Clay–starch combination for micropollutants removal from wastewater treatment plant effluent

M. F. Mohd Amin, S. G. J. Heijman and L. C. Rietveld

ABSTRACT

In this study, a new, more effective and cost-effective treatment alternative is investigated for the removal of pharmaceuticals from wastewater treatment plant effluent (WWTP-eff). The potential of combining clay with biodegradable polymeric flocculants is further highlighted. Flocculation is viewed as the best method to get the optimum outcome from clay. In addition, flocculation with cationic starch increases the biodegradability and cost of the treatment. Clay is naturally abundantly available and relatively inexpensive compared to conventional adsorbents. Experimental studies were carried out with existing naturally occurring pharmaceutical concentrations found and measured in WWTP-eff with atrazine spiking for comparison between the demineralised water and WWTP-eff matrix. Around 70% of the total measured pharmaceutical compounds were removable by the clay–starch combination. The effect of clay with and without starch addition was also highlighted.

Key words | atrazine, clay, flocculations, micropollutant, pharmaceuticals, starch

INTRODUCTION

During the last two decades, interest in the adsorption of polyelectrolytes on clay surfaces for enhanced removal of pharmaceuticals has grown (Radian & Mishael 2012). For example, Churchman (2002) demonstrated the removal of toluene by polystyrene-montmorillonite (MMT) composites. Radian & Mishael (2012) showed that, at high loadings with polydiallyldimethylammonium chloride on MMT, the composite is positively charged, promoting the binding of anionic herbicides. A recent study reported the advantages of composites of poly-4-vinylpyridine-co-styrene and MMT over polydiallyldimethylammonium chloride–MMT composites and activated carbon in the removal of atrazine from synthetic water, even in the presence of spiked dissolved organic matter (Zadaka et al. 2009).

The combination of activated carbon, clays and polymers could therefore play an important role in the removal of pharmaceuticals (Zhao & Vance 1998; Beall 2003; Jiang & Zeng 2003; Dabrowski et al. 2005; Gonen & Rytwo 2006; Ganigar et al. 2010). The application of polymers alone for the purpose of pharmaceutical removal does not have a significant effect (Virkutyte et al. 2010; Huerta-Fontela et al. 2011). The use of clays in particular is advantageous due to their characteristics such as a large specific surface area and cation exchange capacity, and also the low costs, low toxicity and environmental friendliness (Site 2001; Beall 2005; Gonen & Rytwo 2006; Ganigar et al. 2010).

In addition, clay, such as smectite (SME), can act as a coagulant aid and is suitable to be used in wastewater treatment before floc formation with polymer flocculants. Moreover, the enhanced removal of other wastewater parameters (total suspended solids (TSS), chemical oxygen demand (COD), etc.) by the combination of clay and polymer is well documented (Pan et al. 2009; Rytwo 2012; Mohd Amin et al. 2015). This natural ability of the clay, combined with the ability to act as a pharmaceutical adsorbent, is a value-added advantage in reducing the treatment costs. The pharmaceutical adsorption to the clays is influenced by various water quality parameters such as organic matter and particle concentrations in wastewaters. Characteristics such as the exchangeable cations, the distance between the clay mineral layers, and the existence of water molecules between the layers could contribute to the adsorption capacity (Lee 1990; Site 2001; Rytwo 2012). It is expected that pharmaceutical removal mechanisms via hydrophobicity adsorption and charge are predominant with the use of clay (Sotelo et al. 2013; Mohd Amin et al. 2014b). In wastewater matrices, the hydrophobicity-based sorption of
pharmaceuticals is best represented by a solid–water distribution coefficient \( (K_d) \), as it reflects the interaction with the matrix’s conditions (Ternes et al. 2004; Carballa et al. 2004, 2008; de Ridder et al. 2010; Hörsing et al. 2011; Jelic et al. 2011). The sorption of a pharmaceutical onto sediments or sludge as given by its \( K_d \) value, as is shown in Equation (1), has been found to be strongly related to the properties of the sludge and the compound under consideration (Ternes et al. 2004; Carballa et al. 2004, 2008; de Ridder et al. 2010; Hörsing et al. 2011; Jelic et al. 2011).

\[
K_d (L/kg) = \frac{Cs}{Cw}
\]

(1)

where \( Cs \): concentration of pharmaceutical in the sediments or sludge (\( \mu g/kg \)), \( Cw \): concentration of pharmaceutical in dissolved phase (\( \mu g/L \)).

Furthermore, SME has a high cationic exchange capacity (80–150 meq/100 g, in Table 1) and has the ability to attract opposite charges due to its negative surface (Mohd Amin et al. 2014b, 2014c). The addition of a cationic charged polymer such as cationic starch (CS) was expected to provide a positive charge zone. The combination with a polymer is expected to enhance the pharmaceutical removal via this mechanism through the creation of a diffusion layer that can benefit the adsorption of weakly charged or neutral pharmaceuticals (Fleer et al. 1993; Mohd Amin et al. 2014a). Relatively few studies are available on the clay or clay–polymer combination as sorbents for organic pollutants in wastewater (Breen 1999; Churchman 2002; Zadaka et al. 2009). Breen (1999) examined the use of clays as sorbents for organic pollutants and studied the influence of layer charge on pollutant sorption capacity. Churchman (2002) reports on the formation of the polycation–clay combination and its use as a sorbent for non-ionic and anionic pollutants. In addition, studies regarding the use of a clay and biodegradable polymer combination are scarce and its biodegradable capability needs to be investigated (Mohd Amin et al. 2014b). The application of a clay–polymer combination treatment on the natural presence of pharmaceuticals in wastewater treatment plant effluent (WWTP-eff) will provide valuable information regarding optimal treatment conditions including the type and extent of pharmaceutical removal. In addition, removal comparisons of atrazine as a model compound in different types of water matrices (demineralised and wastewater treatment plant effluent (WWTP-eff)) should provide insight into the competition with other organic compounds that are present in wastewater.

The present study was designed as a continuation of a previous study (Mohd Amin et al. 2015) to determine the ability of a combination of SME with CS as a biodegradable polymer in reducing atrazine. In the previous study, a combination of 40 mg/L SME with 20 mg/L CS was viewed as sufficient for the removal of atrazine (80%) in demineralised water. The efficient flocculation by the addition of CS increased the settling of SME and simultaneously increased atrazine removal from the demineralised water. The application of higher dosages did not improve the total atrazine removal. This paper focuses on the efficiency and pharmaceutical removal ability of the developed SME-CS combination method in WWTP-eff. The SME-CS combination method will be tested for its ability and limitation on the model compound (atrazine) removal in the natural presence of particles, organic compounds and pharmaceuticals in the WWTP-eff matrix. The model compound removal performance in WWTP-eff also will be compared to the result from demineralised water. The matrix effect of SME with and without the addition of CS is also reported, to highlight the significance of the combination. Removals of pharmaceuticals and compounds such as caffeine that are naturally found in the WWTP-eff are afterwards highlighted.

**MATERIALS AND METHODS**

Experimental studies were carried out with SME supplied by Tolsa Group (Spain) through Keyser & Mackay (The Netherlands). The SME clay consists of an approximately 1–4 nm thick surface layer and has a total size around <1–5 µm. In addition, NaI cationic starch EX10704 was used and obtained from Nalco Netherlands BV. Atrazine (PESTANAL®, analytical standard) and analytical grade methyl tertiary butyl ether (MTBE) for gas chromatograph measurements, and analytical grade methanol for the solid phase extraction (SPE) column elution method, were purchased.

### Table 1 | Properties of clays used in this study

<table>
<thead>
<tr>
<th>Clay mineralogy</th>
<th>Commercial name</th>
<th>Composition</th>
<th>Surface area (m²/g)</th>
<th>Cations exchange capacity (meq/100 g)</th>
<th>pH</th>
<th>Bulk density (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smectite (SME)</td>
<td>Minclear N100</td>
<td>Hydrous magnesium silicate</td>
<td>200–800</td>
<td>80–150</td>
<td>~8.6</td>
<td>500–600</td>
</tr>
</tbody>
</table>
from Sigma-Aldrich. Properties of the clay and the polymer are listed in Tables 1 and 2. A Whatman Spartan 30/0.45 RC syringe filter (0.45 μm) which was used to filter the sample was purchased from Whatman (UK) for pre-treatment of the samples.

**Wastewater**

The effluent wastewater used in this work was collected from a WWTP located in Leiden Noord (Zuid-Holland, The Netherlands). The WWTP treats the water of the approximate equivalent of 156,000 inhabitants from the centre of Leiden. The average daily flow is about 24,000 m³. At the WWTP, removal of coarse solids takes place, followed by nitrification and denitrification combined with chemical and biological phosphorous removal and finally sedimentation. The main characteristics of the wastewater effluent are: TSS, 100–400 mg/L; COD, 350–500 mg/L; biological oxygen demand, 156.8 mg/L; N-total, 44.5–56 mg/L; P-total, 8.28–9.0 mg/L.

**Compounds**

Atrazine, average concentration of 419 ng/L, was added to the master sample as a reference compound for a comparative study on the performance of clay–starch on the removal of atrazine (demineralised water and WWTP-eff). The properties of the spiked atrazine and other measured pharmaceuticals present in the WWTP-eff, without spiking, are shown in Tables 3 and 4. Caffeine was also included and measured due to it being commonly found in numerous WWTPs (Buerge et al. 2003). The WWTP-eff sample was purposely collected at the secondary clarifier before the sand filtration unit, as highlighted in Figure 1, to reduce the influence of excessive particles that are present in the influent of the WWTP, in order to study the effect of SME-CS combination on the pharmaceuticals.

**Atrazine and pharmaceutical removal by clay flocculation with cationic starch**

The experiments were carried out in batches using a pyrolysed 2,000 mL Duran brown glass bottle. The clay with a concentration range of 10 to 60 mg/L was first dosed to allow for adsorption of the atrazine and pharmaceuticals over 24 h. This was to ensure that equilibrium between atrazine and the pharmaceuticals and the clay was reached. Then the CS with a concentration of 20 mg/L was added and slowly mixed at 40 rotations per minute for 2 h before allowing it to settle for 1 h. All the experiments were carried out at neutral pH (7 ± 0.3). Samples were taken, filtered with a syringe filter (0.45 μm) and prepared for analysis.

**Analytical methods**

Standard wastewater parameters were analysed according to Standard Methods (American Public Health Association 1999).

**Analysis of atrazine with gas chromatography**

The atrazine concentrations were analysed by gas chromatography (Agilent's 7890A) based on the US Environmental

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**Table 2 | Properties of polymer used in this study (with common structure)**

<table>
<thead>
<tr>
<th>Product</th>
<th>Description</th>
<th>Form</th>
<th>Solubility (in water)</th>
<th>Ionic character</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nalco Starch EX10704 (CS)</td>
<td>Modified starch</td>
<td>Flaked solid</td>
<td>Soluble</td>
<td>Cationic</td>
<td>10⁶–10⁸</td>
</tr>
</tbody>
</table>

**Table 3 | Spiked atrazine properties**

<table>
<thead>
<tr>
<th>Charge</th>
<th>Compound</th>
<th>Formula</th>
<th>pKₐ</th>
<th>MW (g/mol)</th>
<th>Log Kₐ (pH 7.4)</th>
<th>Log K₂₀₀ (mean)</th>
<th>Average initial concentration (ng/L)</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral</td>
<td>Atrazine</td>
<td>C₉H₁₄ClN₅</td>
<td>2.27 (base)</td>
<td>215.7</td>
<td>2.63</td>
<td>2.20</td>
<td>419</td>
<td>95</td>
</tr>
</tbody>
</table>

MW, molecular weight; pKₐ, acid dissociation constant; Log K₂₀₀, octanol–water partition coefficient; Log Kₐ, solid–water distribution coefficient.
Protection Agency 551.1 (1995) method. Atrazine in the sample was extracted using liquid–liquid micro-extraction with MTBE as a solvent. The injection sample was 1 mL of the extracted sample. A volume of 2 μL was injected in splitless mode and the injector temperature was 200 °C. The carrier gas was helium (linear velocity was 33 cm/s). The injector temperature was 260 °C. The oven temperature was held at 35 °C for 9 min, and then raised by 15 °C/min to 225 °C. The 225 °C was held for 10 min before being raised by 20 °C/min to 260 °C. The recovery of atrazine was in the range of 90–110%.

### Analysis of pharmaceuticals with UPLC-MS/MS

Pharmaceutical analyses were performed according to Houtman et al. (2015). In short, 10 mL volumes of effluent were diluted 10 times with demineralised water, sand filtered, extracted with SPE (Oasis HLB; 200 mg, 6 cc, 30 μm, Waters) and then eluted with methanol. Extracts were evaporated to 100 μL to which 1 mL MilliQ water was added. The pharmaceuticals were analysed using an ultra performance liquid chromatograph (Waters Acquity).
equipped with a quaternary pump and combined with a Quattro Xevo triple quadrupole mass selective detector (Waters Micromass) with electrospray ionisation. Quantification of the target compounds was performed using an external calibration series of seven concentrations of a stock solution of standards dissolved in MilliQ. Depending on the sensitivity in the mass spectrometry, the individual compounds were included in the stock solution at a low, middle or high concentration (ratio 1:5:30). Concentrations in the calibration series ranged between 1.25, 6.25, and 38 ng/L, for the lowest standard, and 200, 1,000, and 6,000 ng/L, for the highest standard. To compensate for losses during the SPE, the standards were extracted with the same procedure as for the samples.

Recovery of the pharmaceuticals from the WWTP-eff was assessed by analysing the WWTP-eff both unspiked and spiked (and both in two-fold) with standard pharmaceuticals at a concentration of 100, 500 or 3,000 ng/L and substraction from the concentration in the unspiked WWTP-eff. The analysis method contained 43 pharmaceuticals. In the selection, 11 of the top 20 of the most sold pharmaceuticals were included (Buerge et al. 2005; Houtman et al. 2013). Other selection criteria were previous detection, ecotoxicological relevance (e.g. cytostatics, antibiotics and non-steroidal anti-inflammatory drugs), and representation of different therapeutic classes. For all the compounds, a minimum reporting limit was set at 5 ng/L or lower. Table 4 shows the concentrations of the pharmaceuticals selected and measured during the sampling. Recovery of the selected pharmaceuticals was in the range of 40–172%.

RESULTS AND DISCUSSION

Concentrations of pharmaceuticals in the secondary clarifier

The measured concentrations of the pharmaceuticals taken from the secondary clarifier is shown in Table 4. The negatively charged compounds were detected in the range 0.1–47 ng/L. The highest concentration was measured for salicylic acid (47 ng/L) while the lowest concentration was for clofibric acid (0.4 ng/L). For the positively charged compounds, sotalol was quantified with a concentration of 386 ng/L whereas theophylline was the lowest measured at 3.8 ng/L. Regarding the neutral compounds, carbamazepine was the compound with the highest concentration (108 ng/L), while fenofibraat had the lowest concentration (8.7 ng/L).

The obtained concentrations were relatively low if compared to a study done by Rosal et al. (2010). However, the measurement results in Table 4 were in the range of reported occurrences in wastewater across the Netherlands (Schrap et al. 2005). The measured concentrations were also in agreement with the concentrations reported by Zorita et al. (2009).

Atrazine removal

The SME-CS combination was examined for the removal of atrazine from demineralised water and WWTP-eff. The removal of atrazine, by a combination of 20 mg/L CS and a range of SME dosages (0–60 mg/L) with initial concentrations of 500 ± 200 ng/L in the WWTP-eff, is shown in Figure 2. The atrazine removal in the WWTP-eff matrix was 5–65%. The 20 mg/L CS dosage was viewed as sufficient for atrazine removal, which was observed in a previous study (in demineralised water (Mohd Amin et al. 2013)). Compared to WWTP-eff, the removal of atrazine in demineralised water showed a higher removal range (6–85%). It can be expected that competition for attachment sites on the SME surface between other organic pollutants caused the decline in removal efficiency. Moreover, in demineralised water, a high removal can be predicted due to the attachment of CS, which covers the entire clay surface during adsorption of the polymer to the clay, thus creating a diffusion layer that enhances atrazine removal (Fleer et al. 1993; Mohd Amin et al. 2014a). However, this mechanism is expected to be limited in wastewater due to the limited availability of a diffusion layer caused by interference with other particles in the WWTP-eff.

Effect of SME with and without CS dosage on pharmaceutical removal

The relative removal performance of selected pharmaceuticals by the addition of 60 mg/L SME with and without the
addition of CS was compared. From Figure 3, it can be concluded that the application of SME without CS already showed its effectiveness in comparison to the only CS sample. High removal percentage of pravastatin and fenofibrate (66% and 32%, respectively) without the addition of CS demonstrated the ability of the SME surface to adsorb these pharmaceuticals. The addition of CS had the effect on the removability of the compounds; especially removal of atrazine, pravastatin, sotalol and trimethoprim, was further enhanced. However, for compounds such as iopromide and fenofibrate, the addition of CS did not show a change in the removability. The detailed explanations on SME and CS combination are given in the ‘Introduction’.

Wastewater pharmaceutical removal

Removal by SME dosage range 0–60 mg/L

Table 5 shows the removal efficiencies of pharmaceuticals in WWTP-eff with an SME dosage range of 0–60 mg/L and at a fixed CS concentration of 20 mg/L. Generally, for almost all of the compounds the removal increased with a higher SME dosage. Only naproxen and iopromide showed a fluctuating removal percentage. The rest of the compounds listed in Table 4 that were omitted in Table 5 were either not distinctively removed or had a negative removal. The negative removal of some compounds could be attributed to an increase in the concentration of an analysed parent compound. Similar occurrences were reported by several studies (Joss et al. 2005; Wick et al. 2009; Jelic et al. 2011).

Figure 4 shows the pharmaceutical removal based on the Log $K_d$ value. The pharmaceuticals are also arranged by category based on their charge group (in brackets). The pharmaceuticals are expected to be removed by adsorption, mainly due to their hydrophobic property, which is represented by Log $K_d$. The negatively charged pharmaceuticals show a better removal percentage compared to the neutral and positively charged pharmaceuticals. Pravastatin, clofibric acid and ibuprofen had >99% removal with an SME dosage of 20 mg/L despite having a Log $K_d$ value ≤0.8. The high removability could be expected because of charge attraction to the positive charge of the CS polymer adsorbed on the

<table>
<thead>
<tr>
<th>Charge</th>
<th>Micropollutant</th>
<th>Log $K_d$ (pH 7.4)</th>
<th>0</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Negative</td>
<td>Atorvastatin</td>
<td>1.03</td>
<td>0</td>
<td>2</td>
<td>20</td>
<td>75</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Clofibric acid</td>
<td>−0.9</td>
<td>0</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Diclofenac</td>
<td>0.95</td>
<td>2</td>
<td>9</td>
<td>15</td>
<td>50</td>
<td>54</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>Ibuprofen</td>
<td>0.8</td>
<td>7</td>
<td>36</td>
<td>49</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Naproxen</td>
<td>0.47</td>
<td>2</td>
<td>15</td>
<td>10</td>
<td>0</td>
<td>22</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Pravastatin</td>
<td>−1.73</td>
<td>0</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Neutral</td>
<td>Caffeine</td>
<td>−0.13</td>
<td>10</td>
<td>67</td>
<td>67</td>
<td>66</td>
<td>69</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>Fenofibrat</td>
<td>4.8</td>
<td>33</td>
<td>50</td>
<td>53</td>
<td>62</td>
<td>61</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>Tiamulin</td>
<td>3.65</td>
<td>14</td>
<td>69</td>
<td>64</td>
<td>73</td>
<td>76</td>
<td>74</td>
</tr>
<tr>
<td>Positive</td>
<td>Atenolol</td>
<td>−1.99</td>
<td>0</td>
<td>15</td>
<td>15</td>
<td>18</td>
<td>26</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Iopromide</td>
<td>−2.95</td>
<td>6</td>
<td>5</td>
<td>4</td>
<td>2</td>
<td>15</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Metformin</td>
<td>−4.3</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>5</td>
<td>12</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>Metoprolol</td>
<td>−0.31</td>
<td>1</td>
<td>0</td>
<td>14</td>
<td>29</td>
<td>58</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>Paroxetine</td>
<td>1.67</td>
<td>35</td>
<td>65</td>
<td>70</td>
<td>75</td>
<td>88</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>Propranolol</td>
<td>0.98</td>
<td>1</td>
<td>2</td>
<td>12</td>
<td>24</td>
<td>51</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>Sotalol</td>
<td>−1.61</td>
<td>0</td>
<td>7</td>
<td>0</td>
<td>7</td>
<td>9</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>Trimetoprimer</td>
<td>0.67</td>
<td>33</td>
<td>55</td>
<td>60</td>
<td>63</td>
<td>69</td>
<td>72</td>
</tr>
</tbody>
</table>
clay. Pharmaceuticals such as diclofenac (0.95) and atorvastatin (1.03) were not affected by having a slightly higher Log $K_d$ value, which could be caused by other factors, such as compound structure and adsorption competitions. A similar occurrence was also reported by Carballa et al. (2004, 2005, 2008), Ternes (1998), Ternes et al. (2004), Zhang et al. (2008), Hörsing et al. (2011) and Jelic et al. (2011).

For the positively charged pharmaceuticals, an increase in removal can be seen with a higher Log $K_d$. For the lower Log $K_d$ pharmaceuticals, the adsorption of the compounds such as iopromide and metformin was influenced by the repulsion of the compound towards the SME-CS surface, which translated to a low removal (Sawhney & Singh 1997; Lemić et al. 2006; Sánchez-Martín et al. 2006; Mohd Amin et al. 2014a; Mohd Amin et al. 2015). Removal via hydrophobicity of these compounds did not have an effect due to low Log $K_d$ values. For pharmaceuticals such as trimethoprim and paroxetine with higher Log $K_d$, the hydrophobicity was indeed expected to be more dominant, resulting in a better removal (Heberer 2002; Jelic et al. 2011). Neutral pharmaceuticals showed a removal in between the charged compounds (>60%), which could be expected mainly due to the Log $K_d$ values (Heberer 2002; Carballa et al. 2004; Jelic et al. 2011). An exception is caffeine. Approximately 66% of caffeine was removed at 20 mg/L SME (Figure 4), which increased to 87% at 60 mg/L SME dosage (Table 5). Caffeine has a low Log $K_d$ value of −0.13 and theoretically is not predicted to adsorb to particles in wastewater (Buerge et al. 2003; Thomas & Foster 2005; Loos et al. 2009). However, Sotelo et al. (2013) suggested that the adsorption of caffeine to clay (sepiolite) could be caused by diffusion to the boundary layer of the clay.

Compounds such as gemfibrozil, naproxen, and carbamazepine are not removed even though they have a high Log $K_d$ value. They are widely reported in various WWTPs for no removal or a low removal percentage (Ternes 1998; Stumpf et al. 1999; Carballa et al. 2005; Mohd Amin et al. 2014b).

CONCLUSION

The present study was designed to determine the ability of SME in combination with CS to reduce spiked atrazine and other pharmaceuticals that are present in wastewater. Ranges of SME dosages are applied to determine the extent of the compound’s removal within the limit of feasible application in WWTPs. A combination of SME and CS was used to study the effect of polymers on the clays in increasing the removal of pharmaceuticals in wastewater.

The removal of atrazine by the SME-CS combination showed a large drop, around 30–40%, in performance in WWTP-eff compared to demineralised water with the highest achieved removal of 65% at 60 mg/L SME. In general, most of the measured pharmaceutical removal is influenced by its Log $K_d$ value. The rest of the pharmaceutical removal
was either affected by the charge or not removed. The neutral or weakly charged pharmaceuticals are expected to be removed by adsorption. It is also expected that the pharmaceutical removal through this mechanism will be limited, due to polymer attachment to other particles in the wastewater, reducing the removal percentage in wastewater when compared to the removal percentage from demineralised water. Around 70% of the measured pharmaceuticals were removable by SME-CS. The rest of the compounds (30%) showed insignificant or negative removal.

The efficient flocculation by the addition of CS increased the settling of SME and particles present in WWTP-eff and simultaneously increased the pharmaceutical removal from the water. It was observed that dosages of 40 mg/L SME with 20 mg/L CS were sufficient for most of the removable pharmaceuticals.

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