Clay-biodegradable polymer combination for pollutant removal from water

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Abstract

In this study, a new treatment alternative is investigated to remove micropollutants from wastewater effectively and in a more cost-effective way. A potential solution is the use of clay in combination with biodegradable polymeric flocculants. Flocculation is viewed as the best method to get the optimum outcome from the combination of clay with starch. Clay is naturally abundantly available and relatively inexpensive compared to the conventional adsorbents used. Experimental studies were carried out with four different clays to select the best clay for further optimisation. The atrazine removal achieved is in the range of 10–99% based on the clay concentration of 10–50 g L$^{-1}$. Optimisation of the best clay performer leads towards atrazine reduction of > 99% with a dosage of 100 mg L$^{-1}$. The best and underperforming clays were then tested in other experiments with the addition of cationic starch flocculants. In this experiment, the addition of a polymer increased the atrazine removal for the underperforming clay to 46% with only 10 mg L$^{-1}$ clay dosages. The clay flocculation test was also performed to test the flocculation efficiency of clays by the polymer. Approximately 80–84% of the clay is flocculated, which shows exceptional flocculation efficiency in removing both clays and atrazine from the water matrices.

1 Introduction

The wastewater chain is an important source of priority substances into the surface water system and is, therefore, one of the bottlenecks in achieving the European Water Framework Directive objectives (Directive 2001/83/EC, amended by Directive 2004/27/EC (for human pharmaceuticals), and Directive 2001/82/EC, amended by 2004/28/EC (for veterinary pharmaceuticals). At various locations in the Netherlands the standards for priority substances are exceeded. The current concern in detecting these micropollutants in receiving waters may call for new approaches in wastewater treatment (Mohd Amin, 2015). The introduction of an economical and effective method
in removing these compounds from wastewater is therefore crucial (Virkutyte et al., 2010).

The availability of advanced treatment methods has improved the removal of these micropollutants from wastewater and existing conventional wastewater treatments can be upgraded (Ternes, 1998; Stumpf et al., 1999; Heberer, 2002). However, such treatment is often costly. A potential low-cost solution is the use of natural substances for micropollutant removal (Radian and Mishael, 2012), such as clay in combination with biodegradable polymeric flocculants. The application of biodegradable polymers such as cationic starch (CS) to flocculate particles during treatment has the additional advantage of being shear resistant (Singh et al., 2000).

In the last few decades, interest in the adsorption of polyelectrolytes on clay surfaces for enhanced removal of pollutants has grown (Ternes, 1998; Singh et al., 2000). For example, Churchman (2002) demonstrated the removal of toluene by polystyrene–montmorillonite (MMT) composites. Radian and Mishael (2012) showed that, at high loadings of PDADMAC on MMT, the composite is positively charged, promoting the binding of anionic herbicides. In a recent study, the advantages of composites of poly-4-vinylpyridine-co-styrene (PVPcoS) and MMT for the removal of atrazine from water, even in the presence of dissolved organic matter (DOM), were reported (Zadaka et al., 2009).

The combination of clays and polymers can be viewed as a symbiosis interaction, because organic micro-pollutant absorbing clays need to be settled to avoid being flushed out. For that, the dosage of a cationic polymer can be beneficial due to its ability in particle removal (Van Nieuwenhuijzen, 2002). Cationic polymers have also been proven to be efficient in e.g. atrazine reduction from water matrixes, but it requires attachment to a negatively charged surface (Mohd Amin et al., 2014a). The combination of cationic polymers with clays is thus hypothesised to enhance the micro-pollutant reduction by creating a diffuse zone (Eslinger and Pevear, 1988; Mohd Amin et al., 2014c).

Clay such as smectite has a high cationic exchange capacity (80–150 meq (100 g)−1) and can also act as a coagulant aid in wastewater treatment for destabilisation of the
other particles in water before floc formation with polymeric flocculants occurs (Sawhney and Singh, 1997; Mohd Amin et al., 2014b). This paper reports on the direct interaction between clays and a CS with atrazine as a model compound in demineralised water. Four different types of clay were compared and the best performer was selected for optimisation. The flocculation aspect of the clays with CS was also examined in order to find the combined dosage for optimal performance.

2 Material and methods

Experimental studies were carried out with four different clays, which were selected based on their different properties. The attapulgite (ATT), smectite (SME), and sepiolite (SEP) were supplied by Tolsa Group (Spain) through Keyser & Mackay (the Netherlands) while Na-Bentonite (BEN) was purchased from Sigma-Aldrich. All the clays consist of a ∼ 1–4 nm thick surface layer and are around ∼ < 1–5 µm-sized. The Nalco cationic starch EX10704 was used and obtained from Nalco Netherlands BV. Atrazine (PESTANAL®, analytical standard) and analytical grade methyl tertiary butyl ether for gas chromatography measurements were purchased from Sigma-Aldrich. Properties of the clays and the polymer are listed in Tables 1 and 2. Demineralised water was obtained from tap water that was treated with reverse osmosis and ion exchange. Whatman Spartan 30/0.45 RC syringe filters (0.45 µm, Whatman UK) were used to filter the samples as pre-treatment.

2.1 Clay selection and optimisation

Clay selection experiments were prepared by adding a range of clay dosages (0–50 gL⁻¹) to a 200 mL solution with a concentration of 6 ± 2 µgL⁻¹ atrazine in a 500 mL Duran glass bottle. The solutions with the clay were stirred at 40 rpm for 24 h before settling took place for 2 h. After the experiment, the solution was filtered with the sy-
ringe filter (0.45 µm). The collected samples were, after filtration, pre-treated before being analysed for atrazine residues.

The best clay (i.e. SME) from the first experiment was optimised for low dosages to adsorb an initial atrazine concentration of \(2 \pm 0.2 \, \text{µg} \, \text{L}^{-1}\) (normally found in wastewater). The solutions with the clay were stirred at 40 rpm for 8 h before settling took place for 1 h. The rest of the procedure was similar as aforementioned.

### 2.2 Clay flocculation with cationic starch

The clay (SME, ATT) combination with CS was studied to determine the effect on atrazine reduction. The experiments were carried out in a pyrolysed 2000 mL Duran glass bottle. Both clays in concentrations in the range 0–120 mg L\(^{-1}\) (based on previous optimisation experiments) were first dosed to adsorb the atrazine (initial concentration of \(2 \pm 0.2 \, \text{µg} \, \text{L}^{-1}\)) for 8 h. For ATT the adsorption time applied was 24 h, to ensure that equilibrium between atrazine and the clays was reached before flocculation. Then the CS with a concentration of 20 mg L\(^{-1}\) was added and mixed slowly at 40 rpm for 2 h before settling for 1 h. Extended agitation was applied to produce smaller flocs resulting in a higher surface availability especially for atrazine removal by ATT. Samples were taken, filtered with the syringe filter (0.45 µm) and analysed.

ATT in combination with CS was further tested with different starch concentrations (10, 20, 40, 60 mg L\(^{-1}\)) to prove that the atrazine reduction is enhanced by the starch concentration. The experimental procedure was similar as aforementioned.

### 2.3 SME-CS: atrazine removal, flocculant dosage and turbidity relation

The objective of this experiment was to further optimise the flocculation of the clays with CS. The flocculation experiments of the SME using CS (no atrazine added) were carried out in jar test equipment filled with demineralised water (1.8 L). All the jars contain four baffles to increase the energy gradient during stirring. Figure 1 illustrates the specific relationship between the energy gradient (\(G\) value) and the rpm of the
stirrers for this jar tester. The clay dosage used in this experiment was in the range of 0–100 mg L⁻¹ and the CS concentration was fixed at 20 mg L⁻¹. Dosing of the CS was conducted at a stirring velocity of 300 rpm. After a mixing time of 30 s, the stirring velocity was reduced to 40 rpm for 10 min. During this period, floc formation took place. All the jars were observed visually, and after a settling time of 20 min, samples were taken for analysis. Turbidity was measured using a Hach DR5000 spectrophotometer according to APHA (1999) standard methods.

The settled and suspended clay is measured based on the turbidity level of SME from 0–40 mg L⁻¹ dosage based on Fig. 2. The turbidity measurement will be taken after each of the settling periods. The turbidity reading will then be compared to the reading in Fig. 2 in order to determine the SME dosage. This measured SME dosage represents the suspended SME in the water matrix. The rest of the SME in the water matrices will have settled.

The atrazine concentration is determined by calculating the removal from the blank sample (quadruplicate) of SME (40 mg L⁻¹) and atrazine without any polymer addition. On average, 82 % of atrazine is removed and the final turbidity after settling is approximately 5.5 NTU. The turbidity value was used for the determination of SME concentration based on Fig. 2. Based on this turbidity reading and Fig. 2, it can be deduced that 35 mg L⁻¹ is suspended in the water matrixes. The rest of the 5 mg L⁻¹ of SME is expected to settle. With this information, the amount of atrazine attached to the settle clay can be calculated based on Eq. (1).

\[(A/B) \cdot 82\% = C(\%) \tag{1}\]

Where:

- \(A\) : the settled clay concentration
- \(B\) : total concentration of clay
- \(C\) : percentage of atrazine removed by settled clay
The rest of the sample and replicate were measured and calculated based on this equation. The atrazine removal percentage in the solution is the remainder that is removable by clay.

**2.4 Analytical methods**

The atrazine concentrations ($2 \pm 0.2 \mu g L^{-1}$) were analysed by gas chromatography (Agilent’s 7890A) based on the U.S. Environmental 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$^{-1}$). The injector temperature was 260°C. The oven temperature was held at 35°C for 9 min, and then raised at 15°C min$^{-1}$ intervals to 225°C. The temperature of 225°C was held for 10 min before being raised at 20°C min$^{-1}$ intervals to 260°C. The recovery of atrazine was in the range of 90–110%.

**3 Results and discussion**

**3.1 Clay selection and maximising the adsorption of atrazine on clay**

The reduction of atrazine, with initial concentrations of $6 \pm 0.2 \mu g L^{-1}$, for four different clays dosed in the range of 0–50 g L$^{-1}$ is shown in Fig. 3. Atrazine reduction from the water was in the range of 10–99% for three out of the four selected clays. There was no reduction achieved with BEN. BEN has a hydrophilic surface, which attracts water molecules for attachment due to the presence of sodium ions thus limiting the interaction with atrazine. For ATT, atrazine reduction was increased only at dosages larger than 5 g L$^{-1}$ and reached a maximum of 40% at 50 g L$^{-1}$. It is reported that the surface charge of ATT is approximately negative to neutral (White and Hem, 1983), which led to a low atrazine affinity at dosages lower than 5 g L$^{-1}$. This is supported by the...
low cation exchange capacity (CEC) value of ATT being around 20–30 meq(100 g)\(^{-1}\). Similar observations were also reported by Haden (1961). SEP showed a constant increase in removal, with 10 % atrazine reduction at a clay dosage of 0.05 g L\(^{-1}\) to > 99 % at a dosage of 25 g L\(^{-1}\). The ability of SEP in adsorbing organic compounds has previously been reported by Rytwo (2012). SME showed the highest affinity to atrazine removal with reductions > 99 % at dosages lower than 1 g L\(^{-1}\). SME has the highest specific surface area (200–800 m\(^2\) g\(^{-1}\)) and the highest CEC (80–150 meq(100 g)\(^{-1}\)) value compared to the other three clays. It was also reported that SME can adsorb other compounds, such as carbamazepine (Zhang et al., 2010) and naphthalene and phenanthrene (Lee et al., 2004). SME was thus viewed as the most suitable clay for further investigation.

The SME as the best clay and ATT as the low performer reference clays were further tested for optimal dosages in atrazine (initial 2 ± 0.2 µg L\(^{-1}\)) adsorption. In this experiment, more than 86 % atrazine was removed using 60 mg L\(^{-1}\) SME and this reached a maximum of > 99 % at dosages up to 100 mg L\(^{-1}\). Therefore, we limited the dosage in the following experiment to clay dosages below 100 mg L\(^{-1}\).

### 3.2 Clay flocculation with cationic starch

Atrazine reduction from water with SME was 45–99 % before the addition of CS. After the CS addition, the reduction increased at low clay dosages (Fig. 4). The largest effect of the CS addition in enhancing the atrazine reduction was observed at SME dosages of 10–40 mg L\(^{-1}\). The high reduction is expected to be due to the attachment of CS that covers the entire clay surface during floc formation, thus creating a diffuse zone that is able to trap atrazine (Mohd Amin et al., 2014a). At an SME dosage higher than 40 mg L\(^{-1}\), the clay’s own ability in adsorbing the atrazine predominates, thus resulting in a higher removal than without the addition of CS. The ATT alone did not have much ability in reducing the atrazine concentration at low dosages as shown in Fig. 3. However, after the addition of CS, the atrazine reduction was considerably increased,
specifically for the 10 mgL$^{-1}$ clay dosage with an atrazine reduction of 45%. The reduction percentage decreased with the clay dosage increments, to 7.5% at a dosage of 120 mgL$^{-1}$. At a lower clay dosage (10 mgL$^{-1}$), the polymer was expected to cover the entire clay surface. With the clay dosage increment, more flocs were formed, and fewer polymer surfaces were available for atrazine attachment. At higher clay dosages, even more and larger flocs were formed, and less free surface was available which resulted into a lower removal percentage.

From Fig. 4, it is observed that the clay dosages limit the atrazine reduction by ATT. This limitation was further studied at CS concentrations from 10–60 mgL$^{-1}$ (Fig. 5). Best results were obtained at a clay dosage of 10 mgL$^{-1}$ and a CS dosage $> 20$ mgL$^{-1}$. The higher CS dosages did not have a large influence in increasing the atrazine reduction. A further increase in the ATT dosage resulted in a similar pattern. At a limited ATT concentration of 10 mgL$^{-1}$, there was high competition for CS attachment. The extent of CS attachment to the ATT layer is limited by the CS concentration, which translated into different atrazine reduction levels with different CS concentrations. It can also be that, when the ATT dosage increases, a higher surface availability results in less CS multilayer formation and thus in less atrazine diffusion, which leads to less atrazine reduction.

### 3.3 SME-CS: atrazine reduction, flocculation dosage and turbidity relation

In this experiment, the relation between CS dosage and clay is further studied to find a relation between the atrazine reduction, CS dosage and SME turbidity. Atrazine in the water matrix can be divided into three different phases after settling, suspended (adsorbed to SME but does not settle) and remaining in the solution (not adsorbing).

In Fig. 6, it can clearly be seen that the SME had a high ability in atrazine adsorption, which is reflected in the “suspended” phase. At 40 mgL$^{-1}$ without any CS, around 62% atrazine is adsorbed from the solution but suspended and not removed from the wastewater matrix. By increasing the CS dosage, the amount of settled SME that
contains atrazine increased from 10% without any CS dosage to a maximum of 77% with 30 mgL$^{-1}$ dosage. The amount of suspended SME (approximately 2.5 mgL$^{-1}$) was at the lowest at 40 mgL$^{-1}$ CS, which accounted for 5% atrazine removal.

Figure 6 also shows that a further increase in CS dosage did not improve the atrazine reduction although a higher settled clay percentage was observed. The maximum atrazine reduction was 82% at 30 mgL$^{-1}$ CS and was slightly reduced (80%) at higher dosages. The turbidity removal reached a maximum at 40 mgL$^{-1}$ CS with around 92% removal. However, the amount of SME settled was slightly less compared to the settled SME at 30 mgL$^{-1}$ CS dosage.

4 Conclusions

The present study was designed to determine the ability of different clays in combination with a CS to reduce atrazine in water. SME, as the best performing clay, was further optimised to lower the dosage based on atrazine concentrations regularly found in the environment. The effective SME dosage was around 20 mgL$^{-1}$ to reduce about 60% atrazine from demineralised water, and a maximum of > 90% atrazine reduction was reached with a clay dosage > 80 gL$^{-1}$. A combined dosage of SME and CS was performed to study the effect of polymers on the clay’s ability in the reduction of atrazine.

Efficient flocculation by addition of CS increases the settled SME and simultaneously increases atrazine reduction from the water. However, here 20 mgL$^{-1}$ CS dosage was viewed as sufficient for atrazine reduction through the settling of clay (72%) with around 82% of total turbidity removal. Application of higher CS dosages, although improving the turbidity removal and settling the clay, did not significantly improve the total atrazine reduction. It should be noted that the application of inorganic matter such as clay in some countries like the Netherlands is undesirable due to increased waste production, which will increase the disposal cost. However, in certain circumstances, the high sludge productions are also preferable for the production of biogas and can even be
used as fertilizer in some countries. An extended study of the applications of the clay-polymer combination in terms of its performance, reuseability, impact and economic value, is required for more accurate information.

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References


Mohd Amin, M. F.: Polymer for Micropollutants Removal from Wastewater, Delft University of Technology, Delft, 2015.


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⁻¹)</th>
<th>Cation exchange capacity (CEC) (meq (100 g)⁻¹)</th>
<th>pH</th>
<th>Bulk density (g L⁻¹)</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>
<tr>
<td>Attapulgite (ATT)</td>
<td>Minclear N300</td>
<td>Hydrated magnesium aluminium silicate</td>
<td>150</td>
<td>20–30</td>
<td>~ 9.5</td>
<td>310–430</td>
</tr>
<tr>
<td>Sepiolite (SEP)</td>
<td>Pangel s9</td>
<td>Magnesium silicate</td>
<td>~320</td>
<td>4–40</td>
<td>~ 8–9</td>
<td>30–90</td>
</tr>
<tr>
<td>Bentonite (BEN)</td>
<td>Na-Bentonite</td>
<td>Aluminium silicate</td>
<td>220–270</td>
<td>~40</td>
<td>6–9</td>
<td>600–1100</td>
</tr>
</tbody>
</table>
Table 2. Properties of the polymer used in this study.

<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 potato starch</td>
<td>Flaked solid</td>
<td>Soluble</td>
<td>Cationic</td>
<td>$10^6-10^8$</td>
</tr>
</tbody>
</table>
Figure 1. Mixing energy for the jar tester.
Figure 2. Initial turbidity mapping of SME in demineralised water based on the dosage 0–40 mg L\(^{-1}\).
Figure 3. Atrazine adsorption (initial concentration $6 \pm 0.2 \mu g L^{-1}$) by different types of clay with dosages in the range of $50 \text{mg} L^{-1}$–$50 \text{g} L^{-1}$. 
Figure 4. Atrazine reductions by combination of clay and CS (20 mgL$^{-1}$) with a dosage range of 10–100 mgL$^{-1}$; and with SME and ATT as a reference.
Figure 5. Atrazine reductions by combination of ATT and CS (10, 20, 40, 60 mg L\(^{-1}\)) with a dosage range of 10–80 mg L\(^{-1}\).
Figure 6. Atrazine reduction and turbidity removal for 40 mg L\(^{-1}\) SME with different CS dosages. Initial atrazine concentration 2 ± 0.2 µg L\(^{-1}\), initial turbidity 5.5 ± 0.2 NTU.