



Research paper

Pairing micropollutants and clay-composite sorbents for efficient water treatment: Filtration and modeling at a pilot scale



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ABSTRACT

Organically modified clay minerals have been widely developed, tested and employed as sorbents for organic pollutants. However, the process of pollutant-composite pairing is not commonly addressed, which would be valuable for efficient pollutant filtration by such sorbents. This study presents an approach for achieving efficient pollutant removal by large-scale composite filters, based on pairing chemically compatible pollutants and composites and by employing a predictive filtration model. The removal of three organic pollutants, simazine, sulfentrazone and diclofenac by lab-scale filtration columns containing one of three sorbents, a polymer-, micelle- or liposome-clay composite, was measured. Understanding the factors governing pollutant-organic modifier interactions enabled to pair an efficient sorbent to each pollutant. The high removal (80%) of simazine by the polymer composite, was attributed to hydrogen bonds and π - π interactions, compared to less than 20% removal by the surfactant composites. The removal of the anionic diclofenac ($pK_a = 4.1$) was mainly governed by electrostatic attraction, explaining its high removal by the most positively charge sorbent, the liposome composite. Sulfentrazone ($pK_a = 6.5$) removal was mostly affected by micellar solubilization and upon its removal, the zeta potential of the micelle-composite was not reduced as obtained for diclofenac removal. The filtration of the successful pairs was modelled to determine sorbent capacity and adsorption and desorption rate constants. The pilot filtration experiments were well described by the model and demonstrated efficient removal of paired pollutants and sorbents. Model simulations predicted promising treatment at environmental pollutant concentrations in the $\mu\text{g L}^{-1}$ range. This pairing approach along with model calculations can be a strong and valid tool for efficient pollutant-sorbent filtration.

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1. Introduction

The increase in high quality water demand along with the detection of emerging pollutants have brought about an intensification of investments in new approaches and advanced technologies for water treatment (Bixio et al., 2006; Vörösmarty et al., 2010). However, removal of pollutants by adsorption via filtration columns remains a widely used technology since it is advantageous in terms of energy, area demand and cost (Ali and Gupta, 2006). Hence, a large number of new materials have been suggested as sorbents for the treatment of emerging pollutants (Ali, 2012; Jiuhi, 2008; Savage and Diallo, 2005; Unuabonah and Taubert, 2014). In order to achieve high adsorption efficiency during filtration, a sorbent material should possess a high

specific surface area and a large concentration of adsorption sites and/or functional groups that can optimally interact with the pollutants (Qu et al., 2013).

Organically modified clay minerals have been widely developed, tested and constitute a large percent of the recently suggested sorbents (Beall, 2003; Lee and Tiwari, 2012; Unuabonah and Taubert, 2014). The sorptive properties of surfactant based clay composites (Boyd et al., 1988; Jiang et al., 2002; Rathnayake et al., 2015) and of polymer clay composites (Churchman, 2002; Liu, 2007) have been described. The use of such clay composites for the removal of inorganic pollutants (Şölenner et al., 2008), effluent dissolved organic matter (DOM) (Siebdrath et al., 2012), organic pollutants such as dyes (Margulies et al., 1988; Rytwo et al., 1995; Szabo et al., 2011), herbicides (Carrizosa et al., 2000; Cruz-Guzmán et al., 2004; Nir et al., 2000) and pharmaceuticals (Anggraini et al., 2014), have been reported (Park et al., 2011) as well. These studies demonstrate pollutant adsorption in suspension, but recently the employment of optimal sorbents in filtration columns has gained growing interest.

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An efficient filtration of inorganic and organic molecules and micro-organisms by clay composites at the laboratory scale in comparison to the most commonly employed sorbent, granulated activated carbon (GAC), have been reported (Nir et al., 2012; Radian and Mishael, 2012; Shabtai and Mishael, 2016; Undabeytia et al., 2014, 2008), together with an efficient filtration at the pilot/semi-pilot scale (Bleiman and Mishael, 2010; Gardi et al., 2015; Karaman et al., 2012; Nir et al., 2015). For example, the removal of perchlorate from a highly contaminated well (at a concentration of nearly 900 ppb perchlorate) by a surfactant-clay composite in a large filter treated 230 m³ of contaminated water to below the regulation limit of several ppb (Nir et al., 2015).

Routinely, the more successful pollutant-composite pairs were reported, whereas most studies do not elaborate on unsuccessful pairs. A few studies have employed a statistical method. Quantitative Structural Activity Relationships (QSARs), which correlates the experimental adsorption behavior (kd coefficients) and a variety of computationally calculated physicochemical pollutant structural properties, to describe the affinities of a wide range of pollutants to a sorbent, including GAC (Magnuson and Speth, 2005) and a polymer-clay composite (Radian et al., 2015). QSAR is based on a wide range of adsorption measurements, assumptions and calculations. A simplistic approach for matching a specific pollutant to a specific sorbent, which includes a predictive filtration model, would be valuable for efficient water treatment.

The majority of organic water pollutants are neutral or negatively charged molecules usually containing aromatic rings. Therefore, the adsorption of such pollutants by a sorbent can be a result of electrostatic attraction, π electron interactions, hydrogen bonds and Van der Waals interactions. The sorbent capacity towards pollutant molecules is the outcome of the molecules' tendency to leave the aqueous medium, to access the adsorption sites, to substitute pre-sorbed molecules (usually water) and to form specific bonds with the surface (Balmer et al., 2000; Kowalska et al., 1994). One of the major difficulties in developing tailor-made materials is the above-mentioned pairing for maximal pollutant adsorption, as this involves an in depth understanding of the adsorption mechanism of organic pollutants to the new heterogeneous modified clay surface.

This study aims to test a pollutant-sorbent pairing approach for large-scale filtration systems. Based on previous studies, three organo-clay composites were examined: the polymer-clay composite, a poly 4-vinyl pyridine co-styrene modified montmorillonite (HPVP-clay) (Ganigar et al., 2010; Gardi et al., 2015; Radian and Mishael, 2012; Zadaka et al., 2009) and two surfactant-clay composites, octadecyltrimethylammonium-montmorillonite (micelle (ODTMA)-clay) (Katz and Mishael, 2014; Mishael et al., 2002; Nir et al., 2015; Polubesova et al., 2003) and didodecyldimethylammonium-montmorillonite (liposome (DDAB) -clay) (Undabeytia et al., 2008, 2003). Three widely spread water pollutants with various physicochemical properties were paired to the composites. Sulfentrazone (SFZ), a triazolinone herbicide, is strictly limited to control broadleaf and grass weed species both in the US and Europe. Simazine (SMZ), an s-triazine herbicide, is commonly applied as a pre-emergence weed control in the US, whereas in the EU it has been banned since 2003 (Sass and Colangelo, 2003). These herbicides are frequently detected in wells in proximity to agricultural areas years after they have been banned (Fava et al., 2010; Kingston, 2011). Diclofenac, an anti-inflammatory drug, is one of the most evasive pharmaceuticals to outflow wastewater treatment plants and is frequently detected in surface and ground waters (Roberts and Thomas, 2006).

Laboratory scale filtration profiles of all nine combinations (three pollutants with three sorbents) were obtained and based on the understanding of the factors governing the adsorption of the pollutants to the different sorbents, the most efficient sorbent was paired to each pollutant. Model calculations and fitting were employed, for each pair, in order to extract the theoretical capacity as well as the adsorption/desorption rate coefficients. Model calibration was performed on a larger

scale, pilot size system, and simulations of environmental concentrations were performed.

2. Materials and methods

2.1. Materials

Wyoming sodium montmorillonite clay (SWy-2) was obtained from the Source Clays Repository (Clay Minerals Society, Columbia, MO). Bentonil A was kindly supplied by Clariant Iberica S.A. Poly-4-vinylpyridine-co-styrene (HPVP) with average ratio of 9:1 PVP to PS, octadecyltrimethylammonium (ODTMA), didodecyldimethylammonium (DDAB) and benzyl dimethyl hexadecylammonium (BDMHDA) were purchased from Sigma-Aldrich. Simazine was obtained from Makhteshim-Agan Industries Ltd. Sulfentrazone (91.3%) was obtained from FMC (Princeton, NJ). Diclofenac was purchased from Sigma-Aldrich (Sigma Chemical Co., St. Louis, MO).

2.2. Composite preparation

The HPVP-clay composite was prepared as described in Gardi et al. (2015). Briefly, poly-4-vinylpyridine co-styrene was dissolved in H₂SO₄ solution with a molar concentration equivalent to the concentration of the pyridine monomers. Polymer solution at concentrations of 1 g polymer L⁻¹ was added to a clay suspension at a final concentration of 0.834 g clay L⁻¹ and the solid composite was freeze-dried.

Granulated complexes of ODTMA-clay and BDMHDA-clay were prepared as described in Nir et al. (2015). Briefly, the amounts used were multiples of 10 g L⁻¹ clay and 12 mM of ODTMA bromide. A separation of the solid product (cake) was by a filter press. The humidity of the cake was reduced to 42–45% by placing it in 60 °C oven. Granulation of the cake was accomplished by a two stage machine, first a shredder to obtain the desired granule size followed by spherodizing to produce spherical granules. Dry ODTMA-clay granules were sieved to sizes between 0.3 to 2 mm, prior to filtration experiments. Similarly, DDAB-clay granules were obtained from a powdered complex prepared from a suspension of 6 mM DDAB and 5 g L⁻¹ of Bentonil clay as described in Undabeytia et al. (2008), by using a tumbling granulator model G-45 (J Bonals S.A; Barcelona, Spain) equipped with a 1.5 mm mesh sieve.

2.3. Zeta potential measurements

ODTMA-clay and DDAB-clay granules were grounded and suspended in water (1 g L⁻¹) and added to Eppendorf tubes. Different concentrations of sulfentrazone or diclofenac (0–175 mM) were then added to the tubes. After 24 hours the suspended composites were measured using a Zetasizer Nanosystem (Malvern Instruments, Southborough, MA), where the zeta potentials were deduced from the mobility of the particles using the Smoluchowski equation (Smoluchowski, 1941).

2.4. Column preparation and conditioning

2.4.1. Solution preparation and analysis

Simazine solution was prepared by first dissolving simazine in acetone (1000 mg L⁻¹), this solution was then added to distilled water to reach a concentration of 3 mg L⁻¹ (solution pH was adjusted to 3 using H₂SO₄). Sulfentrazone was first dissolved in acetone 100,000 mg L⁻¹, and then the solution was added to water to reach concentrations of 100 or 5 mg L⁻¹. Diclofenac sodium was added to water to reach concentrations of 100 or 5 mg L⁻¹.

Pollutants were quantified using an Agilent Technologies HPLC 1200 system equipped with a photodiode array detector. A C18 XBridge® chromatographic column (4.6 mm × 150 mm, 5 μ m particle size) was used. Chromafil Xtra PTFE® syringe filters 0.2 μ m from Macherey-Nagel GmbH&Co (Germany) were used for all analytical filtration

samples. Simazine mobile phase was acetonitrile and water (70:30), flow rate of 1 mL min⁻¹ and detection at 222 nm (LOD 0.05 mg L⁻¹, LOQ 0.1 mg L⁻¹). Sulfentrazone mobile phase was a mixture 1:1 of acetonitrile and water acidified with 0.1% H₃PO₄; flow rate of 1 mL min⁻¹; UV detection at 230 nm (LOD 0.05 mg L⁻¹, LOQ 0.15 mg L⁻¹). Diclofenac HPLC mobile phase was a mixture (60:40) of acetonitrile and water acidified with 0.1% H₃PO₄; flow rate of 1 mL min⁻¹ and detection at 276 nm (LOD 0.15 mg L⁻¹, LOQ 0.5 mg L⁻¹).

2.4.2. Laboratory experiments

DDAB- or ODTMA-clay (granules) or HPVP-clay composite (powder) were packed in glass columns (1.6 cm in diameter and 20 cm in length) with clean quartz sand (particle size 1 to 1.8 mm). Each column contained 3.6 g sorbent with excess of sand. The columns were slowly saturated with water from below in order to decrease preferential flow. Simazine filtration (3 mg L⁻¹, pH 3) was at a flow rate of 8 mL min⁻¹. Sulfentrazone and diclofenac filtration (100 mg L⁻¹) was at a flow rate of 9.1 mL min⁻¹. Effluent samples were collected over time from the bottom of the columns and emerging concentrations were determined by HPLC.

2.4.3. Pilot size experiment

The larger-scale pilot filtration system consisted of five high-density polyethylene (HDPE) columns 45 mm inner diameter and 980 mm long and a steel grid Ø 0.5 mm or 32 Tyler mesh, at the bottom. These columns were filled with sorbent (120 g of powdered sorbent (HPVP-clay) or 150 g of granulated sorbent (ODTMA-clay or DDAB-clay)) and quartz-sand (particle size 1 to 1.4 mm) in alternating layers. The packed HDPE columns were placed into stainless steel supporting columns provided with a pressure control system and air purge valve (Fig. 1). Each packed column was then slowly saturated at 50 mL min⁻¹ from the bottom to the top with a peristaltic pump until air purging was complete. Solutions containing simazine (3 mg L⁻¹, pH 3), sulfentrazone or diclofenac (5 mg L⁻¹) were pumped through the HPVP-clay, ODTMA-clay and DDAB-clay columns at flow rates of 130, 120 and 625 mL min⁻¹, respectively. Effluent samples were collected over time and emerging concentrations were determined by HPLC.

2.5. Model fitting and model calculations

Filtration results were fitted with an adsorption and convection model (Eq. (1)), first presented by Nir et al. (2012). The model addresses a column with a cross section (A) and (L) in length. The column is filled with a sorbent which has molar concentration of adsorption sites (R₀). The top and bottom of the filter are at the coordinates X = 0 and X = L, respectively. We consider that the pollutant concentration at the inlet, C₀ is constant i.e., C(X, t) = C₀, X ≤ 0, where t denotes time.

$$\frac{dC(X, t)}{dt} = -v \frac{\partial C}{\partial X} - C_1 \cdot C(Xt) \cdot R(Xt) + D_1(R_0 - R(Xt)) \quad (1)$$

Eq. (1): C (X, t), denotes pollutant concentration in the solution at time t (min) and a vertical coordinate X(cm); R(X, t), denotes the unoccupied adsorption sites at time t in coordinate X. C₁, is the adsorption rate constant (M⁻¹ min⁻¹); D₁, is the rate constant of desorption (min⁻¹); v, is the average filtrated flow velocity (cm min⁻¹).

Fitting the model equation to the laboratory scale experimental results yielded the kinetic rate constants (C₁ and D₁). Model calibration for the pilot scale, was performed using the same kinetic constants while adjusting the filter molar capacity (R₀) according to the concentration of the composite and the pore volume. The statistical RMSE was calculated using Eq. (2).

$$RMSE = \sqrt{(n-m)^{-1} \cdot \sum_1^n (y_c - y_e)^2} \quad (2)$$

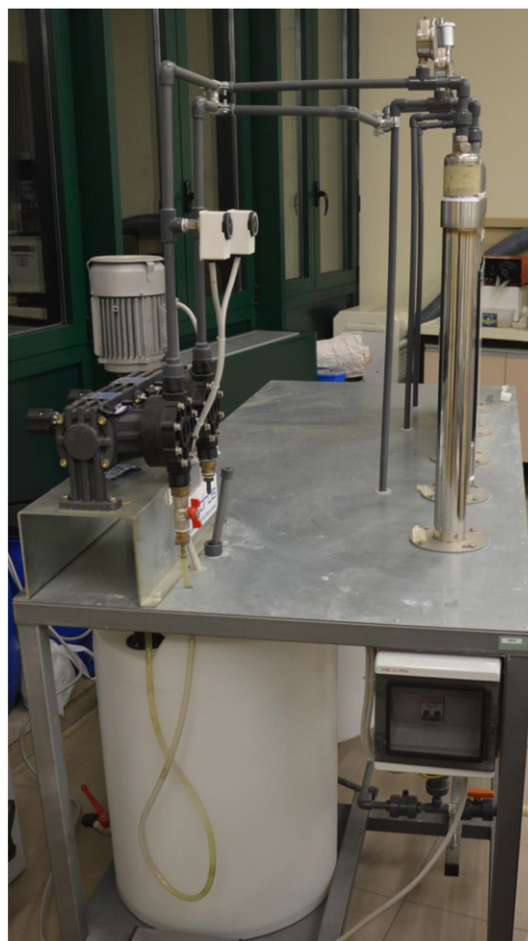


Fig. 1. Pilot scale filtration system consisting of a column filters made of stainless steel, and pump and a plastic reservoir.

Eq. (2): Model fit root mean square error; n is the number of data points; m is the number of free parameters; y_c is the calculated value and y_e is the measured one.

3. Results and discussion

3.1. Pollutants filtration - laboratory scale

Filtration of the pollutants simazine, sulfentrazone and diclofenac through three different columns composed of clay-composites is presented in Fig. 2 A–C. The results exhibit different removal efficiencies of each pollutant by the different composites. Binding mechanisms were proposed by considering the physical chemical properties of the pollutants along with the properties of the composites, such as zeta potentials (Fig. 3), the solubilization capacities of the surfactant composites (Mishael et al., 2002; Undabeytia et al., 2003) and the possible chemical interactions of the organic modifier with the pollutant. The results of the most efficient filtration sorbent per pollutant were modeled to determine sorbent capacity and kinetic adsorption and desorption coefficients (Table 2).

3.1.1. Simazine filtration

Filtration of simazine by HPVP-clay columns was notably higher than the removal by both ODTMA-clay and DDAB-clay columns, which presented similar and rapid breakthroughs (Fig. 2 A). For example, after filtering 0.5 L of the simazine solution only 23% and 32% of the simazine was removed by the ODTMA-clay granules and the

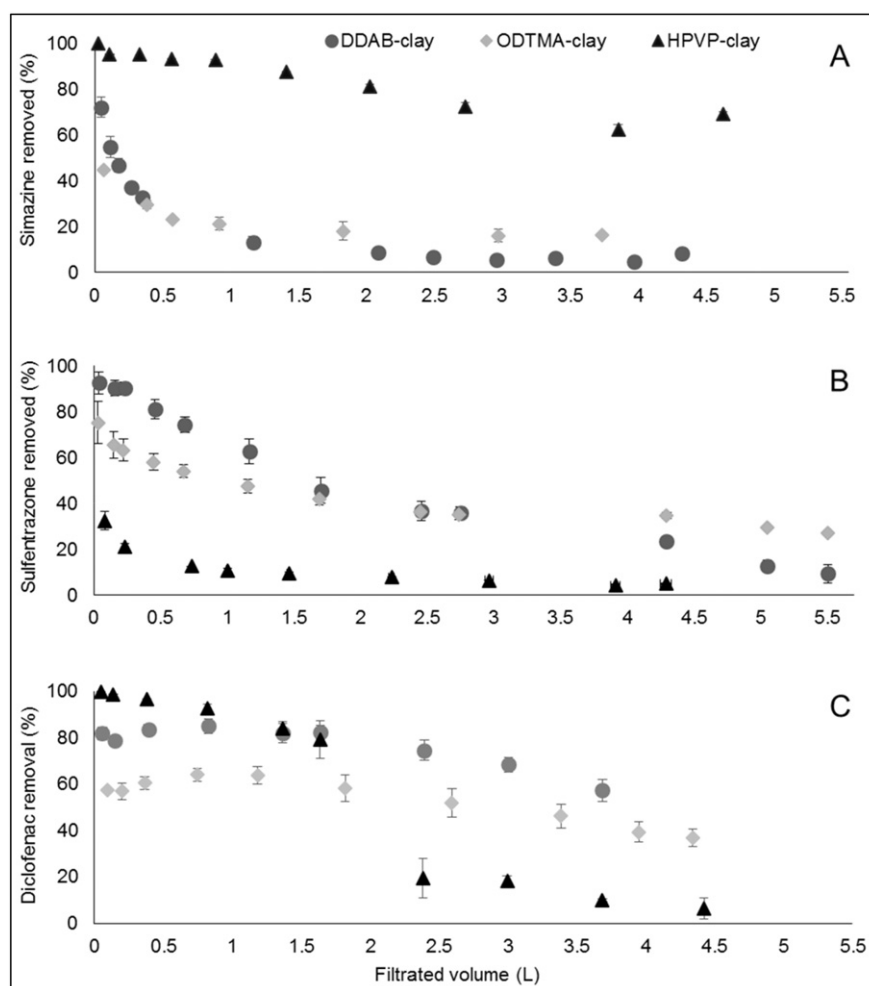


Fig. 2. Filtration of water through columns (1.6*20 cm) containing 3.6 g of DDAB-clay (circles) or ODTMA-clay (diamonds) or HPVP-clay (triangles) Percent removal of; [A] simazine (3 mg L^{-1}), [B] sulfentrazone 100 mg L^{-1} [C] diclofenac 100 mg L^{-1} at flow rate of 8, 9.1 and 9.1 ml min^{-1} . Bars corresponds to the results standard deviations.

DDAB-clay composite, respectively, while 93% was removed by the HPVP-clay composite.

The high affinity of simazine (at pH 3) to HPVP-clay composites was attributed to interactions between the π electrons of simazine and aromatic groups of the polymer along with hydrogen bonds between pyridinium (pH 3) and the nitrogen, a proton acceptor on the simazine ring (Gardi et al., 2015). Therefore, increasing the pH of the simazine solution dramatically reduced its affinity to the polymer composite since the polymer was deprotonated. On the other hand, the pH had no effect

on the affinity of simazine to DDAB-clay and ODTMA-clay composites (results not shown) since they do not tend to form hydrogen bonds. Furthermore, these surfactants lack of aromatic groups explains the low affinity of simazine to these composites, suggesting that simazine adsorption by the surfactant composites is mainly driven by Van der Waals interactions. The contribution of solubilization by these surfaces appears to be minor and not affected by the surfactant type. Therefore, the HPVP-clay composite was selected for simazine filtration and simulation at the pilot scale.

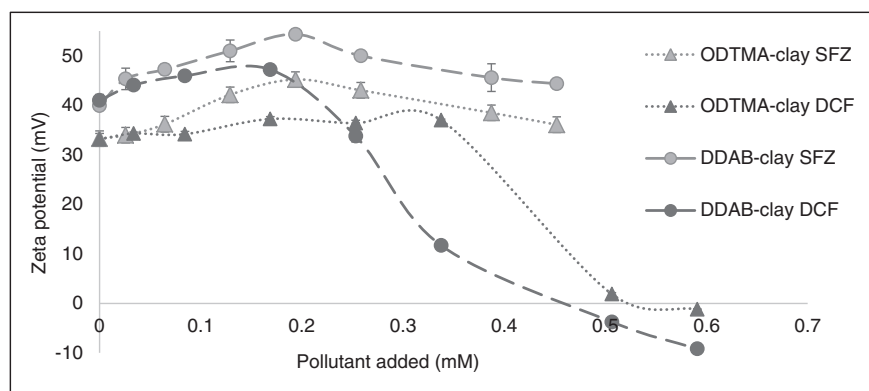


Fig. 3. Zeta potential of composite suspensions (1 g L^{-1}) at increasing concentrations of sulfentrazone (SFZ) or diclofenac (DCF). Bars corresponds to the results standard deviations.

3.1.2. Sulfentrazone filtration

Filtration of sulfentrazone by DDAB-clay columns was slightly and significantly higher than by the ODTMA- and HPVP-clay composites, respectively, especially during the first stage (2 L) of the experiment (Fig. 2B). While DDAB-clay performed slightly better at the first stage of the experiment, than the ODTMA-clay composite, the latter maintained a constant rate of breakthrough, which resulted in similar capacity of the two surfactant composites.

Theoretically, the affinity of sulfentrazone might be much higher to the HPVP-clay composite, since the pollutant has many proton acceptor groups and aromatic moieties, as well as ionizable groups. However, at low pH, in which HPVP is a good proton donor and the composite is positively charged, sulfentrazone is nonionic and its solubility is substantially lower than in the anionic form, resulting in sulfentrazone precipitation (Table 1). Therefore, sulfentrazone filtration was tested from a solution at pH 7.4. At such a pH the HPVP-clay composite is deprotonated, which results in a less positive zeta potential of the composite (40 mV at pH 3 to nearly 0 mV at pH 7), reducing electrostatic or hydrogen bond interactions between the anionic sulfentrazone and the polymer composite. The charge neutralization reduced the affinity of sulfentrazone and resulted in a rapid breakthrough from the HPVP-clay column. For example, after 1 L, the HPVP-clay filtration columns were able to remove only 10% from the initial concentration of sulfentrazone, compared to 54% removal by ODTMA-clay column and 74% by DDAB-clay.

The positive charge of the ODTMA and DDAB composites (33 and 40 mV, respectively) is not pH dependent; hence electrostatic interactions could explain the higher affinity of sulfentrazone to these composites and the slightly higher affinity to DDAB. But such interactions cannot be the only driving mechanism since zeta potential of these composites was not reduced upon sulfentrazone binding (Fig. 3) as obtained

for the binding of diclofenac (discussed below). Indeed, electrostatic attraction between sulfentrazone and ODTMA-clay composites along with intra micelle solubilization was suggested (Ziv and Mishael, 2008) and in a later study we concluded that intra-micellar solubilization has a major role (Katz and Mishael, 2014).

The solubilization of sulfometuron in ODTMA micelles reached 80% while its solubilization, under the same conditions, in DDAB liposomes reached 63% (Mishael et al., 2002; Undabeytia et al., 2003). The advantage of solubilization in ODTMA micelles in the case of sulfentrazone, which has a higher pKa (6.5 compared to 5.2 for sulfometuron) is expected to be even more pronounced. The high solubilization of sulfentrazone in ODTMA micelles, in comparison to another micellar-clay composite, (benzyl dimethylhexadecylammonium (BDMHDA))-clay (zeta potential of 38 mV), is also demonstrated (Table S1).

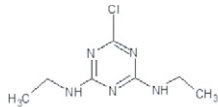
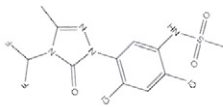
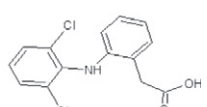
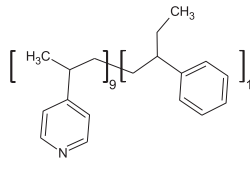
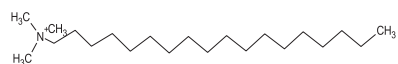
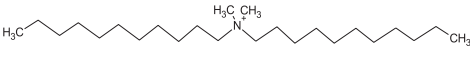
The advantage of sulfentrazone solubilization in ODTMA micelles is perhaps due to greater interactions with the hydrophobic domains of the ODTMA-clay composite, which increases the overall capacity of this column and therefore the ODTMA-clay composite was selected for sulfentrazone filtration and simulation at the larger scale.

3.1.3. Removal of diclofenac

The efficiency of diclofenac removal during the first filtered liter correlated with the positive zeta potentials of the composites as presented in Table 1 (56, 40 and 33 mV for HPVP-clay, DDAB-clay and ODTMA-clay, respectively) suggesting a strong effect of electrostatic interactions. The removal of diclofenac by the HPVP-clay composite column was nearly complete for the first filtered liter. However, the positive surface charge of the composite, which promotes the high binding of diclofenac, is reduced by the natural pH of the solution, resulting in deprotonation of the composite and reduction in composite charge, followed by a rapid breakthrough of the column during the filtration of the second liter

Table 1

Chemical structures of the studied pollutants; simazine, sulfentrazone and diclofenac (log D and pKa) and clay composites organic modifiers HPVP, ODTMA and DDAB and surface zeta potential (mV) at bulk solution.

| Pollutants | Simazine (SMZ) | Sulfentrazon (SFZ) | Diclofenac (DCF) |
|----------------------|---|---|---|
| Structure |  |  |  |
| pKa | 3 | 6.56 | 4.15 |
| Log D ^(a) | 2.18 | 1.42 | 1.89 |
| Clay composites | Poly 4-vinylpyridine co styrene (HPVP) | Octadecyltrimethylammonium (ODTMA) | Didodecyltrimethylammonium (DDAB) |
| Modifiers |  |  |  |
| Zeta potential (mV) | 56 ± 1.0 | 33 ± 0.9 | 40 ± 0.9 |

^a Log D presenting the octanol-water distribution coefficient at the pH of the filtrated solution, pH 3 for simazine and 7.4 for sulfentrazone and diclofenac.

(Fig. 2C). Indeed, the role of electrostatic interaction of diclofenac with polycation-clay composites was emphasized by Kohay et al. (2015).

Similarly to sulfentrazone, the solubility of diclofenac is limited at low pH (pKa 4), which implies that filtration at a low pH is not relevant. The relatively low pKa of diclofenac, indicating a larger fraction of negatively charged molecules at pH 7.4 can explain the high electrostatic dependency and its slower breakthrough from the HPVP-clay column, compared to sulfentrazone. Unlike sulfentrazone, upon the removal of diclofenac by the surfactant composites, a strong decrease in zeta potential of the composites was observed (Fig. 3), suggesting that diclofenac removal was mainly by electrostatic interactions with the shell of the micelles and less affected by solubilization in the hydrophobic domains. These observations can be attributed to the larger fraction of charged molecules of diclofenac (99.9%), compared to only 54.5% of anionic fraction of sulfentrazone at pH 7.4. Low solubilization of diclofenac in ammonium-salt micelles was previously reported, and diclofenac binding was argued to be mainly to the peripheral charged shell at ambient temperature (Mehta et al., 2006). These results support that, despite the similar log D of sulfentrazone and diclofenac, in the case of diclofenac the low pKa dictates a stronger effect of the electrostatic interactions. Therefore, the governing factor attributed to the removal of diclofenac is the surface charge followed by solubilization. Since the DDAB-clay composite showed the highest affinity, it was selected for diclofenac filtration and simulation.

3.1.4. Sorbent selection and model fitting

Specific compatibility between each sorbent and a pollutant gave three optimal pairs. For these pairs, the adsorption and convection model (Eq. (1)) was fitted to the results from the laboratory scale experiments. Adsorption and desorption rate constants as well as the goodness of fit are presented in Table 2. The adsorption affinity coefficients K (M^{-1}) of all three cases were of the same order of magnitude. The kinetic rate constants C_1 ($M^{-1} \text{ min}^{-1}$) and D_1 (min^{-1}) of simazine are significantly larger than those of sulfentrazone and diclofenac. Simazine adsorption and desorption to/from the composite surface is relatively quick due to fast diffusion, while diclofenac (to some extent) and sulfentrazone solubilization to the surfactant phase and diffusion back to the solution is slower. Solubilization into the surfactant phase increases composite capacity R_0 (M) since adsorption is not excluded to external domains. As suggested from the laboratory filtration experiments, solubilization is more dominant in the case of sulfentrazone, in comparison to diclofenac, which is reflected in the higher R_0 of ODTMA-clay for sulfentrazone.

The adsorption of diclofenac by methylated HPVP-clay composite, was previously reported, and the forward adsorption rate constant (C_1) was calculated, $250 (M \text{ min})^{-1}$ (Kohay et al., 2015). This value is notably higher than the value calculated for DDAB-clay (Table 2), explained by the higher zeta potential of that polymer composite (80 mV), which increases diclofenac affinity. On the other hand solubilization into the DDAB-liposome resulted in a lower desorption rate constant D_1 (min^{-1}) which yielded a capacity 260 times higher.

These fitting results were validated and compared to the filtration results from the pilot-scale experiments (see below). Furthermore, based on the calibrated model, the removal of the pollutants at environmental concentrations (ppb) by the pilot scale setting (Fig. 1), was simulated.

3.2. Pilot scale filtration experiments

The removal of simazine, sulfentrazone and diclofenac by a pilot-scale filtration system containing the selected sorbents for each pollutant is presented in Table 3. The molar concentration of available sites in the pore volume of the filter is defined as R_0 (Nir et al., 2012). The increase in the R_0 value for the pilot filter (Table 2 vs. Table 3) is due to the increase in the concentration of sorbent in the filter as well as the lesser proportional increase in pore volume when coarse sand particles are replaced by finer composite particles. The lower removal capacity of diclofenac than sulfentrazone reflects the larger flow velocity in the former case (section 2.4.3). The kinetic constants deduced from laboratory scale experiments (C_1 and D_1) were set fixed while the determination of R_0 values for the pilot filters did not involve fitting of results. Hence, the calculated values may be considered predictions. These predictions appear adequate with RMSE values smaller than experimental error (Table 3). It is noted that the concentrations of initial solutions of sulfentrazone and diclofenac in the pilot were 20-fold smaller than in the laboratory experiments, and the measured concentrations of pollutants in the filtered water were in the ppb range, whereas, in the laboratory experiments they were in the range of ppm or hundreds of ppb.

The filtration at the pilot scale exhibits not only efficient removal of the micropollutants, based on designed pairing between the pollutants and the sorbents, but the results also demonstrate the ability of the model to describe the filtration behavior for a variety of pollutant concentrations, sorbents and filtration set-ups. The results also demonstrate the benefit derived from model calculations, which are not limited to analytical restrictions, such as limit of detection. For example, the limit of quantification of sulfentrazone was $150 \mu\text{g L}^{-1}$ (i.e. 3% from the initial concentration). Thus, the model could predict 97% removal after the filtration of 501 L while experimental measurements are reporting complete removal according to the limit of detection.

An increase in filter capacity (from laboratory- to pilot- scale) was observed for all three scenarios and ranged from 1.25 to 5.23 fold (R_0 Table 2 vs. Table 3). For example, the removal of simazine, given an arbitrary limit that its concentration in the filtered water should not exceed 15% of the initial values. In the laboratory-scale experiment, a column could treat $0.47 \text{ m}^3 \text{ kg}^{-1}$ while in the pilot experiment the corresponding value was $1.42 \text{ m}^3 \text{ kg}^{-1}$.

Due to the good fit between the experimental and calculated results (Table 3) the model was further employed for the estimation of removal of pollutants at environmental concentrations (simazine $5 \mu\text{g L}^{-1}$, sulfentrazone $50 \mu\text{g L}^{-1}$, diclofenac $1 \mu\text{g L}^{-1}$) by using a commercial-size filter at a height of 1.6 m. The capacity is expressed in m^3 of water that can be treated per kg of composite, without being depended on column diameter (i.e., doubling the diameter will increase by 4-fold the treated water volume as well as the composite mass). Model calculations were set to reach the regulation limit of each pollutant (simazine and sulfentrazone $2 \mu\text{g L}^{-1}$, diclofenac $0.5 \mu\text{g L}^{-1}$ (not regulated)) (Hernando et al., 2006; The Council of the European Union, 1998). In the case of sulfentrazone filtration of a $50 \mu\text{g L}^{-1}$ solution yielded filtered concentration below $2 \mu\text{g L}^{-1}$ for $30 \text{ m}^3 \text{ kg}^{-1}$ for a flow velocity of 9.7 m h^{-1} . Under the same conditions the volume capacity of a diclofenac solution $1 \mu\text{g L}^{-1}$ that can be filtered to an emerging concentration below $0.5 \mu\text{g L}^{-1}$ amounts to $39 \text{ m}^3 \text{ kg}^{-1}$. In the case of simazine the estimate is more speculative, since filtration results are only available for a powdered complex. In Nir et al. (2015) it was demonstrated

Table 2
Model parameters for the removal of pollutants by filtration.

| Pollutant | Sorbent | R_0 , molar concentration of adsorption sites | C_1 ($M \text{ min}^{-1}$) | D_1 (min^{-1}) | K (M^{-1}) | R^2 |
|---------------|-----------------------|---|--------------------------------|-----------------------------|------------------|-------|
| Simazine | Powdered HPVP-clay | 0.024 | 68 | 0.00157 | 43300 | 0.95 |
| Sulfentrazone | Granulated ODTMA-clay | 0.130 | 30 | 0.00060 | 50000 | 0.97 |
| Diclofenac | Granulated DDAB-clay | 0.065 | 14 | 0.00025 | 56000 | 0.92 |

Table 3

Model predictions for removal of simazine, sulfentrazone and diclofenac by the pilot filter columns, containing HPVP-clay, ODTMA-clay and DDAB-clay, respectively.

| Simazine | | Sulfentrazone | | | | Diclofenac | | |
|---------------------------|-------------|---------------|------------|-------------|-------|------------|-------------|-------|
| R_0 mol L ⁻¹ | 0.03 | 0.21 | | | | 0.34 | | |
| RMSE% | 2.5 | 1.1 | | | | 1.5 | | |
| Volume (L) | Removal (%) | | Volume (L) | Removal (%) | | Volume (L) | Removal (%) | |
| | Exp. | Calc. | | Exp. | Calc. | | Exp. | Calc. |
| 8 | 100 | 100 | 159 | 100 | 100 | 60 | 100 | 100 |
| 31 | 100 | 100 | 394 | 100 | 98 | 90 | 98 | 97 |
| 55 | 100 | 99 | 501 | 100 | 97 | 110 | 97 | 97 |
| 117 | 100 | 97 | 560 | 96 | 96 | 130 | 96 | 96 |
| 140 | 96 | 96 | 707 | 90 | 91 | 170 | 96 | 96 |
| 187 | 84 | 91 | 750 | 89 | 89 | 200 | 95 | 96 |

(*) R_0 is the calibrated molar capacity for a pilot filter column (4.5 × 98 cm). Experimental error for the measurements of simazine is 6.6% and for sulfentrazone and diclofenac 6%.

that when a powdered complex (ODTMA-clay) and a granulated one are present at the same amounts in a filter, the powdered complex demonstrated a more efficient filtration. This can be rationalized by the longer average distances, which pollutants have to pass by diffusion in order to reach the adsorption sites in a granulated material. However, in accord with analysis (Nir et al., 2012) and experimental results (Nir et al., 2015; Rakovitsky et al., 2016) the volume which can be purified by a filter with more concentrated active material is larger on the basis of filtered volume per mass of active material. The powdered material can rarely support flow in a filter when present at a fraction larger than 10%, whereas a granulated complex can fill the filter exclusively. In the calculations the value of R_0 for a granulated polymer clay complex was estimated by 0.41 M and the values of the kinetic constants were half of those in Table 2. Thus a purification of an initial simazine solution of 5 µg L⁻¹ yielded 11 m³ kg⁻¹ composite to satisfy the regulation of 2 µg L⁻¹. The capacity values mentioned before in this section will be used for discussing the economy of removal of the pollutants studied. Prices considered for the cations ODTMA and DDAB and the clay per 1 kg were for amounts purchased of 1 ton or above. In both cases a first order estimate yields a price of 10 \$ kg⁻¹ for the granulated complexes. In the case of the HPVP composite, a large-scale production has not started yet and estimating costs is premature. Using the above values for the cost of the granulated material ODTMA-clay in removal of sulfentrazone from 50 µg L⁻¹ to 2 µg L⁻¹ yields a value of 10 \$ per 30 m³, i.e., 0.33 \$ m⁻³, whereas for a more realistic case of an initial concentration of 20 µg L⁻¹, the price of material would be 0.09 \$ m⁻³. The corresponding value for reducing diclofenac concentration in water from 1 to 0.5 µg L⁻¹ by DDAB-clay would be 0.07 \$ m⁻³. The price of activated carbon is 2–4 \$ kg⁻¹; however in these two cases removal from water of sulfentrazone (Undabeytia et al., 2008) or diclofenac (Karaman et al., 2012) by using activated carbon in filtration was poor and unacceptable. Similarly, the removal of simazine (10 µg L⁻¹) by activated carbon failed to meet the regulation limit (Gardi et al., 2015).

4. Conclusions

This study paired three commonly detected water micropollutants, simazine, sulfentrazone and diclofenac, with compatible sorbents for pollutant removal by filtration. The filtration efficiency of each sorbent towards the different pollutants were explained by the proposed binding mechanisms. The mechanisms were suggested considering the physicochemical properties of the pollutants along with the properties of the composites such as zeta potentials, the solubilization capacities of the surfactant composites and the chemical interactions of the organic modifier. Strong proton donor sites as well as aromatic groups promoted the efficient adsorption of simazine by HPVP-clay composites.

High solubilization capacity was found to be a major factor in sulfentrazone adsorption by the ODTMA-clay composite. The strictly anionic diclofenac was mostly interacting via electrostatic attraction and was efficiently removed by the DDAB-clay composite.

Based on the nine tested scenarios, tentative guidance may be suggested for sorbent-pollutant pairing. For hydrophobic pollutants solubilization is a dominant mechanism; however, specific interactions, such as hydrogen bonds, can play a major role. For the removal of anionic pollutants by positively charged sorbents, electrostatic interactions are dominant, but Van der Waals interactions contribute as well. For pollutants with an intermediate pKa the pH of the solution governs which mechanism will dominate the adsorption. Filtration of compatible sorbent-pollutant pairs was modeled to determine sorbent capacity, adsorption and desorption rate constants. The pilot filtration experiment was well described by the model and demonstrated efficient removal of paired pollutants and sorbents. Model simulations estimated promising treatment of environmental pollutant concentrations at the µg L⁻¹ range. Model calculations can be a strong and valid tool for estimation of up scaling results as well as emerging pollutants concentrations lower than analytical detection limits.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.clay.2016.12.029>.

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