. Dependence of the adsorption capacity of SMX [mmol/g] on surface area \([m^2/g]\) (A), volume of micro- and meso-pores \([cm^3/g]\) (B), percentage sewage sludge or fish waste (C), and percentage calcium or iron/aluminum/silica in the adsorbent (D).

### 6.1.2.2. Thermal analysis/MS of SMX on 950 °C carbonized waste-based adsorbents

In order to gain further insight, the thermal decomposition patterns of the SMX spent samples were analyzed and compared to those of the initial samples (for detail of the initial samples’ analyses see section 4.3). The DTG curves (Fig. 6.13) were analyzed up to the pyrolysis temperature (950 °C). The subtle peak at 350 °C seen on the DTG curves of the initial samples increases in its intensity for the exhausted samples. This peak may represent the decomposition of the pure pharmaceuticals (see Fig. 6.14). A second peak on the DTG curves at 650 °C, related
to the pharmaceutical decomposition, also shows greater intensity for the exhausted samples. The intensity of these peaks increases with an increase in the content of fish in the composite samples, which is in agreement with the previously discussed importance of the fish component of the materials for the pharmaceutical’s adsorption.

Fig. 6.13. DTG curves in helium for the adsorbents, initial (dotted line) and spent with SMX (solid line).
Fig. 6.14. DTG curve of pure SMX in N₂.

The mass to charge ratio ($m/z$) of the gases released during thermal analysis are shown for initial (for detailed analysis see section 4.3) and SMX exhausted samples S100-II and F100-II (Fig. 6.15). Subtle differences can be noted by comparing the $m/z$ thermal profiles of the initial S100-II sample and the exhausted sample S100-II +SMX. In the S100-II+SMX profile, a broad peak of $m/z$ 44 in the range of 450 to 580 °C can be clearly seen. This peak corresponds to CO₂ released from the decomposition of SMX. No other $m/z$ were detected, which can be due to the small amount of SMX adsorbed on the S100-II adsorbent. The $m/z$ thermal profiles of the exhausted sample F100-II+SMX, in addition to the peaks found for the initial sample, show peaks at 360 °C on $m/z$ 18 and 44, which correspond to the decomposition of SMX. Although sulfones are part of the SMX structure, and would be expected in the thermal profiles of the SMX exhausted samples as they decompose to SO₂ ($m/z$ 64), no signal was detected. This is perhaps due to the low concentration of SO₂ (one sulfur per SMX molecule) released during the pharmaceutical decomposition, which is below the detection limit of our MS instrument.
Fig. 6.15. *m/z* thermal profiles of initial and SMX exhausted adsorbents S100-II and F100-II (multiplication factors: MW-12 x 1000, MW-15 x 500, MW-17 x 25, MW-18 x 10, MW-30 x 100, MW-44 x 200).

### 6.1.2.3. Potentiometric titration of 950 °C carbonized waste-based adsorbents exposed to SMX

Fig. 6.16 shows the proton binding curves of the initial and SMX spent adsorbents. The increased Q value after exposure shows that there is increased proton uptake after exposure to SMX. The pH<sub>PZC</sub> values of the samples after SMX exposure were more basic than the initial of the same composition, yet remained in the range of 8.5 – 10.5. The trend observed in the initial
materials (of being more basic with an increased fish content), was maintained after pharmaceutical exposure.

Fig. 6.16. Proton uptake curves for the waste-based adsorbents carbonized at 950 °C, initial and spent with SMX.

The pKₐ distributions for adsorbents exhausted with SMX are shown in Fig. 6.17, and the peak positions and number of groups specified in Table 6.7. The amount of groups increases 15 to nearly 24 fold after adsorption of SMX. The increase was greatest for the samples where sewage sludge was the predominant component. The surface of the initial adsorbent F100-II (the sample with the highest adsorption capacity for SMX) reveals four groups at pKₐs of 4.75, 5.76, 6.90, and 7.79. After SMX adsorption six types of groups are detected at pKₐs of 3.85, 4.78, 6.38, 7.72, 8.91, and 10.51. Most of the increase in the number of total groups is due to the presence of a large amount of the strongly acidic groups of low pKₐ values. This indicates the acidification of
the surfaces after pharmaceutical adsorption. These groups must represent the adsorbed pharmaceuticals.

Fig. 6.17. The comparison of the pKₐ distributions for the waste-based adsorbents carbonized at 950 °C, initial and after SMX adsorption.

Table 6.7. Peak positions and numbers of groups (in parentheses; [mmol/g]) for 950°C carbonized waste adsorbents exhausted with SMX.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>pKₐ 3-4</th>
<th>pKₐ 4-5</th>
<th>pKₐ 5-6</th>
<th>pKₐ 6-7</th>
<th>pKₐ 7-8</th>
<th>pKₐ 8-9</th>
<th>pKₐ 9-10</th>
<th>All</th>
</tr>
</thead>
<tbody>
<tr>
<td>S100-II + SMX</td>
<td>8.32</td>
<td>3.75</td>
<td>5.38</td>
<td>6.34</td>
<td>7.12</td>
<td>8.38</td>
<td></td>
<td></td>
<td>1.749</td>
</tr>
<tr>
<td>S90F10-II + SMX</td>
<td>9.86</td>
<td>3.73</td>
<td>5.44</td>
<td>6.34</td>
<td>7.67</td>
<td>9.48</td>
<td></td>
<td></td>
<td>2.323</td>
</tr>
<tr>
<td>S75F25-II + SMX</td>
<td>9.96</td>
<td>3.84</td>
<td>5.40</td>
<td>6.10</td>
<td>7.56</td>
<td>9.24</td>
<td>10.09</td>
<td></td>
<td>2.960</td>
</tr>
<tr>
<td>S50F50-II + SMX</td>
<td>10.12</td>
<td>3.75</td>
<td>5.28</td>
<td>6.49</td>
<td>7.77</td>
<td>9.25</td>
<td>10.20</td>
<td></td>
<td>4.045</td>
</tr>
<tr>
<td>F100-II + SMX</td>
<td>10.47</td>
<td>3.85</td>
<td>4.78</td>
<td>6.38</td>
<td>7.72</td>
<td>8.91</td>
<td>10.51</td>
<td></td>
<td>7.690</td>
</tr>
</tbody>
</table>
6.1.2.4. XRD of SMX on 950 °C carbonized waste-based adsorbents

Fig. 6.18 shows the X-ray diffraction patterns for the initial and SMX spent samples. For interpretation of the initial samples, see section 4.6. The XRD profiles of the spent samples can be compared to the diffraction patterns for the pure pharmaceuticals (Fig. 6.19). Identification of the pharmaceutical peaks on the diffractograms of the spent samples is difficult due to the overlapping of the signals with those from the initial adsorbents. However in sample S50F50-II + SMX, on which a marked amount of SMX was adsorbed, the appearance of a peak at 2θ 28 can be clearly seen. This signal can be attributed to SMX adsorbed on the surface.
Fig. 6.18. X-Ray diffraction patterns for the sewage sludge/fish waste-based adsorbents, carbonized at 950 °C; initial and exposed to SMX.

\[
\begin{align*}
&\text{SiO}_2; \quad \text{Fe}_2\text{P}; \quad \text{Ca}_{10}(\text{PO}_4)_{6}(\text{Cl}, \text{OH})_2; \quad \text{CaAl}_2\text{Si}_2\text{O}_8; \quad \text{AlPO}_4; \quad \text{Ca(OH)}_2; \quad (\text{NH}_4)_2\text{CaSO}_4; \quad \text{Ca}_{10}(\text{PO}_4)_6\text{CO}_3
\end{align*}
\]
6.1.2.5. Summary of SMX adsorption on the waste-based adsorbents carbonized at 950 °C.

Surface area and porosity are typically important for the adsorption process [90]. The sewage sludge/fish waste materials, however, are of a low surface area and pore volume. This, combined with the fact that no correlation between their adsorption capacities and these features was found, suggests that the adsorption of SMX is not predominantly governed by a physical adsorption process. Therefore, the surface chemistry of the materials must be driving the adsorption. Overall the high pyrolysis temperature likely decreased the quantity of surface oxygen groups, but some acidic oxygen groups (such as carboxylic, phenolic, lactonic), and basic (such as pyronic) would remain and participate in acid-base reactions [90]. However, the carbon phase is a minor component of our adsorbents and the interactions with the inorganic polar phase likely predominate. This is especially a consideration for the adsorbents obtained at a higher pyrolysis temperature as they have a proportionally higher amount of the inorganic phase (71 % of the

Fig. 6.19. X-Ray diffraction patterns for pure SMX.
inorganic phase in the adsorbents obtained at 950 °C versus 62 % for the samples obtained at 650 °C).

Since the pKₐs of SMX (1.6, 5.7) are below the pH of the equilibrium suspensions (pH between 8 and 11 – see Table 6.1), SMX is mainly present in its deprotonated forms. Therefore it could be attracted to the acidic sites via acid-base interactions. In the samples containing primarily sewage sludge, SiO₂ is the main component and it can act as a Lewis acid, accepting electrons from the amine groups. This silica phase would also provide hydroxyl groups specifically interacting with the polar sites of the adsorbates.

**6.1.3. Trimethoprim**

**6.1.3.1. Adsorption isotherms of TMP on the waste-based adsorbents carbonized at 950 °C.**

Fig. 6.20 shows the adsorption isotherms of TMP on the waste derived adsorbents. The experimental data was fitted to Langmuir-Freundlich equation (R² and SSE values can be found in Table 6.8). The waste-based materials adsorbed TMP in the range of 0.070 to 0.312 mmol/g. Of the samples pyrolyzed at 950 °C, the best adsorption performances were on S90F10-II and F100-II.

Table 6.8. Fitting parameter to L-F equation of TMP adsorption isotherms on waste-based adsorbents carbonized at 950 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>qm (mmol/g)</th>
<th>K (L/mmol)</th>
<th>n</th>
<th>R²</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>S100-II</td>
<td>0.312</td>
<td>0.033</td>
<td>0.34</td>
<td>0.9755</td>
<td>7.28x10⁻⁵</td>
</tr>
<tr>
<td>S90F10-II</td>
<td>0.073</td>
<td>30.213</td>
<td>0.55</td>
<td>0.9675</td>
<td>6.07x10⁻⁵</td>
</tr>
<tr>
<td>S75F25-II</td>
<td>0.113</td>
<td>2.237</td>
<td>0.31</td>
<td>0.9666</td>
<td>6.77x10⁻⁵</td>
</tr>
<tr>
<td>S50F50-II</td>
<td>0.151</td>
<td>0.349</td>
<td>0.29</td>
<td>0.9832</td>
<td>3.21x10⁻⁵</td>
</tr>
<tr>
<td>F100-II</td>
<td>0.070</td>
<td>52.753</td>
<td>0.44</td>
<td>0.9569</td>
<td>8.23x10⁻⁵</td>
</tr>
</tbody>
</table>
Fig. 6.20. Adsorption isotherm of TMP on the waste-based adsorbents carbonized at 950 °C. Solid lines represent the fitting to the L-F equation.

The impact of using the composite adsorbents over the single component materials on the adsorption capacity can be seen in Fig. 6.21. The numbers express the differences (in %) between the measured capacity and the hypothetical one calculated assuming the physical mixture of the components. For the adsorption of TMP, the benefit of using composite materials can be seen. Sample S90F10-II has a higher adsorption capacity than the materials obtained solely from the single precursors, and it performs 17% better than would the hypothetical physical mixture of its components.
Fig. 6.21. Comparison of measured (based L-F fittings at a $C_{eq}$ of 0.1 mmol/L) and hypothetical $q_e$ values (with percent difference between them) of adsorption capacity for TMP. The hypothetical values were calculated assuming a physical mixture of the components and taking into account their % contributions in the composites.

The comparison can be made of the surface area and pore volumes of the initial (Table 4.2) and the samples after TMP adsorption (Table 6.9). All the adsorbents showed a decrease in the porosity after the adsorption process, with the exception of the fish-derived material. This may be due to leaching of soluble components, which would cause an increase in the surface area.

Table 6.9. The parameters of porous structure for the adsorbents exhausted with TMP, calculated from nitrogen adsorption isotherms.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ [m$^2$/g]</th>
<th>$V_{mic}$ [cm$^3$/g]</th>
<th>$V_{meso}$ [cm$^3$/g]</th>
<th>$V_t$ [cm$^3$/g]</th>
<th>$V_{mic}/V_t$ [cm$^3$/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S100-II + TMP</td>
<td>58</td>
<td>0.026</td>
<td>0.080</td>
<td>0.106</td>
<td>0.25</td>
</tr>
<tr>
<td>S90F10-II + TMP</td>
<td>55</td>
<td>0.027</td>
<td>0.100</td>
<td>0.127</td>
<td>0.21</td>
</tr>
<tr>
<td>S75F25-II + TMP</td>
<td>50</td>
<td>0.025</td>
<td>0.081</td>
<td>0.116</td>
<td>0.22</td>
</tr>
<tr>
<td>S50F50-II + TMP</td>
<td>48</td>
<td>0.026</td>
<td>0.072</td>
<td>0.098</td>
<td>0.27</td>
</tr>
<tr>
<td>F100-II + TMP</td>
<td>43</td>
<td>0.022</td>
<td>0.089</td>
<td>0.111</td>
<td>0.20</td>
</tr>
</tbody>
</table>
The impact of the adsorbent’s surface features on the adsorption capacity of TMP was examined (at an arbitrarily chosen C<sub>eq</sub> of 0.1mmol/g). The 950 °C pyrolized adsorbents demonstrate a slight decrease in the amount adsorbed with an increased surface area (Fig. 6.22.A, R<sup>2</sup> = 0.61). As mesopores (Fig. 6.22.B) are responsible for the majority of the surface area, the trends in the effect of mesoporosity on the amount adsorbed (R<sup>2</sup> = 0.54) are similar to those for the surface area, demonstrating a decreased amount adsorbed with an increased mesopore volume.

6.1.3.2. Thermal analysis/MS of TMP on 950 °C carbonized waste-based adsorbents

The thermal decomposition patterns of the samples exhausted with TMP were analyzed and compared to those of the initial samples in order to gain further insight into the interactions between the adsorbates and the adsorbent surfaces. The DTG curves are shown in Fig. 6.23, and were analyzed up to the pyrolysis temperature of the materials (for details on the analysis of the initial samples, see section 4.3). A peak at 350 °C on the DTG curves (that was subtle for the initial samples) increased in intensity after the TMP exposure, and can be related to the decomposition of the pure TMP (see Fig. 6.24). A second peak on the DTG curves at 650 °C, is
also related to the TMP decomposition and shows greater intensity for the exhausted samples. The intensity of these peaks increases with an increase in the content of fish in the composite samples, which is in agreement with the previously discussed importance of the fish component for TMP adsorption.

Fig. 6.23. DTG curves in helium for the adsorbents, initial (dotted line) and spent with TMP (solid line).
Fig. 6.24. DTG curve of pure TMP in N₂.

The mass to charge ratio (m/z) thermal profiles of the gases released during thermal analysis are shown for the initial (for a detailed analysis see section 4.3) and the exhausted S100-II and F100-II samples after TMP adsorption (Fig. 6.25). There is a broad peak on the m/z 12 thermal profile for S100-II+TMP in the range of 300 to 400 °C, which can be attributed to the decomposition of TMP. In the thermal profile of sample F100-II exhausted with TMP, displays peaks at 360 °C which correspond to CO₂ (m/z 12, 44) and H₂O (m/z 18). At the same temperature, there is also peak of m/z 15. It is possible this signal is due to the detection of NH, and therefore along with m/z 17 and 18, correspond to the NH, NH₃, and NH₄⁺, fragmentation series, respectively [192]. All of these signals can be related to the decomposition of TMP, since the only nitrogen source in the exhausted materials is due to the TMP adsorption. At high temperatures (660-890 °C) a peak on the m/z 30 thermal profile appears, which can indicate the formation of NO, therefore suggesting a strong reactive adsorption of TMP nitrogen groups.
Fig. 6.25. *m/z* thermal profiles of initial and SMX exhausted adsorbents S100-II and F100-II (multiplication factors: MW-12 x 1000, MW-15 x 500, MW-17 x 25, MW-18 x 10, MW-30 x 100, MW-44 x 200).

**6.1.3.3. Potentiometric titration of 950 °C carbonized waste-based adsorbents exposed to TMP**

Fig. 6.26 shows the proton binding curves of the initial adsorbents and those exposed to TMP. The Q value increased after TMP exposure, indicating an increased proton uptake. Although the pH$_{PZC}$ of the TMP exposed samples was more basic, it remained in the range of 9.9 to 10.2. In
the initial materials it was observed that samples with increased fish content were more basic, and this trend continued with the samples exposed to TMP.

![Proton uptake curves for the waste-based adsorbents carbonized at 950 °C, initial and spent with TMP.](image)

Fig. 6.26. Proton uptake curves for the waste-based adsorbents carbonized at 950 °C, initial and spent with TMP.

The pKₐ distributions for the adsorbents exposed to TMP are shown in Fig. 6.27, and the peak positions and number of groups are specified in Table 6.10. The amount of groups increases 12 to nearly 26 fold after adsorption of TMP. The increase was greatest for the samples where sewage sludge was the predominant component. The initial sample S90F10-II had three groups at pKₐs of 5.39, 6.30, and 7.57, which after TMP adsorption increased to five groups at pKₐs of 3.97, 5.28, 6.36, 7.42, and 9.14. The surface of the initial adsorbent F100-II reveals four groups at pKₐs of 4.75, 5.76, 6.90, and 7.79, which after TMP adsorption led to the appearance of five groups at pKₐs of 3.82, 4.96, 5.91, 7.52, and 8.95. Most of the increase in the number of the total groups is due to the presence of a large amount of the strongly acidic groups of low pKₐ values.
This indicates the acidification of the surfaces after pharmaceutical adsorption. These groups must represent the adsorbed pharmaceuticals.

Fig. 6.27. The comparison of the pK\textsubscript{a} distributions for the waste-based adsorbents carbonized at 950 °C, initial and after TMP adsorption.
Table 6.10. Peak positions and numbers of groups (in parentheses; [mmol/g]) for 950°C carbonized waste adsorbents exhausted with TMP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>pKₐ 3-4 (mmol/g)</th>
<th>pKₐ 4-5 (mmol/g)</th>
<th>pKₐ 5-6 (mmol/g)</th>
<th>pKₐ 6-7 (mmol/g)</th>
<th>pKₐ 7-8 (mmol/g)</th>
<th>pKₐ 8-9 (mmol/g)</th>
<th>pKₐ 9-10 (mmol/g)</th>
<th>All</th>
</tr>
</thead>
<tbody>
<tr>
<td>S100-II + TMP</td>
<td>7.92</td>
<td>3.57</td>
<td>5.05</td>
<td>6.11</td>
<td>7.03</td>
<td></td>
<td></td>
<td></td>
<td>1.990</td>
</tr>
<tr>
<td>S90F10-II + TMP</td>
<td>9.62</td>
<td>3.97</td>
<td>5.28</td>
<td>6.36</td>
<td>7.42</td>
<td></td>
<td></td>
<td></td>
<td>9.14</td>
</tr>
<tr>
<td>S75F25-II + TMP</td>
<td>9.79</td>
<td>3.82</td>
<td>5.68</td>
<td>7.83</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.821</td>
</tr>
<tr>
<td>S50F50-II + TMP</td>
<td>10.25</td>
<td>4.00</td>
<td>5.12</td>
<td>5.78</td>
<td>6.45</td>
<td>7.84</td>
<td></td>
<td></td>
<td>3.317</td>
</tr>
<tr>
<td>F100-II + TMP</td>
<td>10.19</td>
<td>3.82</td>
<td>4.96</td>
<td>5.91</td>
<td>7.52</td>
<td>8.95</td>
<td></td>
<td></td>
<td>6.310</td>
</tr>
</tbody>
</table>

6.1.3.4. DRIFTS of 950 °C carbonized waste-based adsorbents exposed to TMP.

The DRIFTS analysis results are presented in Fig. 6.28. The spectra of the initial and spent S100-II samples (not shown) did not demonstrate any difference between them, which is likely due to the small amounts of pharmaceuticals adsorbed. However, differences can be seen between the initial F100-II sample and that exposed to TMP. The spectrum for initial F100-II shows a wide band between 1600 and 1350 cm⁻¹, which represents the C=C stretch in the aromatic ring of the carbon [193]. With the adsorption of TMP, the intensity of the wide band increases, corresponding to C-N stretching [193]. Also, there is an increase in the intensity of the band at 875 cm⁻¹, related to N-H wagging [193]. Both these signals are associated with the primary amines of adsorbed TMP. This analysis confirms the TMP physical adsorption on the materials.
Fig. 6.28. DRIFT spectra of F100-II, initial and exposed to TMP.

6.1.3.5. XRD of 950 °C carbonized waste-based adsorbents exposed to TMP.

Fig. 6.29 shows the X-ray diffraction patterns for the initial adsorbents and those exposed to TMP. For interpretation of the initial samples, see section 4.6. The XRD profiles of the spent samples can be compared to the diffraction patterns for the pure pharmaceuticals (Fig. 6.30). For the samples exposed to TMP, the appearance of the pharmaceutical-related peaks can be seen. The diffractogram of F100-II+ TMP (F100-II adsorbed the highest quantities of TMP) exhibits a large increase in the intensity of the peak at 30 2θ, as does S50F50-II. These results indicate that the pharmaceutical is retained on the surface without being transformed into a crystalline product.
Fig. 6.29. X-Ray diffraction patterns for the sewage sludge/fish waste-based adsorbents, carbonized at 950 °C, initial and exposed to SMX.

\[ \text{\(\Delta SiO_2, \bigcirc Fe_2P, \blacklozenge Ca_{10}(PO_4)_6(Cl, OH)_2, \blacksquare CaAl_2Si_2O_8, \bigtriangleup AlPO_4, \triangleleft Ca(OH)_2, \triangledown (NH_4)_2CaSO_4, \square Ca_{10}(PO_4)_6CO_3\)} \]
6.1.3.6. Summary of TMP adsorption on the waste-based adsorbents carbonized at 950 °C

The high preparation temperature of the adsorbents results in a greater degree of aromatization of the carbon phase. This would facilitate π-stacking between the aromatic rings of the pharmaceuticals and the carbon layers of the adsorbent materials and thus provide a contribution of the physical adsorption process. Yet in understanding the adsorption mechanism, it should be taken into account that the waste-based materials have a low surface area and pore volume. Additionally, there was no correlation between the adsorption capacity and surface features, therefore the adsorption of TMP is not predominantly a physical process. For physical adsorption, porosity and adsorbate size would be important factors, but it was found that even though TMP has a larger molecular size than the other compounds in this study (and therefore the most pore diffusion constraint), it was adsorbed in a greater quantity than was SMX. Therefore, the surface chemistry of the materials must be driving the adsorption of TMP.

Fig. 6.30. X-Ray diffraction patterns for pure TMP.
The organic phase of the waste-based materials is a minor component, and the interactions with the inorganic polar phase likely predominate during adsorption. Since the pKₐ of TMP (7.1) is below the pH of the equilibrium suspensions (pH between 9 and 11 – see Table. 6.1), TMP is mainly present in its deprotonated form. In the samples containing primarily sewage sludge, SiO₂ is the main component and it can act as a Lewis acid, accepting electrons from the amine groups. This silica phase could also provide hydroxyl groups specifically interacting with the polar sites of the adsorbates. The other inorganic components, such as iron, aluminum, and calcium, of the adsorbent provide metal ions for chelation. On the TMP molecule two amine groups are present, and it’s possible that chelation could occur between the amines and the metals of the adsorbent, including the calcium phase [194], which is abundant in the well-performing fish waste materials. In the samples containing primarily sewage sludge, SiO₂ does not contribute to chelation as the other inorganic components do, and therefore the fish waste-based adsorbents in general, demonstrate a better adsorption performance. It seems that the addition of fish to the sewage sludge caused a beneficial synergistic effect, and thus composite sample S90F10-II demonstrated the highest adsorption capacity. However, an examination of the other composite samples prepared at 950 °C indicates that the synergistic effect is non-linear. Overall, the composite samples demonstrate a performance that is superior to that of the adsorbent composed of sewage sludge alone. Therefore the results suggest that the introduction of the fish waste leads to an adsorbent that facilitates chelation, and thereby increases the adsorption capacity.

6.2. Adsorption from multi-component solution

To simulate complex pollutant conditions encountered in wastewater treatment plant influents, adsorption of pharmaceuticals from a multi-component solution on waste-based adsorbents was conducted. The objective was to compare the differences in the performance of the materials in
terms of their adsorption capacity and selectivity, as compared to the single-solute adsorption study.

6.2.1. Adsorption isotherms of multiple pharmaceuticals on waste-based adsorbents

Fig. 6.31 shows the adsorption isotherms of CBZ, SMX, and TMP from the multi-component solution on the sewage sludge/fish waste derived adsorbents. The experimental data was fitted to the L-F equation. To check for consistency of results, the trials were conducted in triplicate (see Fig. 6.32), and standard error of the mean did not exceed 0.003 mmol/g. On all our waste-derived adsorbents CBZ is adsorbed in the greatest quantity, and SMX in the smallest.

Fig. 6.31. Adsorption isotherms of waste-based adsorbents from multi-component pharmaceutical solution, containing CBZ, SMX, and TMP. Lines represent the fitting to the L-F equation.
Fig. 6.32. Reproducibility between trials as indicated by the adsorption isotherms of 950 °C pyrolyzed waste-based adsorbents exposed to multi-component pharmaceutical solution, containing CBZ, SMX, and TMP. Lines represent goodness of fit to the L-F equation. Bars represent S.E. over 3 trials.

Since developed porosity and surface area have been shown to beneficially impact the adsorptive performance of a material [191], the effect of these features on the performance of our adsorbents has to be analyzed. S100-II shows the best adsorption performance from the multi-component solution. This material has a surface area of 101 m²/g and a pore volume of 0.145 cm³/g. Its surface area and porosity is much greater than that of F100-II (34 m²/g and 0.098 cm³/g, respectively). Since S100-II performed the poorest in the trials with single component pharmaceutical solutions (see section 6.1), it is unlikely that the physical adsorption in the pores would represent the main mechanism of pharmaceutical removal from the aqueous phase.

The adsorption trend amongst the pharmaceuticals, wherein CBZ is adsorbed in greatest quantity and SMX in the smallest, is opposite to the trend in the polarity of the pharmaceuticals, where CBZ is the least polar, and SMX the most (K_{ow} values provided in chapter 1, Fig. 1.2). Therefore the less polar CBZ would have a greater attraction to the carbon phase of the adsorbents, due to π-π electron-donor-acceptor interactions, where the CBZ acts as an electron donor. A similar
trend has been observed by Morisette et al. [195] who noted that the adsorption onto organic matter of substances with a higher $K_{ow}$ exceeds that of those with a lower $K_{ow}$. Interestingly, the carbon content of sample F100-II is higher than that of the other adsorbents. Generally, an increased carbon content would facilitate $\pi-\pi$ interactions, and thus increase the adsorption capacity. However, in the case of F100-II, we see a decreased adsorption of CBZ. This could be due to the high calcium content of the fish waste, which increases the alkalinity of the suspension. The polarity of the CBZ molecule would be affected by this pH increase, which would render CBZ more polar, and in turn decrease the affinity of the carbons surface to interact with CBZ. On the other hand, the higher polarity of SMX could explain its significantly lower adsorption on the hydrophobic carbon surfaces. Additionally, as the pH of the adsorption is greater than the $pK_{a}$ of SMX, it causes the pharmaceutical to exist mostly in its deprotonated form, which leads to more marked hydrophilic properties [196]. In the single-component experiments, it was noted that acid-base interactions were the main mechanism for SMX adsorption on the waste-derived materials [197]. In the multi-component solution, SMX is deprotonated as well as competing with TMP for adsorption sites on the (basic) inorganic material, which ultimately results in a low removal rate for SMX.

It is interesting to compare the performance of the adsorbents exposed to multicomponent adsorption (Fig. 6.33) to that from the single component pharmaceutical solutions. In the former case, S100-II had the best performance for all pharmaceuticals, however in the latter case the optimal material varied depending on the nature of the pharmaceutical. The amount of the pharmaceuticals absorbed from the individual solutions exceeded those from the multi-component one. When only a single pharmaceutical was present in the solution, S90F10-II was
the best adsorbent for CBZ, while F100-II had the best performance with regards to SMX, and both F100-II and S90F10-II had equal capacities for TMP.

![Bar chart showing adsorbed amounts of CBZ, SMX, and TMP from different adsorbents.](image)

Fig. 6.33. Amounts adsorbed (at q_e of 0.1) of CBZ, SMX and TMP from single and multicomponent solutions on the 950 °C carbonized waste-derived adsorbents.

It is evident is that there is competition for available adsorption sites, which is demonstrated by a decrease in the adsorption efficiency of each pharmaceutical when in the presence of additional pharmaceuticals. SMX was the pharmaceutical where the removal from aqueous phase was most negatively impacted, displaying a 77 % decrease on average (Table 6.11). The adsorption of TMP was the least affected by competition in the multi-component experiments. As noted in sections 6.1.2 and 6.1.3, the main mechanism of SMX and TMP adsorption involves interactions with the inorganic components of the material; for SMX by acid-base reactions and for TMP by chelation. It was found that TMP has greater binding capabilities to the waste-based adsorbents.
than SMX, which can be attributed to the chelating properties of the diamino-pyrimidine moiety in TMP [198]. The results from the multi-component adsorption experiments, as compared to the single-component, showed a shift to optimal adsorption on S100-II. This is likely due to the higher inorganic content of this material, as well as the more favorable (less basic) pH of the S100-II suspension which favors adsorption of these species.

Table 6.11. Comparison of the adsorption capacity of the waste-derived adsorbents (at $q_e$ at 0.1 mmol/L, as determined by L-F fitting) for each pharmaceutical when in single versus multi-component solution, and the percent difference.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$q_{e,0.1}$</th>
<th>$q_{e,0.1}$</th>
<th>% diff.</th>
<th>$q_{e,0.1}$</th>
<th>$q_{e,0.1}$</th>
<th>% diff.</th>
<th>$q_{e,0.1}$</th>
<th>$q_{e,0.1}$</th>
<th>% diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CBZ (mmol/g)</td>
<td>CBZ (mmol/g)</td>
<td></td>
<td>SMX (mmol/g)</td>
<td>SMX (mmol/g)</td>
<td></td>
<td>TMP (mmol/g)</td>
<td>TMP (mmol/g)</td>
<td></td>
</tr>
<tr>
<td>S100-II</td>
<td>0.056</td>
<td>0.035</td>
<td>37</td>
<td>0.010</td>
<td>0.005</td>
<td>55</td>
<td>0.026</td>
<td>0.028</td>
<td>-6</td>
</tr>
<tr>
<td>S90F10-II</td>
<td>0.115</td>
<td>0.026</td>
<td>77</td>
<td>0.014</td>
<td>0.003</td>
<td>81</td>
<td>0.047</td>
<td>0.026</td>
<td>46</td>
</tr>
<tr>
<td>S75F25-II</td>
<td>0.079</td>
<td>0.027</td>
<td>66</td>
<td>0.012</td>
<td>0.002</td>
<td>83</td>
<td>0.043</td>
<td>0.020</td>
<td>54</td>
</tr>
<tr>
<td>S50F50-II</td>
<td>0.072</td>
<td>0.026</td>
<td>63</td>
<td>0.013</td>
<td>0.002</td>
<td>81</td>
<td>0.042</td>
<td>0.023</td>
<td>46</td>
</tr>
<tr>
<td>F100-II</td>
<td>0.084</td>
<td>0.024</td>
<td>71</td>
<td>0.018</td>
<td>0.003</td>
<td>83</td>
<td>0.047</td>
<td>0.018</td>
<td>63</td>
</tr>
</tbody>
</table>

It is clear that the fish waste-derived phase of the adsorbents has a significant impact on the adsorption mechanism, which is illustrated in Fig. 6.34. It can be seen that 10 % fish waste is beneficial for the adsorption capacity of pharmaceuticals from a single component solution. This trend is true for all three pharmaceuticals, however CBZ in particular, adsorbed favorably on the S90F10-II composite. It benefitted from the inorganic phase, where complexation of CBZ on metal oxides could occur, while the addition of the fish waste increased the carbon phase
content and allowed for π-π interactions, yet without any significant effect on the pH (due to the small amount of alkaline fish waste content). A decreased adsorption removal of all the pharmaceuticals is noted as the fish waste content of the adsorbent was augmented to 25 and 50 %, due to increasing and unfavorable pH conditions. The adsorbent composed of 100 % fish waste also shows a good adsorption performance, particularly for SMX. Despite the elevated pH, the inorganic content (principally calcium) provided by the fish waste enables the occurrence of the acid-base reactions that are mainly responsible for the adsorption of SMX. Interestingly, when adsorbing multiple pharmaceuticals simultaneously, the fish content has less impact upon the adsorption capacity. This is likely due to the overall competitive effect and the involvement of all adsorption sites to various extents.

![Graph](image)

Fig. 6.34. The impact of fish content on the adsorption of pharmaceuticals for the single and multi-component solutions.

### 6.2.2. Thermal analysis/mass spectrometry of waste-based adsorbents exposed to multi-component solution.

In order to gain further insight into the surface chemistry changes as a result of pharmaceutical adsorption, the thermal decomposition patterns of the samples exhausted in multi-component adsorption were analyzed and compared to those of the initial samples (for detail of the initial
samples’ analyses see section 4.3). The DTG curves (Fig. 6.35) were analyzed up to the pyrolysis temperature (950 °C). For all samples, the total weight loss ranged between 3 and 12%. The two high temperature peaks, at 630 and 900 °C, become more intense after exposure to the pharmaceuticals. This might be due to an increase in the carbon phase after the adsorption of the organic adsorbates, and the higher extent of the iron reduction process by the carbon phase. As all three pharmaceuticals have decomposition temperatures between 200 and 400 °C (see Figs. 6.5, 6.14, 6.24), the increased peak at around 360 °C represents their removal from the material.

Fig. 6.36 shows the mass to charge ratio (m/z) of the gases released during thermal analysis of the initial (for detailed analysis see section 4.3) and the multi-component exhausted S100-II and F100-II samples. The peak on m/z 17 and 18 for S100-II at 100°C intensifies after adsorption from the multi-component mixture, likely due to the increased release of ammonia/ammonium from the amine groups. After adsorption on S100-II, the peaks on m/z 12 and 44 at 360, 620 and 900 °C become more intense. These temperatures correspond to those of the iron reduction mentioned previously in the thermal analysis section. Since CO₂ would be a product of the iron reduction with carbon, the increased amount of CO₂ detected supports the hypothesis of the iron involvement during pharmaceuticals uptake. Peaks on m/z 48 and 64, between 200 and 500 °C (maxima at 300°C), are related to the removal of SMX (SO and SO₂ from SMX). Note that this overlaps with the decomposition temperature reported for SMX (Fig. 6.14).
Fig. 6.35. DTG curves in helium for the waste-derived adsorbents; initial, used for the adsorption from single component solution and in the multi-component solution.

After the adsorption of pharmaceuticals, the peak on m/z 17 and 18 thermal profiles at 100 °C for F100-II becomes more intense due to the contribution of amine groups from the pharmaceuticals, and thus the peak at 370 °C is barely noticeable. After adsorption of the pharmaceutical mixture, and particularly TMP which was adsorbed in marked quantity, intense peaks are seen on F100-II+CBZ/SMX/TMP at 360 and 670 °C on the thermal profiles for m/z 12 and 44. Unlike for the sewage sludge-derived adsorbent, the m/z 48 and 64 thermal profiles for F100-II+CBZ/SMX/TMP don’t show pronounced peaks owing to the small amount of SMX adsorbed on this sample.

The absence of a stronger signal related to the adsorbates, particularly to CBZ that adsorbed in the greatest quantity on the waste-based adsorbents, is likely due to the limit of our instrument
(m/z 100). The main spectra for CBZ, SMX and TMP would have peaks on m/z 237, 254, and 182 thermal profiles, respectively [199].

Fig. 6.36. m/z thermal profiles for the initial and TMP exhausted samples, S100-II and F100-II. Multiplication factor: MW-12x1000, MW-17x25, MW-18x10, MW-44x100, MW-48x50,000, MW-64x20,000.

6.2.3. Potentiometric titration of waste-based adsorbents exposed to multi-component pharmaceutical solution.

To gain insight into changes in acidity occurring on the surface of the materials as a result of adsorption, potentiometric titration was conducted. The number of groups detected on the surface of the initial materials, as well as after adsorption from either the single or multi-component
solution is presented in Fig. 6.37. After the multi-component adsorption, the total number of groups was greater for the samples with higher fish waste content. However, the amount of the increase was greater for the sample containing predominantly sewage sludge content, such that the number of groups on S100-II increased 39-fold, while on F100-II the increase was 13-fold. After adsorption from single pharmaceutical solution, few groups were detected after CBZ exposure, as compared to the samples exposed to SMX and TMP, therefore it’s likely that SMX and TMP contribute more groups to those detected after multi-component exposure.

![Graph showing number of groups detected on various adsorbents](image_url)

Fig. 6.37. Total numbers of groups detected on the surface of the waste-derived adsorbents by potentiometric titration; initial, exposed to the single pharmaceuticals and to the multi-component solution.

The pKₐ distributions (Fig. 6.38) show the appearance of new groups, particularly at pKₐ 3-4, after exposure to the multi-component solution. The same species are present after exposure to the single SMX or TMP solution, indicating that these pharmaceuticals contribute to
acidification of the material. However, as the amount of SMX adsorbed from the multi-component solution was small, TMP might be a larger contributor of the resultant surface acidification.

Fig. 6.38. pKₐ distributions for the sewage sludge/fish waste-based adsorbents; initial, exhausted used in the single pharmaceutical solution and in the multi-component solution.

It is interesting that the trend in adsorption of the pharmaceuticals from the multi-component solution (CBZ is adsorbed in the greatest quantities, followed by TMP, and then SMX) follows the pKₐ values of the pharmaceuticals. CBZ has the highest pKₐ (13.9), followed by TMP (7.1), and then SMX (1.6, 5.7). As such, the basic pH values of the suspensions of adsorbent and pharmaceutical solution (Table 6.1), would have resulted in unfavorable adsorption conditions for SMX. A previous study reported that the optimum adsorption of SMX on activated carbon occurred at pH 2 [200]. When the experimental pH is below the pKₐ of SMX, it will exist in a
stable protonated form, but at higher pH values, the amine group will dissociate, resulting in decreased hydrophobicity, and thus poorer adsorption. The \( pK_a \) of CBZ is greater than the pH of the suspension, which means that CBZ will have a net neutral charge at the experimental conditions, thus the pH will have a minimal impact upon its adsorption capacity. In fact, in a previous study [201], it was shown that altering the solution pH from 5 to 9 caused only a 4% change in the adsorption of CBZ on resin. Moreover, as discussed above, the adsorption of CBZ is not driven by the electrostatic interactions affected by pH changes, but by the \( \pi-\pi \) interactions of the aromatic moiety of CBZ, or H-bonding of the urea moiety [202]. TMP, on the other hand, is not neutral, and is affected by the experimental pH. In a study by Dominguez et al., pH was adjusted from 5 to 9, which caused TMP adsorption to increase more than 10-fold [201]. Basic compounds, like TMP, have shown increased adsorption in basic pH [201]. Thus in the current research, the pH conditions proved to be favorable for the adsorption of TMP, unfavorable for SMX, and little effect on CBZ. Based on this, SMX should have adsorbed in the lowest quantity onto F100 as it had the highest pH, however, the SMX’s performance was optimal on F100. And by the same token, TMP, which should adsorb best in basic conditions, had the greatest amount adsorbed on S90F10, which was the more acidic of the materials. This suggests that the pH is not the only factor driving adsorption of the pharmaceuticals undergoing ionization.

6.2.4. Summary of adsorption on the waste-based adsorbents from multi-component solution

Ultimately, the removal efficiency of pharmaceuticals from an aqueous phase depends on the affinity between the adsorbate and adsorbent. The characteristics of the adsorbate, such as hydrophobicity and charge, must be well-matched to the surface chemistry of the adsorbent to achieve an optimal removal. For the present study, polarity was an important feature impacting
the adsorption success where the least polar substance, CBZ, adsorbed in nearly 10-fold greater quantity than the most polar pharmaceutical, SMX. The removal of TMP and SMX benefitted from the presence of the inorganic phase in the adsorbent, due to adsorption resulting from chelation and acid-base reactions, respectively. However, for CBZ, where π-π interactions are thought to be the primary mechanism of the removal, the presence of the carbon content is essential. The current results indicate a decreased quantity of pharmaceutical removal from the multi-component over single-component solution (by 0 – 83 %), and the efficacy varied greatly depending on the adsorbent features.
7. Comparison of adsorption capacity between waste-based adsorbents prepared at 650 and 950 °C

The previous chapters indicated the differences in surface area, pore volume, as well as compositional variation of the inorganic and carbon phases that resulted from the difference in pyrolysis temperature. It is interesting to consider how these differences affect the adsorption capacities of the materials.

7.1 Adsorption of carbamazepine

The performance of the materials carbonized at 950 °C exceeds that of their low temperature-prepared counterparts, and the amounts adsorbed are 2 to 8 times greater. Interestingly, the best CBZ adsorption performance for the 950 °C samples was on S90F10-II, yet its low temperature carbonized counterpart, S90F10-I, demonstrated the poorest adsorption performance.

A comparison of the measured (based on L-F fitting) and hypothetical (based on L-F fitting for the sludge and fish waste based adsorbent and assuming their physical mixtures showed that the composites exceeded their predicted adsorption. This indicates a synergistic effect in the composite materials, for both preparation temperatures. However, this synergistic effect is much more pronounced for the materials prepared at 950 °C, where the measured amount exceeded the predicted by up to 96 %, versus 15 – 20 % for the 650 °C materials. Thus it can be concluded that at the lower carbonization temperature, the development of synergistic features affecting adsorption is not as pronounced.

A comparison of the CBZ adsorption capacities of the 650 and the 950 °C pyrolyzed samples can be seen in Fig. 7.1. The largest difference is seen in the S90F10 samples, which when carbonized at 950 °C had the best adsorption capacity, but when carbonized at 650 °C adsorbed the smallest
amount of CBZ. There was about 10 times more CBZ adsorbed onto the S90F10 material pyrolyzed at 950 °C. Of the 650 °C prepared samples, S50F50-I had the best adsorption performance, yet in comparison to its high temperature counterpart, the lower temperature material adsorbed less than half the amount.

Fig. 7.1. Amounts adsorbed of CBZ on waste-based adsorbents, pyrolyzed at 650 and 950 °C.

Taking into consideration the low porosity of the materials, physical adsorption does not appear to be the predominant mechanism of adsorption. In comparing the 950 °C carbonized samples to those prepared at 650 °C it was observed that F100-II demonstrated a higher adsorption capacity than that of F100-I, despite F100-I having the larger surface area and porosity. The 650 °C materials have a proportionally larger content of the carbon phase than the 950 °C prepared materials, however it is of a lower level of aromatization, thus the 650 °C materials are not able to attract the aromatic rings of CBZ as effectively. And moreover, the 650 °C materials contain lower amounts of the inorganic phase, which also negatively impacts the adsorption of CBZ. Therefore all compositions of the 650 °C carbonized adsorbents demonstrated a lower adsorption capacity than their higher temperature counterparts.
7.2. Adsorption of sulfamethoxazole

Of the materials pyrolized at 650 °C, S100-I has the highest SMX adsorption capacity, and F100-I has the lowest. This is interesting because for the same materials pyrolized at 950 °C, the relationship shifts such that F100-II is the best performing adsorbent, and S100-II is the worst one. Overall, it can be noted that the adsorption capacity improved with an increased carbonization temperature. At an arbitrarily chosen equilibrium concentration of 0.1 mmol/L, the materials prepared at 650 °C adsorbed SMX in the range of 0.5 – 3.0 µmol/g while the ones at 950 °C, 10.0 – 18.5 µmol/g. The high adsorption capacity of the materials that contain a high content of silica (from the sewage sludge precursor) can be linked to the interactions of SMX with hydroxyl groups [189].

A comparison of the adsorption capacities of the 650 and the 950 °C pyrolized samples at the specific equilibrium concentration of 0.1 mmol/L can be seen in Fig. 7.2. Sample F100 (pure fish waste-derived adsorbent) has the greatest adsorption of SMX when pyrolized at 950 °C. The amount adsorbed is over 30 times greater than that on the material of the same composition when pyrolized at 650 °C.
Fig. 7.2. Amounts of SMX adsorbed on waste-based adsorbents (pyrolized at 650 and 950 °C) at a $C_{eq}$ of 0.1 mmol/L.

The lower pyrolysis temperature results in a greater content of the carbon phase. However, this did little to improve the adsorption capacity, as the main adsorption mechanism is an attraction to the inorganic phase. The 650 °C pyrolyzed materials contain lower inorganic content, in particular SiO$_2$, which would have an important role in the removal of SMX via acid-base interactions with the amine group. However, the overall low inorganic content of the 650 °C pyrolyzed adsorbents in comparison to the 950 °C prepared materials, combined with the unfavorable conditions of the pH (SMX is deprotonated at the experimental pH), resulted in low adsorption capacity on the 650 °C carbonized materials.

### 7.3 Adsorption of trimethoprim

Comparing the adsorption capacities of the waste-based materials for the removal of TMP was interesting in that the best performance was achieved by the material of the same waste composition, regardless of preparation temperature. S90F10, prepared at either carbonization
temperature, performed the best for TMP removal, and S100, the worst. This is distinct from CBZ and SMX, where adsorption capacity was affected by both pyrolyzation temperature and composition of the adsorbent.

The benefits of the higher pyrolysis temperature can be visualized in a comparison of the amounts adsorbed at the specific equilibrium concentration of 0.1 mmol/L (Fig. 7.3). The best performing material with respect to TMP adsorption in each pyrolyzation temperature was the S90F10 composite, however the total amount of TMP adsorbed varied greatly between the S90F10 materials prepared at different temperatures. The 950 °C pyrolysis temperature resulted in an adsorbent with 2.8 times higher adsorption capacity than on the sample pyrolized at 650 °C. Across all the samples, those prepared at the higher temperature demonstrated the better adsorption performance. At an equilibrium concentration of 0.1 mmol/L, the samples pyrolized at 650 °C adsorbed TMP between 9.6 and 16.6 µmol/g, and those at 950 °C, 26.3 – 47.4 µmol/g.

Fig. 7.3. Amounts of TMP adsorbed on waste-based adsorbents (pyrolized at 650 and 950 °C) at a C_{eq} of 0.1 mmol/L.
It is interesting that for both the 650 °C and 950 °C materials that S90F10 had superior adsorption capacity. This indicates the important role of the synergistic effect of the addition of 10 % fish waste in the composite materials. The fish waste would increase opportunities for chelation to occur between the amines and the metals of the adsorbent. The high calcium content is also the reason that the F100 materials of both pyrolization temperatures resulted in higher adsorption capacity on these materials as well. This highlights the importance of the inorganic phase, which is a smaller proportion of the content in the 650 °C prepared materials, and therefore is likely linked to the lower adsorption quantities on these materials.

7.4. Summary of adsorption on waste-based adsorbents from single component solution

The adsorption capacity of the various pharmaceuticals do not correlate to the porosity of the materials. In addition, there is no evidence that molecular size resulted in lowered adsorption amounts due to pore size constraints. This indicates that physical adsorption does not govern the removal of these pharmaceutical species, and thus points to the importance of chemical removal.

A very interesting shift in adsorption can be noted by comparing Fig. 7.1 to Fig. 7.3. On the 950 °C prepared adsorbents it was noted that CBZ adsorbed from single solute at about twice the amount as compared to TMP. However, when adsorption was carried out on the 650 °C carbonized adsorbents, this relationship changes such that TMP adsorbs in slightly greater quantity than CBZ. Clearly the distinct surface chemistry of the low temperature adsorbents possess some characteristic that favors the adsorption of TMP on these materials. Although the slightly decreased inorganic content of the low temperature adsorbents could have a negative impact on chelation with TMP, the low preparation temperature also causes less aromatization of the carbon phase. This decrease in aromaticity would decrease the hydrophobicity of the material, which could negatively impact the removal of CBZ by these low temperature materials.
SMX adsorption was low on the materials of both pyrolysis classes, although the 950 °C adsorbents did remove greater quantities from aqueous phase than the low temperature materials. The acid-base interactions between the SiO2 of the material and the amine group of SMX would have been facilitated by the higher inorganic content of the 950 °C prepared materials.

7.5 Simultaneous adsorption of multiple pharmaceuticals

Similar to the adsorbents prepared at 950 °C, the ones pyrolyzed at 650 °C demonstrated clear decrease in pharmaceutical adsorption from multi-component solution (Fig. 7.4) as a result of competition for adsorption sites. The trend in decreased adsorption from multi-component solution is evident on the adsorbents from both pyrolysis temperatures, however, the effect is more pronounced with the 950 °C materials, with a maximum reduction of 81 %, as compared to 73 % for the 650 °C materials. This is likely due to the fact that the amounts adsorbed on the 650 °C from single solution were low, and therefore the decrease from the competitive adsorption had less impact.
Fig. 7.4. Amounts adsorbed (at $q_e$ of 0.1) of multicomponent solutions on the 650 and 950 °C waste-derived adsorbents.

Although CBZ from the multi-component solution adsorbed at higher quantities onto the 950 °C pyrolyzed adsorbents than the other pharmaceuticals, for the 650 °C materials, there was no trend in adsorption. Additionally for the 950 °C prepared materials it was noted that TMP was the least impacted by competition, however on the 650 °C materials there was no trend observed for this either. Common to the adsorbents prepared at both temperatures is that SMX was adsorbed in the lowest quantity of all the pharmaceuticals, both from single and multi-component solution. As the pH values of the 650 °C adsorbent/adsorbate suspensions matched those of their respective compositions prepared at 950 °C, the same unfavorable conditions would have been found for SMX adsorption for all samples. SMX would be deprotonated at the experimental pH, resulting in increased hydrophobicity and low adsorption quantities.
8. Adsorption on commercial activated carbons

To determine whether the waste derived carbons are a viable economical alternative for use in wastewater treatment plants, it was necessary to compare the performance of the waste-based adsorbents to that of commercially available carbons that are currently used in wastewater treatment (note that only the better performing waste-derived adsorbents, those pyrolyzed at 950 °C, were used in comparison).

Two carbons were selected to represent adsorbents that are commercially available; WVA and S208. Due to different source materials and preparation methodologies, they each possess diverse physical and chemical characteristics. WVA is a wood-based carbon, chemically activated with phosphoric acid, and S208C is derived from coconut shells, and activated physically with steam.

First the initial carbons were characterized in terms of surface area and porosity. Then adsorption trials were carried out, using the single-solute and a multi-component solutions. Finally, in order to understand the adsorption mechanism and especially the role of specific interactions/reactive adsorption, the changes on the surfaces of our carbons after interactions with the pharmaceuticals were thoroughly analyzed. Insight into the adsorption mechanism can indicate which characteristics provide an adsorption advantage of one material over another, as well as aid in better tailoring of the adsorbent features in the production process.

8.1 Surface area and porosity of commercial carbons

Table 8.1 shows the surface areas and pore volumes for WVA and S208. The surface area of WVA is 60 % larger than that of S208. A similar trend (50 % difference) is found for the volume of micropores. On the other hand, the volume of pores smaller than 10 Å is 40 % higher in S208.
than that in WVA. While the smallest pores should be more active in physical adsorption as they create high-energy physical adsorption centers, functional groups can exist only in larger pores and thus they may affect the surface interactions at higher surface coverages [203].

In comparison to the waste-derived adsorbents, the commercial carbons have a surface area that is 10 to 16 times greater than the waste-derived sample with the largest surface area. The porosity of the commercial carbons is also more developed, with microporosity that is 9 to nearly 14 times greater than that of the most developed waste based adsorbent. Due to the well-developed porosity of the commercial carbons, it is anticipated that physical adsorption would play a more prominent role in the pharmaceuticals adsorption on WVA and S208 than it did on the waste based adsorbents.

Table 8.1. The parameters of porous structure for the commercial carbons calculated from nitrogen adsorption isotherms.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ [m$^2$/g]</th>
<th>$V_{mic}$ [cm$^3$/g]</th>
<th>$V_{mic} &lt; 10 , \text{Å}$ [cm$^3$/g]</th>
<th>$V_{meso}$ [cm$^3$/g]</th>
<th>$V_{t}$ [cm$^3$/g]</th>
<th>$V_{mic}/V_{t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WVA</td>
<td>1648</td>
<td>0.61</td>
<td>0.11</td>
<td>0.54</td>
<td>1.15</td>
<td>0.53</td>
</tr>
<tr>
<td>S208</td>
<td>1042</td>
<td>0.40</td>
<td>0.27</td>
<td>0.13</td>
<td>0.53</td>
<td>0.75</td>
</tr>
</tbody>
</table>

8.2. Adsorption from single component solution

Prior to the equilibrium adsorption measurements, kinetics studies were carried out to determine the time needed to reach equilibrium. The concentration decay curve (Fig. 8.1) shows a plateau after 72 contact hours with the commercial carbons, indicating that the equilibrium was reached. This duration was used in measuring the adsorption isotherms.
8.2.1. Carbamazepine

8.2.1.1. Adsorption isotherms of CBZ on the commercial activated carbons

Fig. 8.2 shows the adsorption isotherms with the experimental points fitted to the L-F equation (for equation details see section 1.3.3). The fitting parameters and the SSE errors are presented in Table 8.2. CBZ is adsorbed on both materials following the Langmuir-Freundlich isotherm model, where high-energy centers are responsible for a steep rise in the amount adsorbed at low surface coverage. At low surface coverage, slightly more CBZ is adsorbed on S208 than WVA. Then, for both samples, the gradual occupation of the centers with decreasing adsorption energy takes place. As equilibrium concentration is reached, slightly more CBZ is adsorbed onto WVA than S208.
Fig. 8.2. Adsorption isotherm of CBZ on WVA and S208. Solid lines represent the fitting to the L-F equation.

Table 8.2. Fitting parameter to L-F equation of CBZ adsorption isotherms on commercial carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$q_m$ (mmol/g)</th>
<th>K (L/mmol)</th>
<th>n</th>
<th>$R^2$</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>WVA+CBZ</td>
<td>1.41</td>
<td>36.64</td>
<td>1.10</td>
<td>0.9799</td>
<td>3.5x10^{-2}</td>
</tr>
<tr>
<td>S208+CBZ</td>
<td>1.27</td>
<td>3.62</td>
<td>0.58</td>
<td>0.9761</td>
<td>2.3x10^{-2}</td>
</tr>
</tbody>
</table>

8.2.1.2. Thermal analysis/mass spectrometry of commercial carbons exhausted with CBZ

The DTG curves are collected in Fig. 8.3. For comparison, and to eliminate any effect of possible solvent-adsorbent chemical interactions TA experiments were also run on the carbons exposed to water. No changes after water adsorption were noticed in comparison with the initial samples. During the thermal decomposition of pure CBZ, the weight loss was observed as a two-component peak between 200–400 °C (Fig. 6.5). Interestingly, the main weight loss is between the melting (190 °C) and boiling (411 °C) points of CBZ.
The weight loss pattern for CBZ on WVA shows a broad peak between 100 and 500 °C, with three maxima at 190, 290 and 430 °C. The first peak at 190 °C, represents the removal of the product of CBZ reactive adsorption, likely urea. The peak at 290 °C might represent the removal of CBZ physically/weakly adsorbed in the pore system. The higher temperature peak at 430 °C represents the reactive adsorption of CBZ on the surface of the carbon. Support for this can be found in the fact that the low temperature peaks are much smaller than the peak at 430 °C.

On the DTG curve for S208 two peaks are revealed, at about 200 °C and between 450 and 600 °C. The low temperature peak at 200 °C is linked to the changes in the chemistry of the adsorbed species, likely caused by oxidation reactions. It is well known that an activated carbon surface catalyzes the formation of superoxide ions [204]. These ions could oxidize urea moiety in some CBZ molecules resulting in the formation of either urea, or when oxidation goes further, of ammonia and CO₂ [205]. In the broad temperature range between 400 °C and 600 °C thermal transformations of CBZ strongly adsorbed/reacted with the carbon surface takes place, and the removal of decomposition products is detected. The large shift in the removal temperature suggests the occurrence of specific interactions of CBZ with the carbon surface. The broad peak appearing at the higher temperatures could be related to the consumption of reacted surface oxygen groups, such as quinones, which are known to participate in oxygen activation [206], or groups reacting directly with the amine groups of CBZ, such as phenols.
More qualitative information about the desorption/decomposition of the products adsorbed on the surface of the carbons can be derived from the analysis of $m/z$ thermal profiles of the species removed from the surface. They are collected in Fig. 8.4. Only $m/z$ 15 and 17 were chosen since they can represent CH$_3$ and/or NH, and NH$_3$ and/or OH, respectively. These species are expected to be released when CBZ decomposes/desorbs from the surface. In the case of the initial WVA sample, the most intense peak at $m/z$ 17 represents the removal of physically adsorbed water and water from the decomposition of carboxylic acids. Adsorption of CBZ decreases the intensity of the peak, which might be related to the involvement of the carboxylic acids in the surface reactions with the urea moiety. CBZ adsorption on S208 results in the release of water and ammonia at temperatures lower than 200 °C. The $m/z$ profiles are featureless at high temperature, even though well-defined weight loss is found on the thermal analyses between 400- 600 °C (Fig. 8.3). The absence of signals might be related to the removal of high molecular weight products of surface reactions, which are not detected by our MS ($m/z$ limit is 100).
Fig. 8.4. *m/z* thermal profile in helium for WVA and S208, initial and exhausted with CBZ.

8.2.1.3. FTIR of commercial carbons exhausted with CBZ

The results of FTIR analysis are presented in Fig. 8.5. Unfortunately, the data for S208 cannot be interpreted as the featureless spectra obtained are due to a high level of condensation of aromatic rings in this carbon, which results in absorption of almost all infrared radiation. On the other hand, on the spectra for the WVA samples several bands can be clearly distinguished. On the spectrum for the initial sample the bands visible at 1560, 1150, 1050 and 885 cm\(^{-1}\) (as indicated by the arrows) represent quinones, carboxyl/carbonates, C-O, and C-H vibrations, respectively. After CBZ adsorption the intensities of bands related to carbon oxygen groups decrease and a new strong band appears at 756 cm\(^{-1}\), which corresponds to the NH\(_2\) out-of-plane-bend [207].
Fig. 8.5. Comparison of FTIR spectra for WVA, initial and after CBZ adsorption.

8.2.1.4. Potentiometric titration of commercial carbons exhausted with CBZ

The potentiometric titration results confirm the differences in the chemistry of WVA and S208 carbons. Fig. 8.6 shows the proton binding curves of the carbons, initial and after exposure to CBZ. WVA has an initial $pH_{PZC}$ of 7.3, which decreases to 6.1 after adsorption. The decreasing $Q$ value indicates decreased proton uptake after exposure. The $pH_{PZC}$ of S208. is 9.4 initially, but increases to 9.9 after CBZ adsorption, highlighting the differences in the chemistry of the two commercial carbons.
Fig. 8.6. Proton uptake curves for commercial carbons, WVA and S208, initial and spent with CBZ.

The proton uptake curves (Fig. 8.7) show that the adsorption of CBZ on WVA does not change the surface in a marked way, as there is only a slight acidification of the surface. However, there are significant changes on the surface of S208 after CBZ adsorption with a 30% decrease in the number of groups, as well as surface alkalization. This supports the data from TA analysis which showed the consumption of groups which decompose at high temperatures, and which might represent phenols with pKₐ greater than 9.
8.2.1.5. X-ray photoelectron spectroscopy of commercial carbons exhausted with CBZ

The elemental compositions, in atomic %, on the surface of the carbons are presented in Table 8.3. The P and Na detected on WVA are residual from the activation step of the preparation procedure. After CBZ adsorption, N was detected on both the surface of WVA and S208, with a slightly higher amount detected on S208. Since the differences in the adsorption capacities between these two carbons are rather small, these differences may be linked to the reactivity of the WVA surface. It is possible that some nitrogen got released from the surface as a result of urea oxidation to ammonia and CO₂.
Table 8.3. Content of elements on the surface of the commercial carbons, initial and exhausted with CBZ (in atomic % from XPS analysis). ND = not detected.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>S</th>
<th>P</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>WVA</td>
<td>89.9</td>
<td>8.4</td>
<td>ND</td>
<td>ND</td>
<td>0.59</td>
<td>1.08</td>
</tr>
<tr>
<td>WVA+CBZ</td>
<td>89.5</td>
<td>8.2</td>
<td>1.8</td>
<td>ND</td>
<td>0.42</td>
<td>ND</td>
</tr>
<tr>
<td>S208</td>
<td>92.6</td>
<td>7.4</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>S208+CBZ</td>
<td>91.4</td>
<td>6.5</td>
<td>2.1</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

The complexity of the chemical environment of nitrogen remaining on the surface is evidenced from the deconvolution of N1 \( s \) core energy level spectra for the carbons after CBZ adsorption (Table 8.4). Apparently pyridine species are formed, and the ratio of conversion from amines is much greater on WVA than that on S208. The results support the hypothesis formulated based on the results of surface analyses discussed above. Thus ammonia evolved from the decomposition of the carbamazepine/urea moiety must contribute to pyridine functionality formation in the acidic environment of these carbon pores. The content of some oxygen groups decreased after CBZ adsorption, which may be linked to the consumption of these groups in the surface reactions.
Table 8.4. The results of deconvolution of C 1s, O 1s, N 1s and S 2p core energy levels, initial and after CBZ exposure.

<table>
<thead>
<tr>
<th>Energy, eV</th>
<th>Bond assignment</th>
<th>S208 Initial</th>
<th>+CBZ</th>
<th>WVA Initial</th>
<th>+CBZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>284.8</td>
<td>C-(C, S) (graphitic carbon)</td>
<td>83.7</td>
<td>84.3</td>
<td>86.9</td>
<td>83.1</td>
</tr>
<tr>
<td>285.9</td>
<td>C-(O, N, H) (phenolic, alcoholic, etheric)</td>
<td>11.6</td>
<td>10.5</td>
<td>7.2</td>
<td>9.6</td>
</tr>
<tr>
<td>286.9</td>
<td>C=O (carbonyl or quinone)</td>
<td>4.7</td>
<td>5.3</td>
<td>3.6</td>
<td>4.6</td>
</tr>
<tr>
<td>288.7</td>
<td>O-C=O (carboxyl or ester)</td>
<td></td>
<td></td>
<td>2.2</td>
<td>2.8</td>
</tr>
<tr>
<td>O 1s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>530.7</td>
<td>Ketone, lactone, carbonyl</td>
<td>43.5</td>
<td>22.2</td>
<td>37.7</td>
<td>22.0</td>
</tr>
<tr>
<td>532.1</td>
<td>O=C/O=S (in carboxyl/carbonyl or sulfoxides/ sulfones)</td>
<td>56.5</td>
<td>33.7</td>
<td>34.5</td>
<td>48.3</td>
</tr>
<tr>
<td>533.6</td>
<td>O-C (in phenol/epoxy, ether, ester, anhydride, carboxyls)</td>
<td>44.1</td>
<td>27.8</td>
<td>29.7</td>
<td></td>
</tr>
<tr>
<td>N 1s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>398.7</td>
<td>N-6 (in pyridine)</td>
<td>3.7</td>
<td></td>
<td>33.7</td>
<td></td>
</tr>
<tr>
<td>400.2</td>
<td>N-5 (in pyrrolic/pyridone and amide, amines)</td>
<td>96.3</td>
<td></td>
<td>66.3</td>
<td></td>
</tr>
</tbody>
</table>

8.2.2. Sulfamethoxazole

8.2.2.1. Adsorption isotherms of SMX on commercial activated carbons

Fig. 8.8 shows the adsorption isotherms of SMX on the commercial carbons, with the experimental points fitted to the L-F equation (for equation details see section 1.3.3). The fitting parameters and SSE errors are presented in Table 8.5. For the adsorption of SMX on WVA, the isotherm is nearly linear, suggesting that at higher concentrations more SMX will be retained. The isotherm of SMX on S208 follows the L-F isotherm model, indicating the presence of a significant amount of high-energy adsorption centers. Overall the results indicate that SMX has a higher affinity for WVA. The fitting parameters (Table 8.5) indicate that adsorption of SMX on WVA was 3.5 times higher than on S208, which is related to the linear shape of the isotherm. The difference is also noted in the $n$ values, which indicate an increased heterogeneity as the value lowers from 1. After SMX adsorption, S208 has $n$ fitting values that are lower than that for WVA, therefore the mechanism for adsorption on S208 is more complex.
Fig. 8.8. Adsorption isotherms of SMX on WVA and S208. Solid lines represent the fitting to the L-F equation.

Table 8.5. Fitting parameter to L-F equation of SMX adsorption isotherms on commercial carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>qm (mmol/g)</th>
<th>K (L/mmol)</th>
<th>n</th>
<th>R^2</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>WVA+SMX</td>
<td>26.55</td>
<td>0.44</td>
<td>0.99</td>
<td>0.9924</td>
<td>8.5x10^{-1}</td>
</tr>
<tr>
<td>S208+SMX</td>
<td>7.51</td>
<td>0.09</td>
<td>0.48</td>
<td>0.9810</td>
<td>1.5x10^{-2}</td>
</tr>
</tbody>
</table>

8.2.2.2. Thermal analysis/mass spectrometry of commercial carbons exhausted with SMX

When the thermal decomposition of pure SMX was tested, the weight loss was observed as a two-component peak between 200-400 °C (Fig. 6.14), which falls between the melting (166 °C) and boiling (482 °C) points of SMX. For both carbons after SMX adsorption (Fig. 8.9), similar weight loss patterns are found with the main peak between 200-400 °C and a long tail throughout almost the whole temperature range. The tail is also visible on the decomposition pattern of pure SMX, which can be linked to its dimerization [208] during heating and to the decomposition of
the dimers/polymers formed. This can be deduced from the ratio of its intensity to the intensity of the main peak on the carbons studied, which is much greater than that for the pure substances. This effect is especially visible for S208, which is likely due to an inaccessibility of the small pores to the formed dimers, which then block the pore entrances. The weight loss pattern for WVA at temperatures higher than 600 °C was not analyzed since this carbon was not exposed to these temperatures during its production. The first peak on the DTG curve for WVA exposed to SMX is linked to the removal of physically adsorbed SMX, and the enhanced tail, to the decomposition of the species formed as a result of its dimerization/polymerization and chemical interactions with the surface groups of carbons. The involvement of carboxylic groups in these reactions can be difficult to discern owing to the overlap of their decomposition temperatures [209] with that of SMX decomposition.

Fig. 8.9. DTG curves in helium for WVA and S208, initial (dotted line) and exhausted (solid line) with SMX.

The m/z thermal profiles of the species removed from the surface of the carbons are presented in Fig. 8.10. The m/z 15, 17, 48 and 64 are shown, which represent CH₃ and/or NH, NH₃ and/or OH, SO and SO₂, respectively. These species are expected to be released when SMX
decomposes/desorbs from the surface. After SMX adsorption on WVA, the removal of ammonia at a low temperature is detected indicating that some decomposition reactions take place on the surface. On both carbons, a peak from the removal of SO₂ is noticed between 250 and 450 °C with the maximum at 350 °C. This overlaps with the most intense weight loss for the samples, which was linked to the removal/sublimation and boiling of SMX. Some traces of SO are also removed at temperatures over 800 °C and must be related to the removal of dimers and thermal transformations of sulfones on the surface.

Fig. 8.10. MS patterns during thermal analysis in helium for WVA and S208, initial and exhausted after SMX adsorption.
8.2.2.3. FTIR of commercial carbons exhausted with SMX

The results of the FTIR analysis of carbons exposed to SMX are presented in Fig. 8.11. The data for S208 is not shown due to a featureless spectra resulting from the absorption of almost all infrared radiation. The initial sample contains the bands visible at 1560, 1150, 1050 and 885 cm\(^{-1}\), representing quinones, carboxyl and carbonates, C-O, and C-H vibrations, respectively. SMX adsorption, besides decreasing the intensity of the C-O and C=O bands, also results in the appearance of new bands at 1590, 1510, 1160, 1090 and 825 cm\(^{-1}\). They are linked to the presence of C=N, C-N, N-H, and -SO\(_2\)- bonds [210]. The appearance of these bands and the decrease in the intensity of carbon-oxygen bands, especially those at 1560 cm\(^{-1}\) and 1050 cm\(^{-1}\) representing quinones and C-O bonds, supports the reactivity of SMX with the WVA surface.

![Fig. 8.11. Comparison of FTIR spectra for WVA, initial and after SMX adsorption.](image-url)
8.2.2.4. Potentiometric titration of commercial carbons exhausted with SMX

Positive values of $Q$ represent a proton uptake on basic groups and a negative proton release from the acidic groups [211]. After exposure to SMX the pH$_{PZC}$ values decrease for WVA, and the shape of the proton uptake curve is significantly altered (Fig. 8.12), indicating an increase in surface acidity. For S208 there is little change in the pH$_{PZC}$ or the shape of the proton binding curve after SMX adsorption.

![Proton uptake curves for commercial carbons, initial and spent with SMX.](image)

Fig. 8.12. Proton uptake curves for commercial carbons, initial and spent with SMX.

The pK$_a$ distributions (Fig. 8.13) show that for WVA there are nearly twice as many surface groups after exposure to SMX as on the initial material, and surface groups dissociating at pH $> 5$ are introduced. When SMX is adsorbed on S208, only a small decrease in the amount of basic groups dissociating at pH $< 6$ is noticed.
Fig. 8.13. The comparison of the pKₐ distributions for WVA and S208, initial and after SMX adsorption.

8.2.2.5. X-ray photoelectron spectroscopy of commercial carbons exhausted with SMX

In Table 8.6 are presented the elemental compositions (in atomic %) of the carbons’ surfaces. S208 is richer in carbon in C-C bonds and has less oxygen than WVA. The trace of P and Na in WVA are the results of its activation with phosphoric acid followed by neutralization during the manufacturing process of this carbon. After adsorption of SMX the ratio of nitrogen to sulfur on WVA is nearly 5:1, and on S208 is about 6:1. Taking into account that this ratio for SMX is 3:1, these results suggest significant transformations of the adsorbate on the surface towards the incorporation of nitrogen molecules. This is especially visible for the WVA carbon. More nitrogen and sulfur on the surface of this carbon can be also linked to its higher affinity to retain SMX than that of S208.
Table 8.6. Content of elements on the surface of the commercial carbons, initial and exhausted with SMX (in atomic % from XPS analysis). ND = not detected.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>S</th>
<th>P</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>WVA</td>
<td>89.9</td>
<td>8.4</td>
<td>ND</td>
<td>ND</td>
<td>0.59</td>
<td>1.08</td>
</tr>
<tr>
<td>WVA+SMX</td>
<td>88.7</td>
<td>9.1</td>
<td>1.8</td>
<td>0.37</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>S208</td>
<td>92.6</td>
<td>7.4</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>S208+SMX</td>
<td>90.3</td>
<td>7.9</td>
<td>1.6</td>
<td>0.25</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

Examination of the deconvolution (Table 8.7) of the N1s core energy level for the carbons after SMX adsorption shows that the conversion of nitrogen groups to pyridine is similar on both carbons. Since an acidic environment catalyzes pyridine formation, the appearance of sulfonic acids on the carbon surface can trigger these transformations. Oxidation of sulfones to sulfonic acids is more pronounced on WVA than on S208, which may be linked to the formation of superoxide ions, and enhanced electron transfer on a more aromatized carbon surface. The presence of sulfones/sulfonic acid is also visible as an increase in the oxygen content after SMX adsorption.
Table 8.7. The results of deconvolution of C 1s, O 1s, N 1s and S 2p core energy levels, initial and after SMX exposure.

<table>
<thead>
<tr>
<th>Energy, eV</th>
<th>Bond assignment</th>
<th>S208 Initial</th>
<th>+SMX</th>
<th>WVA Initial</th>
<th>+SMX</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C 1s</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>284.8</td>
<td>C-(C, S) (graphitic carbon)</td>
<td>83.7</td>
<td>81.6</td>
<td>86.9</td>
<td>87.0</td>
</tr>
<tr>
<td>285.9</td>
<td>C-(O, N, H) (phenolic, alcoholic, etheric)</td>
<td>11.6</td>
<td>13.0</td>
<td>7.2</td>
<td>9.1</td>
</tr>
<tr>
<td>286.9</td>
<td>C=O (carbonyl or quinone)</td>
<td>4.7</td>
<td>5.4</td>
<td>3.6</td>
<td>4.6</td>
</tr>
<tr>
<td>288.7</td>
<td>O=C=O (carboxyl or ester)</td>
<td></td>
<td></td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td><strong>O 1s</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>530.7</td>
<td>Ketone, lactone, carbonyl</td>
<td>43.5</td>
<td></td>
<td>37.7</td>
<td>20.9</td>
</tr>
<tr>
<td>532.1</td>
<td>O=C/O=S (in carboxyl/carbonyl or sulfoxides/sulfones)</td>
<td>56.5</td>
<td>57.0</td>
<td>34.5</td>
<td>47.8</td>
</tr>
<tr>
<td>533.6</td>
<td>O-C (in phenol/epoxy, ether, ester, anhydride, carboxyls)</td>
<td>43.0</td>
<td></td>
<td>27.8</td>
<td>31.3</td>
</tr>
<tr>
<td><strong>N 1s</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>398.7</td>
<td>N-6 (in pyridine)</td>
<td>11.9</td>
<td></td>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td>400.2</td>
<td>N-5 (in pyrrolic/pyridone and amide, amines)</td>
<td>88.1</td>
<td></td>
<td>89.5</td>
<td></td>
</tr>
<tr>
<td><strong>S 2p3/2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>167.8</td>
<td>R₂-S=O/R-SO₂-R (in sulfoxides, sulfones)</td>
<td>56.0</td>
<td></td>
<td>42.7</td>
<td></td>
</tr>
<tr>
<td>168.3</td>
<td>R-SO₃H (in sulfonic acids)</td>
<td>44.0</td>
<td></td>
<td>57.3</td>
<td></td>
</tr>
</tbody>
</table>

8.2.3. Trimethoprim

8.2.3.1. Adsorption isotherms of TMP on commercial activated carbons

Fig. 8.14 shows the adsorption isotherms with the experimental points fitted to the L-F equation (for equation details see section 1.3.3). The fitting parameters and the SSE errors are presented in Table 8.8. At low surface coverage, TMP adsorbs with greater affinity to S208, however at higher concentrations TMP adsorbed somewhat better on WVA.
Fig. 8.14. Adsorption isotherm of TMP on WVA and S208. Solid lines represent the fitting to the L-F equation.

Table 8.8. Fitting parameter to L-F equation of TMP adsorption isotherms on commercial carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( q_m ) (mmol/g)</th>
<th>K (L/mmol)</th>
<th>( n )</th>
<th>( R^2 )</th>
<th>( SSE )</th>
</tr>
</thead>
<tbody>
<tr>
<td>WVA+TMP</td>
<td>4.49</td>
<td>1.73</td>
<td>0.59</td>
<td>0.9904</td>
<td>6.7x10^{-3}</td>
</tr>
<tr>
<td>S208+TMP</td>
<td>4.11</td>
<td>0.07</td>
<td>0.30</td>
<td>0.9874</td>
<td>8.4x10^{-3}</td>
</tr>
</tbody>
</table>

### 8.2.3.2. Thermal analysis of commercial carbons exhausted with TMP

The decomposition/desorption of the surface species can be observed in the DTG curves in Fig. 8.15. The DTG curve for TMP on both WVA and S208 demonstrate a broad peak between 150 and 800 °C, with a maxima at 400 °C. This can be compared to the thermal decomposition of pure TMP (Fig. 6.24), which shows a single peak between 200 and 400 °C, with a tail throughout the rest of the temperature range. The first low temperature shoulder likely represents the removal of physically adsorbed TMP, as this shoulder is not present on the DTG of the pure...
pharmaceutical. The main peak reflects the melting (197 °C) and boiling (526 °C) points of pure TMP, therefore this peak represents the decomposition of the pure pharmaceuticals. The long tail found at the higher temperatures of the DTG curve, are also present on the thermal decomposition curve of pure TMP, and at much higher intensities, indicating that the tail visible on the decomposition curves likely represents the decomposition of polymers formed during heating.

![DTG curves](image)

Fig. 8.15. DTG curves in helium for WVA and S208, initial (dotted line) and exhausted (solid line) with TMP.

### 8.2.3.3. FTIR of commercial carbons exhausted with TMP

The results of the FTIR analysis of carbons exposed to TMP are presented in Fig. 8.16. The bands of the initial sample have been identified in the previous section. TMP adsorption results in the appearance of new bands at 1498, 1447, 1326, 1227 and 1118 cm\(^{-1}\). The bands at 1447, 1326, and 1227 cm\(^{-1}\) have been reported previously [212] to pertain to the deformation of the CH\(_2\) group, vibrations of C-N in the amine aromatic primary, and OCH\(_3\) aromatic group vibrations, respectively. The bands at 1498 and 1118 are linked to the presence of C=C and C-O
bonds, respectively [187]. The appearance of these bands supports the reactivity of TMP with the WVA surface.

![FTIR spectra comparison](image)

**Fig. 8.16.** Comparison of FTIR spectra for WVA, initial and after TMP adsorption.

### 8.2.3.4. Potentiometric titration of commercial carbons exhausted with TMP

The results of the potentiometric titration were analyzed to better understand the surface changes after TMP exposure. For WVA, initially there is an increase in the Q value (Fig. 8.17) after exposure to TMP, and the pH\textsubscript{PZC} increases to 8.3 from 7.3. After the exposure of S208 to TMP, the Q value decreases, and the pH\textsubscript{PZC} increases from 9.4 to 10.5, in relation to the initial material. The shape of the proton binding curve also changes significantly.
The number of groups on the surface of WVA (Fig. 8.18) after TMP exposure increases more than two-fold, with new groups appearing at both low and high pK\textsubscript{a} values. For S208 after TMP exposure, the number of groups is about half that of the initial sample, and there is the appearance of a new group around pK\textsubscript{a} 4.7.

Fig. 8.18. The comparison of the pK\textsubscript{a} distributions for WVA and S208, initial and after TMP adsorption.
8.3 Adsorption from multi-component solution

8.3.1. Adsorption isotherms of multi-component solution on commercial activated carbons

Fig. 8.19 depicts the adsorption of multi-component pharmaceutical solution onto commercial carbons. The experimental data was fitted to the L-F equation. From multi-component solution onto WVA, CBZ was adsorbed in highest quantity, followed by TMP, and lastly SMX. Adsorption on S208 is very distinct. The overall amount adsorbed is lower than on WVA, and the trends of pharmaceutical removal change such that TMP is adsorbed in highest quantity, followed by CBZ and finally SMX.

Fig. 8.19. Multicomponent adsorption isotherms on WVA and S208. Solid lines represent the fitting to the L-F equation.

Fig. 8.20 considers the physical characteristics of the carbons, and their impact on the adsorption of the pharmaceuticals from multi-component solution. It can be seen that 2.2 times more CBZ is adsorbed, and 1.8 times more TMP is adsorbed on WVA than on S208. Interestingly, the adsorption of SMX is the same on both carbons. For WVA (Fig. 8.20A), there is a trend of
increased adsorption capacity with an increased surface area. There is also a positive trend between the increased volume of micropores of WVA and increased adsorption capacity (Fig. 8.20B). The increased adsorption capacity (Fig. 8.20C) is linked with increased oxygen content. This highlights the important contribution of the oxygen-containing surface groups during adsorption.

Fig. 8.20. Dependence of adsorption capacity from the multi-component solution [mmol/g] on surface area [m²/g] (A), volume of micropores [cm³/g] (B), and oxygen content (C) of the commercial carbons.

The performance of the carbons when adsorption occurred from a single-solute solution as compared to that from a multicomponent solution can be seen in Fig. 8.21. WVA adsorbed higher quantities of pharmaceuticals, both from the single-solute and multi-component solutions. All the pharmaceuticals were adsorbed in greater amounts from single solute solution than from the multi-component solution. On WVA, the adsorption of SMX was decreased by 69 % when in multi-component solution, which was more than the decrease experienced by CBZ (34 % decrease in adsorption) or TMP (41 % decrease in adsorption) (Table. 8.9). On S208, the trends are distinct, with all the pharmaceuticals adsorbing in similar quantities from the single-solute solutions. The decreased amount adsorbed on S208 from the multi-component solution, as
compared to single solute adsorption, is similar for CBZ and SMX (62 and 66 % decrease, respectively), while TMP was less impacted (49 % adsorption decrease).

Fig. 8.21. Amounts adsorbed (at $q_e$ of 0.1) of CBZ, SMX and TMP from single and multicomponent solutions on the commercial carbons.

Table 8.9. Comparison of the adsorption capacity of the commercial carbons (at $q_e$ at 0.2 mmol/L, as determined by L-F fitting) for each pharmaceutical when in single versus multicomponent solution, and the percent difference.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>$q_{e,0.1}$ CBZ (mmol/g)</th>
<th>$q_{e,0.1}$ SMX (mmol/g)</th>
<th>$q_{e,0.1}$ TMP (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WVA</td>
<td>1.068</td>
<td>0.856</td>
<td>1.180</td>
</tr>
<tr>
<td>S208</td>
<td>0.802</td>
<td>0.720</td>
<td>0.741</td>
</tr>
</tbody>
</table>
8.3.2. Thermal analysis of commercial carbons after adsorption from the multi-component solution

The thermal decomposition patterns of the exhausted samples were analyzed and compared to those of the initial samples. The DTG curves (Fig. 8.22) were analyzed up to the pyrolysis temperature (600 °C for WVA and 800 °C for S208). The total weight loss was 12 and 21 % for S208 and WVA respectively. All three pharmaceuticals have decomposition temperatures between 200 and 400 °C. The peak in this temperature range on WVA is linked with an increased percentage of weight loss (based on the TG analysis), reflecting the high quantities of pharmaceuticals adsorbed on this sample. The quantities of pharmaceuticals adsorbed on S208 from the single as compared to the multi-component solution did not vary much, resulting in the weight loss remaining the same between trials. On this sample the maxima that correspond to each respective pharmaceutical are evident in the multi-component peak.

Fig. 8.22. DTG curves in helium for WVA and S208, initial, exposed to the single and multi-component solutions (CBZ/SMX/TMP).
8.3.3. Potentiometric titration of commercial carbons after adsorption from the multi-component solution

Analysis of the potentiometric titration revealed the number of groups present on the surface of the initial materials, as well as after adsorption from either the single or multi-component solution (Fig. 8.23). For both carbons, the number of groups decreases when adsorption occurs from the multi-component solution. This is interesting because on the waste-derived materials, there was an increase in the number of groups after multi-component adsorption. This highlights how distinct the surfaces and the adsorption mechanisms of the two groups of adsorbents are. In comparing the results on the commercial carbons, there is no trend between the number of groups and the amount of pharmaceuticals adsorbed. Nor is there a common trend between adsorption of a particular pharmaceutical on WVA and S208. Thus, TMP has the more groups than SMX on WVA, but the reverse is true on S208. This indicates that the surface adsorption mechanisms are also different between the two commercial carbons. It is interesting to note that the total amount adsorbed on S208 after exposure to multi-component solution was greater than for any single solute solution on this material, however, the former has nearly a complete disappearance of all surface groups after adsorption, indicating a reaction between the carbon’s surface groups and the pharmaceuticals.
8.23. Total numbers of groups detected on the surface of the commercial carbons by potentiometric titration; initial, exposed to the single pharmaceuticals and to the multi-component solution.

Another way to view these surface changes is in the pK$_a$ curves depicted in Fig. 8.24. The number of groups on the surface of WVA after exposure to the multi-component solution increases 1.5 times. It is mainly due to the appearance of new groups at low pK$_a$ values. On the surface of S208, there is a disappearance of all groups except for one at pK$_a$ 6.6.
Fig. 8.24. The comparison of the pK\textsubscript{a} distributions for WVA and S208, initial and after adsorption from the multi-component solution.

### 8.3.4. Mechanisms of pharmaceutical adsorption on commercial carbons

Although physisorption can account for some of the pharmaceutical removal from aqueous phase, the surface characterizations of the exhausted carbons indicate that chemisorption occurs as well.

Based on the surface analysis, disproportionation of the amide bond of CBZ with a subsequent release of phenanthrene and urea can take place on the surface of the carbons as a result of oxidation with superoxide ions formed in the process of oxygen activation [204]. This is presented in Fig. 8.25. That disproportionation of the amide bond of carbamazepine can even go further, and NH\textsubscript{3} and CO\textsubscript{2} can be released. Released ammonia can be incorporated by the aromatic ring on the surface of carbons, especially for WVA which has a low degree of aromatization and is rich in oxygen species such as aldehydes and carboxylic acids.
Fig. 8.25. Disproportionation of the amide bond of CBZ with the release of urea (A) and ammonia (B).
Another scenario is the reaction of the amine group(s) of the pharmaceuticals with surface carboxylic acids (Fig. 8.26). The reaction is depicted for SMX, but could also occur for CBZ or TMP.

Fig. 8.26. Reactions of amine groups with surface carboxylic acids.
A decrease in the number of high temperature decomposing groups (carbonyl/quinone/phenol) can be explained by their reactions with the amine moieties of the pharmaceuticals (Fig. 8.27).
8.4. Comparison of the adsorption capacity of waste-based adsorbents and commercial carbons

The adsorption performance of the commercially available carbons is higher than that of the waste-derived adsorbents. Adsorption of CBZ from a single solute solution, at an equilibrium concentration of 0.1 mmol/L, on WVA and S208 was 1.07 and 0.80 mmol/g, respectively. The best performing of the waste-based adsorbents adsorbed one order less (0.1 mmol/g). At the equilibrium concentration of 0.1 mmol/g the SMX adsorption capacity on WVA was 0.86 mmol/g, whereas on S208 was 0.72 mmol/g. Whereas the highest amount adsorbed of SMX on the waste-derived materials was 0.02 mmol/g. And finally, the amount of TMP adsorbed was 1.18 and 0.74 mmol/g for WVA and S208, respectively, as compared to 0.05 mmol/g on the waste-based adsorbents. However, the adsorbents should be evaluated not only in terms of adsorption capacity. The waste-based materials offer a means to a water treatment method that is economical to produce, and also aids in reducing the accumulation of undesired waste products.

If the pharmaceutical removal on the sewage sludge/fish waste adsorbents are compared to other alternatively-sources adsorbents, it becomes clear that their performance is on par with these other waste-based materials. CBZ was removed by pillared clays in the amount of 0.11 mmol/g [120]. On activated walnut shell, maximum adsorption capacity for SMX was 0.002 mmol/g of SMX [213], which is an order of magnitude less than the sewage sludge/fish waste adsorbent. The maximum capacity of TMP adsorption on Montmorillonite clay was 0.14 – 0.44 mmol/g [214], and on activated lotus stalks, 0.41 – 1.19 mmol/g of TMP was adsorbed [215].

From multi-component solution, the best performing of the waste-based adsorbents removed a total of 0.07 mmol/g, as compared to 1.65 and 0.93 mmol/g, respectively on WVA and S208. A broader comparison is challenging, as studies on multi-component adsorption are limited.
However, some recent articles noticed similar trends with respect to multi component studies demonstrating decreased adsorption quantities as compared to the pharmaceuticals present in a single solution. CBZ removal was diminished by 38 – 63 %, (depending on the concentration of bisphenol A) when in a bi-solute solution [119]. SMX removal decreased by 73 % when in a multi component solution with acetaminophen and diclofenac [117]. On the sewage sludge/fish waste adsorbents, the decreases in the removal of pharmaceuticals from a multicomponent solutions for CBZ and SMX are 37 -77% and 55-83 %, respectively, in comparison to their removal from single solutions. Although with some pharmaceuticals complementary adsorption is possible, when the molecular structure and physiochemical properties are similar, competition for the same adsorption sites usually takes place [119]. Across all studies that considered CBZ adsorption from a multi component solution, CBZ was adsorbed in greater quantity than numerous other pharmaceuticals [201, 216, 217].

Although the commercial carbons demonstrate greater maximum adsorption capacity than the waste-based adsorbents, their surface is at least ten fold larger. Taking into account the surface activity and the amount adsorbed per unit surface area, the waste-based adsorbents performance can match that of the commercial activated carbons. Moreover, the attractiveness of waste recycling for sewage sludge/fish waste-based adsorbent precursors shows promise as an economical and environmental approach to meet waste water remediation needs.
9. Conclusion

The primary goal of this work was to develop an adsorbent from repurposed waste precursors that offers a viable alternative to the current standard of commercial activated carbon for the treatment of wastewater. By carbonizing a combination of sewage sludge and fish waste, adsorbents were produced that possess unique characteristics. The two precursor materials were used in varying proportions, and carbonized at two temperatures, to evaluate which preparation resulted in the most effective adsorbent for the removal of three model pharmaceuticals (CBZ, SMX and TMP) from aqueous phase.

Due to the chemical nature of the precursor materials, the waste-based adsorbents are composed of 55 – 74 % inorganic content after pyrolysis. The inorganic content primarily consists of SiO$_2$ from the sewage sludge, and CaO from the fish waste. Based on the adsorption isotherms of the waste-based materials with CBZ, SMX and TMP, altering the proportions of the adsorbent’s precursor content did not show a clear trend with respect to the removal of the pharmaceuticals from the water phase, as optimum performance varied by pharmaceutical. However, for the removal of CBZ and TMP, it was evident that the addition of fish waste to the sewage sludge led to an improved adsorption capacity over the application of adsorbents produced from a single precursor. Clearly a synergistic effect occurred in producing the S90F10-II composite material, and the results were beneficial for the pharmaceutical removal capacity.

For the removal of CBZ, the highly dispersed inorganic phase can interact by means of polar attraction and acid-base reactions. There would also be a strong effect of the π-π interactions between aromatic rings of the CBZ with the carbon phase of the materials. SMX on the other, is quite polar, and therefore would not adsorb as well onto the carbon phase. Therefore the
inorganic content of the waste-based adsorbent plays an important role in the removal of SMX from aqueous phase. SMX adsorbed in greatest amounts on F100-II, due to acid-base reactions between the amine/amide group of the SMX and the Lewis acidic sites of the adsorbent. The adsorption of TMP on the waste-based materials would be driven by the chelation mechanism that occurs between the amine group of the pharmaceutical and the metals of the inorganic content, particularly calcium and iron. It was found that SMX was adsorbed in lower quantities than either of the other pharmaceuticals. The polar nature of SMX, combined with unfavorable pH conditions that deprotonated the molecule, resulted in less of this pharmaceutical removed from the water phase.

The removal of pharmaceuticals from multi-component solution, as compared to single component solution, resulted in a lesser total amount (by 0 – 83 %) of each pharmaceutical adsorbed on the waste-based adsorbents. It is clear that there is competition between the pharmaceuticals for the adsorption sites. For all adsorbent materials, SMX was adsorbed in the lowest quantity from the multi-component solution due to once again to the polarity of the molecule, and unfavorable pH conditions.

The effect of the carbonization temperature on adsorption capacity was also investigated. The adsorbents prepared at 950 °C resulted in a more effective removal of all of the pharmaceuticals from the aqueous phase. The materials prepared at 650 °C adsorbed 64 – 87 % less than the materials carbonized at 950 °C. Although the materials prepared at the lower temperature had less development of pore volume and surface area (by 17 % and 20 %, respectively), no correlation was observed between these characteristics and the adsorption capacity. The lower adsorption capacity of the 650 °C prepared materials is mainly due to the proportionally lower inorganic content, as compared to the 950 °C materials, which is significant in light of the
governing role the inorganic content plays in the removal of the pharmaceutical species.

Additionally, the carbon phase of the adsorbents prepared at the lower temperature would be less aromaticized, which would affect hydrophobicity and thus pharmaceutical removal as well.

The total quantities of pharmaceuticals removed by the commercial carbons were an order of magnitude greater than the amount adsorbed on the waste-based materials. However, based on the fact that the time required to reach adsorption equilibrium for the waste-based adsorbents was 5 hours, as compared to the 72 hours required by the commercial carbons, the application of the waste-based materials would facilitate treatment in large-scale plants where minimal treatment times are desirable. The waste-based materials’ adsorption capacities were comparable to that measured for other adsorbents produced from alternative precursor materials. Ultimately the performance of the waste-based materials should not be evaluated solely on the basis of the adsorption capacity, but also their economical production and the ability to diminish the accumulation of undesired waste products by repurposing them. The application of sewage sludge and fish waste for the production of adsorbents for waste water treatment is a promising technology in this regard. The waste-based adsorbents have shown that their unique surface chemistry can enable removal of pollutants that might be resistant to removal with more traditional adsorbents. Moreover, once the mechanisms of adsorption are understood, the composition of an adsorbent can be tailored to optimize for removal of adsorbates with certain characteristics.
10. Future perspectives

Carbon-based adsorbents have been used since 1500 B.C. [90], and therefore they do not represent a novel technology. However, adsorption continues to be one of the most commonly used water treatment methodologies nowadays because it’s effective and simple to use in the removal of a wide array of contaminants. To keep adsorption a current waste water treatment technology, here are some considerations:

- Adsorption can provide both an environmental as well as an economical benefit. Rather than harvesting costly raw materials, such as wood, to serve as precursors, continuous research into abundant and low cost precursors should be conducted. A particular focus should be placed on the reuse of materials that may be toxic, even for disposal purposes, but that through the process of carbonization can be rendered benign. One such material is the sewage sludge that was the focus of the current project. Sewage sludge can tend to accumulate heavy metals and other persistent toxic compounds resultant from industrial discharge and commercial activities [218]. The toxic content of sewage sludge can limit its reuse, however with carbonization it is possible to reuse this otherwise accumulating waste. The development of adsorbents from toxic refuse is a novel field that will continue to grow, however even at this early stage has yielded some interesting precursor materials, such as circuit boards and other electronic waste that contains heavy metals [219].

- Research into the further tailoring of adsorbents should be conducted to meet specific micropollutant removal needs. It is well-recognized that the properties of an adsorbent are determined by the pyrolysis temperature, residence time, and precursor materials [118]. The current research showed the importance of surface chemistry in adsorption.
The composition of the surface functional groups and the active sites, as well as other characteristics, such as pH, can be controlled by altering the preparation conditions. After an assessment of pollutant removal needs, an adsorbent can be tailored to maximize removal of a particular contaminant. The use of waste-based adsorbents can be beneficial in the generation of adsorbents with particular characteristics. As was seen in the current work, pharmaceuticals are a varied and complex class, and therefore their removal requires adsorbents that match. Waste-based adsorbents have an advantage over commercial carbon in that the waste precursor lends particular polarity, hydrophobicity or the presence of cations which can be tailored to specifically remove recalcitrant pollutants which were not effectively removed by traditional carbon adsorbents.

- The recycling of waste materials is an environmentally friendly technology, however the environmental and cost benefits can further be extended by regeneration of spent adsorbent materials. Regeneration has been accomplished by solvent washing [220], chemical treatment [221] or thermal treatment [89]. However, further research could be done into developing new, or improving existing regeneration methods to extend the life of an adsorbent.

- The current research indicated the degree to which pollutant behavior can be altered by the presence of additional compounds. As the simultaneous existence of multiple contaminants represents a realistic challenge faced by waste water plants, there is a need to better understand the alterations in pollutant behavior brought on by the competition for adsorption sites. If the competitive interactions were better understood, it would be possible to more effectively apply adsorption technology. Currently there is a gap in knowledge in this area, and future research should include this area of focus.
Bibliography


