

in removing these compounds from wastewater is therefore crucial (Virkyute 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

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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 $\sim 1\text{--}4$ nm thick surface layer and are around $\sim < 1\text{--}5$ 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 filtrate 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-

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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 $2 \pm 0.2 \mu\text{g L}^{-1}$ (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 $2 \pm 0.2 \mu\text{g L}^{-1}$) 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

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Table 2. Properties of the polymer used in this study.

Product	Description	Form	Solubility (in water)	Ionic character	Molecular weight
Nalco Starch-EX10704 (CS)	Modified potato starch	Flaked solid	Soluble	Cationic	10^6 – 10^8

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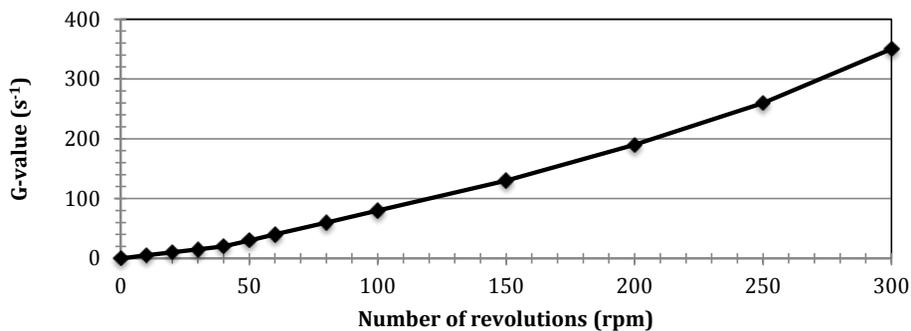


Figure 1. Mixing energy for the jar tester.

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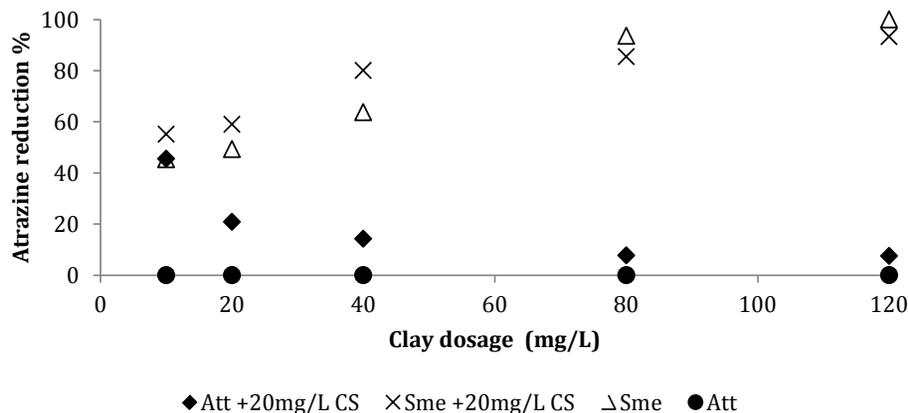


Figure 4. Atrazine reductions by combination of clay and CS (20 mg L^{-1}) with a dosage range of $10\text{--}100 \text{ mg L}^{-1}$; and with SME and ATT as a reference.

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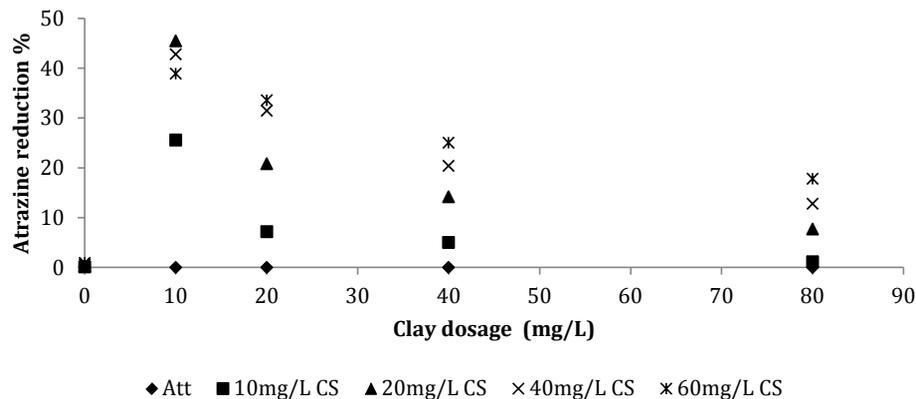


Figure 5. Atrazine reductions by combination of ATT and CS (10, 20, 40, 60 mgL⁻¹) with a dosage range of 10–80 mgL⁻¹.

