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Filtration of triazine herbicides by polymer-clay sorbents: Coupling an experimental mechanistic approach with empirical modeling

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ABSTRACT

Triazine herbicides detected in surface and groundwater pose environmental and health risks. Removal of triazine herbicides (simazine, atrazine and terbuthylazine) by polymer-clay composites was studied and modeled. Their binding by a poly 4-vinyl pyridine co styrene-montmorillonite (HPVP–CoS–MMT) composite was especially high due to specific interactions between the herbicides and polymer, mainly hydrogen bonds and π-π stacking. The binding kinetics to the composite was in the order of simazine > atrazine > terbuthylazine, which was in accord with their equilibrium Langmuir binding coefficients; 44,000, 17,500 and 16,500 M^{-1}, respectively, which correlated with herbicide accessibility to form specific interaction with the polymer. Simazine binding kinetics to the composite was significantly faster than to granulated activated carbon (GAC), reaching 93% vs 38% of the maximal adsorption within 10 min, respectively. Herbicide filtration by composite columns was adequately fitted by a model which considers convection and employs Langmuir formalism for kinetics of adsorption/desorption. Filtration of simazine (10 $\mu g\ L^{-1}$) by composite columns (40 cm long, which included 26 g composite mixed with sand 1:40 (weight ratio)), was well predicted by the model with nearly 120 L purified, i.e., effluent concentrations were below regulation limit (3 $\mu g\ L^{-1}$). Effluent concentrations from GAC columns exceeded the limit after filtering 5 L. Experimental results and model predictions suggest that while GAC has a high capacity for simazine binding, the composite has higher affinity towards the herbicide and its adsorption is faster, which yields more efficient filtration by composite columns.

1. Introduction

Pesticides provide substantial agronomic and economic benefits. However, pesticide migration may cause soil, surface and ground-water contamination (Werf, 1996). For example, tens of thousands of tons of triazine herbicides are being manufactured and applied to fields all over the world, and are frequently detected in high concentrations in surface and groundwater (Pionke and Glotfelty, 1989; Pucarević et al., 2002). Due to its stability, high concentrations of atrazine have been detected in groundwater under fields years after it

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was banned by the EU (Armstrong et al., 1967; Fava et al., 2010). Triazines are categorized as potential carcinogenic (Gammon et al., 2005; Kettles et al., 1997) and their regulation limits in drinking water are 3 ppb and 0.1 ppb in the US and EU, respectively (EPA, 2003; Sass and Colangelo, 2003).

Triazine herbicide removal from water by oxidation or coagulation was found to be ineffective (Jiang and Adams, 2006) and photo catalytic degradation using TiO_2 did not achieve mineralization (Pelizzetti et al., 1990). The isolation of bacteria (*Pseudomonas* sp. *strain ADP*) that utilize atrazine as a nitrogen source and can efficiently degrade atrazine was reported (Mandelbaum, 1995). This report prompted a large number of studies which demonstrated the biodegradation of triazine compounds found in water (Feakin et al., 1995; Katz and Dosoretz, 2000). However, biodegradation is not the most suitable technology, and the EPA recommendation for treating triazine contaminated drinking water is by filtration with granular activated carbon (GAC) (EPA, 2012).

The development of sorbents which may remove organic pollutants from water, more efficiently than GAC, has been addressed and sorbents such as organo-clays, in which the hydrophilic clay surface is modified by organic cations to form a more organophilic surface, have been suggested (Beall, 2003; Mortland et al., 1986; Ruiz-Hitzky and Serratosa, 1998). More recently, polymer-clay composites have drawn attention as attractive sorbents (Alexandre and Dubois, 2000; Yue et al., 2007). The first study to acknowledge the sorptive properties of polymer-clay composites was published by Churchman (2002), which suggested that the polymer can form specific interactions with the pollutant, therefore enhance its binding. Indeed, specific interactions between a pollutant (imazapyr, picric acid and MTBE) and the adsorbed polymer have shown to enhance pollutant removal (Ganigar et al., 2010; Radian and Mishael, 2008; Zadaka-Amir et al., 2012).

Concerning atrazine, we have reported (Zadaka et al., 2009) its efficient removal by an acidified poly-4-vinylpyridine co styrene-montmorillonite composite (PVP–CoS–MMT). Filtration tests demonstrated enhanced removal of atrazine by composite columns in comparison to its removal by GAC columns. Atrazine removal by the composite columns was extremely efficient from an acidic solution (pH~4), but was dramatically compromised at a higher pH, which was attributed to polymer desorption at a neutral pH. However, further investigation of filtration by these composite columns showed that the removal of pyrene was high at a wide range of pH (Radian and Mishael, 2012). These studies demonstrated the high potential of the PVP–CoS–MMT composite to bind aromatic pollutants, but indicated that the mechanism of pollutant binding to the composite is complex, pollutant specific and not fully understood.

In addition to shedding light on the binding mechanism of atrazine to the composite, we aimed to elucidate the mechanism of simultaneous binding of pairs of triazine herbicides. Only a few studies have looked at simultaneous binding of pollutants to natural sorbents (Matsui et al., 2003) or to engineered ones, such as GAC (Xing and Pignatello, 1997; Xing et al., 1996), organo-clays (Lee and Tiwari, 2012; Rytwo et al., 2002) and micelle clay composites (Nir et al., 2012). Several studies have reported the promising potential of new sorbents by batch experiments (Zhu et al., 2010) and in some cases also by filtration tests (Li et al., 2002). However, when extrapolating results obtained from laboratory filters to the pilot scale filters, it is essential to be able to yield reliable estimates for filter capacities under a variety of pollutant concentrations, flow rates, column size etc. For this purpose a semi-empirical model for the kinetics of filtration, (Nir et al., 2012) which could yield predictions, was developed and employed.

In the current study we explore experimentally and by modeling the removal of three triazine herbicides (simazine, atrazine and terbuthylazine) by PVP–CoS–MMT composites and GAC, attempting to shed light on the binding mechanism and study the complex simultaneous removal of the herbicides. We aim to model the removal of simazine by filtration with composite columns, at a wide range of concentrations. Furthermore, the removal of simazine by the composite columns will be compared to the removal by GAC filters.

2. Materials and methods

2.1. Materials

Na-montmorillonite clay (SWy-2) (MMT) was purchased from Source Clays Repository of The Clay Mineral (Columbia MO). S-triazine herbicides: simazine (6-chloro-2N,4N-diethyl-1,3,5-triazine-2,4diamine), atrazine (6-chloro-N2-ethyl-N4-isopropyl-1,3,5triazine-2,4-diamine), terbuthylazine (N2-tret-buthyl-6-chloro-4N-ethyl-1,3,5-triazine-2,4-diamine) were obtained from Makhteshim-Agan Industries Ltd. Their physical–chemical properties ("PPDB: Pesticide Properties DataBase," 2007) are shown in Table 1. Poly-4-vinylpyridine-co-styrene (PVP–CoS) with average ratio of 9:1 PVP to PS, was purchased from Sigma–Aldrich. Granular activated carbon, Hydraffin 30N was purchased from Benchmark Ltd.

2.2. Analytical methods

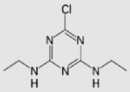
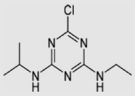
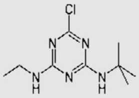
Polymer concentration in water was determined by spectrophotometer measurements (Thermo–UV–Vis) (see details below). Herbicide concentrations were measured by an Aglient 1200 series HPLC instrument equipped with a G1315D UV–vis Diode Array Detector ($\lambda = 222$ nm) with a Lichrospher® RP-18 (25 cm) column; the mobile phase was acetonitrile and water 70:30 v/v, flow rate of 1 mL min^{-1} (LOD 0.05 mg L^{-1}, LOQ 0.1 mg L^{-1}). Herbicide concentrations lower than 0.1 mg L^{-1} were determined by LC-MS using EPA standard method number 525.2 (LOQ 0.1 μg L^{-1}).

2.3. Experimental methods

2.3.1. Batch experiments

2.3.1.1 Preliminary tests showed that the binding of atrazine (10 mg L^{-1}) was positively correlated with PVP–CoS loading on the clay (0–0.25 g polymer per g clay) at a composite concentration of 0.834 g L^{-1}. The binding of the herbicides by the bare clay was relatively low. A polymer loading higher than 0.2 g polymer per g clay showed only minor improvement in herbicide binding; therefore this loading was selected. A similar optimal loading was reported for atrazine binding, by Zadaka et al. (2009).

Table 1 – Chemical properties of three s-triazine herbicide tested ("PPDB: Pesticide Properties DataBase," 2007).

s-triazine herbicides	Formula	MW ($g\ mol^{-1}$)	Solubility in water ($mol\ L^{-1}$)	Log Kow
Simazine		201.66	$2.48 * 10^{-5}$	2.3
Atrazine		215.68	$3.25 * 10^{-4}$	2.7
Terbuthylazine		229.71	$3.70 * 10^{-5}$	3.4

2.3.1.2 To prepare PVP–CoS–MMT clay composites, the polymer was dissolved in a H_2SO_4 solution with a molar concentration equivalent to the concentration of the pyridine monomers to protonate the pyridine monomers and positively charge the polymer. Protonated PVP–CoS will be denoted as HPVP–CoS. Quaternary PVP–CoS was prepared by methylation (CH_3I as reactant) of all the pyridine monomers, using similar reaction as published by Singh et al. (2010); consequently the polymer had a constant, pH independent, positive charge. Quaternary PVP–CoS will be denoted as QPVP–CoS.

Clay composites (0.2 g polymer per g clay) were prepared by adding the polymer solution to a Na-montmorillonite clay (MMT) suspension reaching final concentrations of 1 g polymer L^{-1} and 0.834 g clay L^{-1}. Upon reaching equilibrium (within 2 h); suspensions were centrifuged for 25 min (4500 rpm), supernatants were separated and measured by a spectrophotometer ($\lambda = 260$ or 222 nm for HPVP–CoS and QPVP–CoS, respectively). The amount of adsorbed polymer was calculated. The precipitated HPVP–CoS–MMT or QPVP–CoS MMT were freeze-dried using a lyophilizer. In order to test herbicide binding to un-protonated HPVP–CoS (PVP–CoS), following the composite preparation as mentioned, the composite was repeatedly washed with distilled water and the solution pH was adjusted to 7 by a dilute NaOH solution.

2.3.1.3 Herbicide binding to HPVP–CoS–MMT and QPVP–CoS–MMT composites in batch experiments was tested in triplicates. Simazine, atrazine or terbuthylazine solutions were added to the composites (final concentration of 1 g L^{-1}) reaching final concentrations of 0.5–4 mg L^{-1} for simazine and terbuthylazine and 0.5–20 mg L^{-1} for atrazine. The samples were agitated for 48 h (reaching equilibrium), centrifuged and filtered by 0.45 μm PTFE filters and herbicide concentrations in the supernatants were measured by HPLC. Binding isotherms were constructed, the results were then fitted to the Langmuir model using numerical solutions (Nir, 1986) and the binding coefficients were extracted.

2.3.1.4 For the preparation of composites of HPVP–CoS, PVP–CoS, QPVP–CoS and PAM 1, 1, 1.2, 1 g L^{-1} polymer solutions were added to 0.83 g L^{-1} clay (final concentrations), mixed for 4 h, centrifuged and the supernatant was discarded. Binding of atrazine (5 mg L^{-1}) to four polymer-MMT composites (0.2 g polymer per g clay, 1 g composite L^{-1}) was tested (in triplicates) at equilibrium (48 h). Herbicide concentrations in the supernatants were measured by HPLC.

2.3.1.5 The kinetics of herbicide binding to HPVP–CoS–MMT composites and to GAC in batch experiments was tested (in triplicates) by adding simazine, atrazine or terbuthylazine solutions (3 mg L^{-1}) to the composites, or to GAC (1 g L^{-1}) under constant stirring. Simultaneous binding kinetics of simazine and terbuthylazine (1.5 mg L^{-1} each, i.e., a total of 3 mg L^{-1}) to HPVP–CoS–MMT composites and to GAC in batch experiments (1 g L^{-1}) were tested under constant stirring. Using a syringe, the suspensions were sampled (0–120 min at intervals of a few minutes), filtered by 0.45 μm PTFE filters and herbicide concentrations were measured by HPLC.

2.3.2. *Filtration experiments*

2.3.2.1 Filtration of water containing triazine herbicides was conducted using glass columns (diameter- 1.6 cm, length –22 cm). The columns were filled with 3.6 g HPVP–CoS–MMT or GAC mixed with sand at 1:20 (weight ratios). All filtration experiments were in duplicates. Herbicide solutions (1 mg L^{-1}) were prepared with distilled water; pH was adjusted to 3.5 using sulfuric acid in a large glass container (22 L). Under constant stirring and temperature (27 °C) the water was spiked with 1000 mg L^{-1} herbicide in acetone solution. The columns were slowly saturated from the bottom to eliminate trapped air and prevent channeling. The herbicide solutions were pumped through the columns (6 mL min^{-1}) using a peristaltic pump. The effluent from each column was collected over time and analyzed by HPLC. The results were fitted by model calculations according to Equation (1) below.

This model deals with adsorption and convection in a column filter. The adsorption and convection are described by Equation (1). whose numerical solutions were executed by a FORTRAN program described in (Nir et al., 2012). Briefly, a column of length L is filled with material whose initial molar concentration of adsorbing sites is R_0, whose concentration changes later to $R(X,t)$. The beginning and end of the filter are at the coordinates $X = 0$ and $X = L$, respectively. We consider that the pollutant concentration at the inlet, C_0 is constant i.e., $C(X, t) = C_0$, $X \le 0$, where t denotes time. The adsorption convection model can describe inert solutes such as anions. Since the binding coefficients of these solutes are very small (i.e., low forward coefficient or high backward coefficient) the model converges to the mass convection, resulting in zero retardation for inert solutes.

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

Equation (1): C_1 (M^{-1} $\min^{-1}$) (rate constant of forward adsorption), D_1 ($\min^{-1}$) (rate constant of desorption), υ (cm $\min^{-1}$) (flow velocity).

The statistical criteria for the goodness of the fits were the closeness of R^2 to unity, and RMSE, the root mean square error.

2.3.2.2 Simazine filtration model validation was performed under different conditions from the ones mentioned above (i.e., twice the column length, more than three times the width, one fifth of the sorbent concentration and higher initial simazine concentration). A solution at an initial concentration of 1.5 mg L^{-1} simazine (pH − 3.5) was pumped (16 mL $\min^{-1}$) through duplicates of two sequential columns (20 cm in length and 2.5 cm radius) both filled with 6 g of HPVP–CoS–MMT or GAC mixed with sand at 1:100 weight ratios. The effluent was collected over time from the first (20 cm) and second (40 cm) columns and simazine concentrations were measured.

2.3.2.3 Filtration of simazine at an environmental concentration (10 μg L^{-1}) was performed. Plexiglas columns (40 cm long and 5 cm in diameter) were filled with 26 g of HPVP–CoS–MMT or GAC mixed with sand at 1:40 (weight ratio) in duplicates. Simazine solution was prepared in a 300 L tank; pH was adjusted as mentioned in the previous section. Solution was pumped through the columns (35 mL $\min^{-1}$) using a peristaltic pump. The effluent from the column was collected over time and blindly tested by Mekorot (National Water Carrier of Israel) Central Laboratory, Jordan region; using LC-MS and according to the EPA method 525.2. Preliminary model calculations were made, in order to evaluate the breakthrough point at which more than 3 μg L^{-1} of simazine (the regulation limit for simazine in U.S drinking water) will emerge. The results were compared to the model predictions.

3. Results and discussion

3.1. *Adsorption isotherms of triazine herbicides on HPVP–CoS–MMT composites*

Adsorption isotherms of simazine, atrazine and terbuthylazine on HPVP–CoS–MMT (1 g L^{-1}) were obtained (Fig. 1) and well described by the Langmuir equation ($R^2 = 0.99$–0.96). The estimated capacity of the HPVP–CoS–MMT composite to s-triazine herbicides, 0.2 mmol g^{-1} at least, was calculated from the maximal adsorption of atrazine (of highest solubility among the triazine herbicides Table 1). The binding affinities of the herbicides to HPVP–CoS–MMT followed the sequence simazine > atrazine > terbuthylazine with binding coefficients of 44,000, 17,500 and 16,500 M^{-1}, respectively; i.e., the binding affinity increased with a decrease in molecular weight. The herbicides differ by an additional methyl group on the side chains (Table 1). These results suggest that spatial interference reduces the accessibility of the larger herbicides to form interactions with the adsorbed polymer.

3.2. *Interactions of triazine herbicides with HPVP–CoS–MMT composites*

Most studies on atrazine adsorption by soil or soil organic matter (Kovaios et al., 2006; Weber et al., 1969) suggest that hydrophobic partitioning and/or hydrogen bonds are involved.

The interactions between the herbicides and the adsorbed polymer may include; Van Der Waals, π-π stacking interactions and hydrogen bonds (Table 2). Triazine herbicides have both H–acceptor and H-donor groups (a side chain NH performs as an H-donor and the pyridine as an H–acceptor) and therefore have high potential to form hydrogen bonds with strong H-donors or acceptors (Welhouse and Bleam, 1993). To further explore the contribution of Van Der Waals, π-π interactions and hydrogen bonds to the interactions

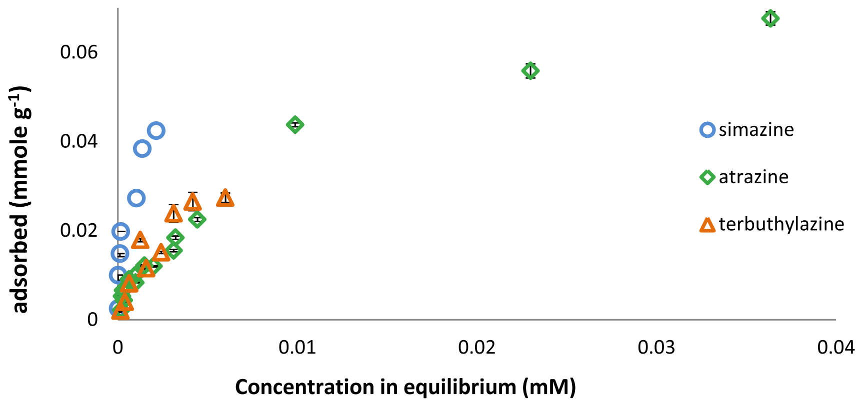
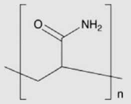
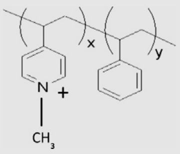
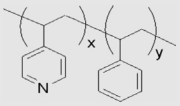
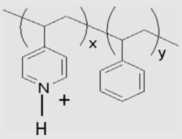


Fig. 1 – Adsorption isotherms of simazine (circles), atrazine (diamonds) and terbuthylazine (triangles) by 1 g L^{-1} HPVP–CoS–MMT composite (0.2 g polymer per g clay). Vertical bars represent the standard deviations of the measured results.

Table 2 – Atrazine (5 mg L^{-1}) removal by polymer-clay composites (0.2 g polymer/g clay) 1 g L^{-1}, and suggested interactions between the adsorbed polymer and herbicide.

Polymer in complex	Structure	Solution pH	Interaction possible	(5 mg L^{-1} ATZ) % removal (±SD)
PAM		6.5	Van Der Waals Weak Hydrogen bonds	17 ± 1
QPVP–CoS		6	Van Der Waals π-π	65 ± 4
PVP–CoS		6.5	Van Der Waals Weak Hydrogen bonds π-π	81 ± 2
HPVP–CoS		3.7	Van Der Waals Hydrogen bonds π-π	97 ± 2

between the herbicides and the adsorbed polymer; the binding of atrazine to polymers with different functional groups, was tested.

Binding of 5 mg L^{-1} atrazine to four polymer-MMT composites (0.2 g polymer per g clay) 1 g L^{-1} in suspension at equilibrium was explored (Table 2). Atrazine binding to the poly acryl amide (PAM) composite was low (16%) while its binding to the polymer composites with aromatic rings (QPVP–CoS, PVP–CoS and HPVP–CoS) was significantly higher (65%, 81%, 97%, respectively). This indicates that π-π stacking interactions are dominant and that hydrogen bonds and van der Waals interactions, which may form in the case of PAM, are not the main interactions contributing to atrazine binding. However, within the group of aromatic polymers atrazine showed the highest affinity to HPVP–CoS–MMT, which can be attributed to the formation of hydrogen bonds in addition to the π-π interactions. As mentioned above herbicide affinity to the composite increased with a decrease in herbicide molecular weight (Fig. 1 and Table 1). The reduction in molecular weight is coupled with an increase in accessibility of the pyridine of the herbicides (the hydrogen acceptor group) to form interactions with the pyridinum group of the polymer (a hydrogen donor). Therefore, it is most likely that the forming hydrogen bonds involve the herbicide as H-acceptor and the polymer as an H-donor. This conclusion is in agreement with previous studies on atrazine forming hydrogen bonds (Welhouse and Bleam, 1992, 1993) and with the weaker binding of atrazine to the PVP–CoS–MMT composite in comparison to the HPVP–CoS–MMT composite. Furthermore, preventing the formation of hydrogen bonds by adding a methyl group on the N-pyridine i.e., synthesizing a QPVP–CoS composite, yielded even lower atrazine binding.

Hydrogen bonds between the herbicides and the polymer did not only affect the binding of the herbicides at equilibrium but also the kinetics of binding. Simazine binding to HPVP–CoS and to PVP–CoS–MMT (1 g L^{-1}) at pH 3 and 6, below and above the pKa of the pyridine monomers, respectively, was measured as a function of time. Within 4 min simazine (1 mg L^{-1}) binding reached 0.6 mg g^{-1} HPVP–CoS–MMT while only 0.1 mg g^{-1} PVP–CoS–MMT, which are 66% and 16% of the amounts bound at equilibrium, respectively. These results indicate that hydrogen bonds, which increase triazine herbicide binding at equilibrium, also enhance the kinetics, which is crucial in filtration. Therefore, the HPVP–CoS–MMT composite was selected for removing triazines from solution.

3.3. *Kinetics of triazine herbicide binding by the composite and GAC*

Binding kinetics of triazine herbicides to the HPVP–CoS–MMT composite and to GAC are shown in Fig. 2. The binding kinetics of the three triazine herbicides (3 mg L^{-1}) to the HPVP–CoS–MMT composite was significantly faster than to GAC (1 g L^{-1}). The three herbicides presented similar binding rates to GAC (Fig. 2) with terbuthylazine binding somewhat faster, which is in line with the assumption that the binding to GAC is not very selective and resembles a hydrophobic partitioning (terbuthylazine has the highest Kow (Table 1)). In contrast, the binding rates to the HPVP–CoS–MMT composite were in the order of simazine > atrazine > terbuthylazine, i.e., in the same order as their affinity in equilibrium (Fig. 2A) supporting the suggestion that binding rates increase with the accessibility of the herbicide to the proton donor group of the

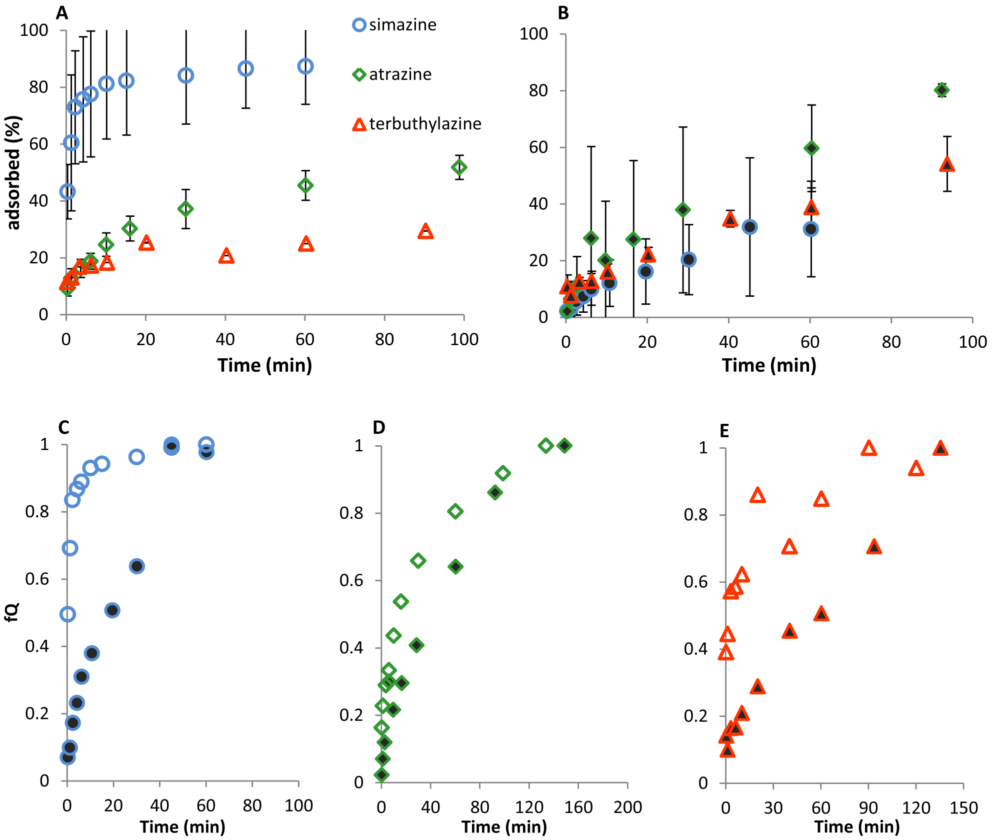


Fig. 2 – Binding kinetics of simazine (circles), atrazine (diamonds) and terbuthylazine (triangles) (3 mg L^{-1}) to HPVP–CoS–MMT [A] and to GAC [B] 1 g L^{-1}. Vertical bars represent the standard deviations of the measured results. Temporal adsorbed fraction of simazine [C], atrazine [D] and terbuthylazine [E], the ordinate; fQ, is defined as fraction of the maximum adsorbed by HPVPCoS–MMT (hollow symbols) or GAC (full symbols).

polymer. This kinetic advantage of the binding of herbicides to the composite is clearer when presenting herbicide removal as a fraction of the maximal removal (Fig. 2C–E). The results of the binding kinetics emphasize the superior removal of simazine by the composite. Within 1.5 h simazine and atrazine binding to HPVP–CoS–MMT composites reached equilibrium while their binding to GAC did not (complete binding within 48 h-not presented).

To explore the effect of competition on triazine binding, we focused on simazine and terbuthylazine. These herbicides have the highest and lowest affinity to HPVP–CoS–MMT, respectively, whereas their affinity to GAC is the lowest for simazine and highest for terbuthylazine (Fig. 2). The kinetics of simultaneous binding of simazine and terbuthylazine (1.5 mg L^{-1} each) to GAC and to HPVP–CoS–MMT composite (1 g L^{-1}) are shown in Fig. 3. The binding rate of terbuthylazine to HPVP–CoS–MMT was not affected in the presence of simazine (Fig. 3C), whereas, the rate of simazine binding to HPVP–CoS–MMT was reduced in the presence of terbuthylazine (Fig. 3A), but upon approaching equilibrium the effect of competition was minor. The binding of simazine and of terbuthylazine to GAC in the presence of each other demonstrated a synergistic effect. Even so, the rate of simazine binding to HPVP–CoS–MMT was higher than to GAC also under competition conditions (Fig. 3B,D).

3.4. *Filtration of triazine herbicides by composite and GAC filtration columns*

3.4.1. *Filtration of triazine herbicides: experiments and modeling*

The removal of simazine, atrazine and terbuthylazine by filtration through columns filled with HPVP–CoS–MMT or GAC mixed with sand at 1:20 (weight ratio) was tested (Fig. 4). The removal efficiency of simazine was higher than that of terbuthylazine by filtration with the composite columns, whereas the trend was reversed with GAC columns, which is in agreement with the batch kinetics results (Fig. 2).

The adsorption and convection model (Equation (1)) was employed in order to extract the appropriate forward (adsorption) and backwards (desorption) coefficients (C_1 [M^{-1} min^{-1}]) and (D_1 [min^{-1}]) to be used later for model simulations and predictions. The model fits to the filtration results of simazine, atrazine and terbuthylazine by the composite columns were very good (Table 3), and described well the breakthrough volume at which the concentration eluted from the HPVP–CoS–MMT column exceeded the chosen limit. An arbitrary limit of 5% from the initial concentration was chosen (marked by dash line) Fig. 4. Simazine filtration by columns including the composite was extremely efficient (7 L before reaching the limit) in comparison with the

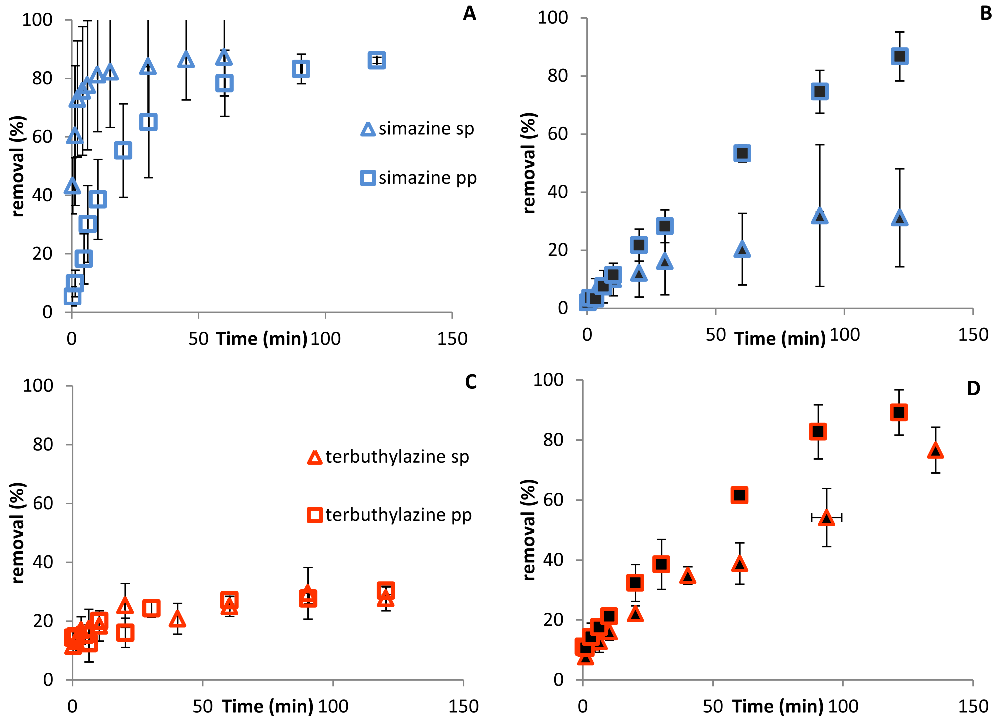


Fig. 3 – Binding kinetics of 1.5 mg L^{-1} simazine and/or terbuthylazine by 1 g L^{-1} HPVP–CoS–MMT composite [A, C] or GAC [B, D]. Binding kinetics of single pollutant [SP] triangles and of the pollutant in the presence of the other pollutant [PP] squares. Vertical and horizontal bars represent the standard deviations of the measured results.

GAC filters (0.07 L before reaching the limit). Terbuthylazine filtration was more efficient by the GAC columns (0.5 L before reaching the limit) in comparison with the composite one (0.07 L before reaching the limit).

The model fitting was better in the earlier stages of the filtration experiments both for simazine and atrazine (R^2 for-up to 20% emerging was 0.983 and 0.999 for simazine and atrazine, respectively), which is important in order for the

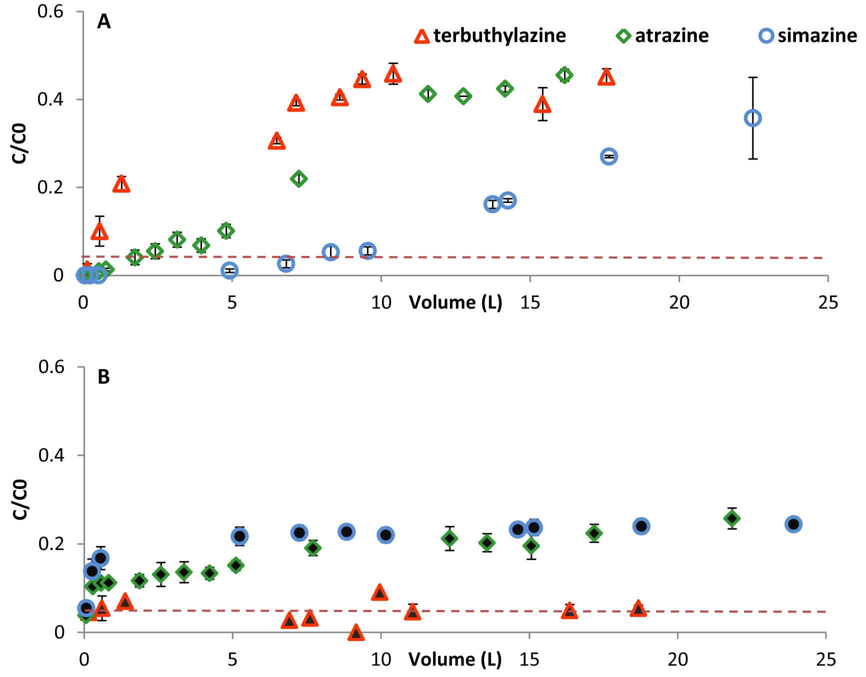


Fig. 4 – Filtration of 1 mg L^{-1} simazine (circles), atrazine (diamonds) and terbuthylazine (triangles) by columns which included 3.6 g HPVP–CoS–MMT [A] or GAC [B] mixed with sand at 1:20 (weight ratios). The dash line represents an emerging concentration of 5% from the initial value. Vertical bars represent the standard deviations of the measured results.

Table 3 – Adsorption and Convection model Equation 1, (Nir et al., 2012), goodness of fit and coefficients; C_1 [M^{-1} min^{-1}] forward adsorption, D_1 [min^{-1}] backward adsorption (desorption).

Herbicide	C_1 [M^{-1} min^{-1}]	D_1 [min^{-1}]	R^2
Simazine	68	0.00157	0.955
Atrazine	40	0.0016	0.961
Terbuthylazine	24	0.0013	0.906

model to accurately estimate the stage at which the emerging pollutant concentration exceeds the regulation limit.

It is of interest to note that the binding coefficients *K* (= $C_1 D_1^{-1}$, see Table 3) deduced from the kinetics of filtration, (e.g., for simazine 43,300 M^{-1}) was very close to the values deduced from the adsorption isotherms (44,000 M^{-1}) in suspension.

3.4.2. *Filtration of simazine: validation of model predictions*

In order to validate and test the predictions of the model, a filtration experiment with very different starting conditions (i.e., twice the column length, more than three times the width, one fifth of the sorbent concentration and higher initial simazine concentration) was performed.

The advantage of the HPVP–CoS–MMT filtration columns in comparison to the GAC columns is evident even at higher simazine concentrations and lower sorbent concentrations (Fig. 5). For comparison, after more than 30 L the percentage of simazine removed by the HPVP–CoS–MMT columns was 90.8% compared to 77.8% by GAC.

Even though the model was constructed for very different filtration conditions, applying the model yielded a good fit (i.e., $R^2 = 0.995$, RMSE = 7.8% see Table 4). Considering the satisfying prediction of the filtration experiment (and breakthrough point of the columns) we deduce that the model parameters are adequate to describe the filtration of simazine under wide range of conditions. Therefore, it is likely that the fitted model can further be employed for other scenarios.

3.4.3. *Simazine filtration – environmental concentrations: comparing experimental results and model predictions*

The filtration of nearly 120 L per column of 10 μg L^{-1} simazine, by composite and GAC columns mixed with sand at 1:40 weight ratios, was tested (Fig. 6). The emerging concentrations of simazine in the effluent from the HPVP–CoS–MMT columns throughout the entire experiment were lower than the USA regulation (3 μg L^{-1}), whereas the concentrations of simazine in the effluent from the GAC columns were above the limit reaching 3–4.5 μg L^{-1}.

Model predictions for the emerging simazine concentrations from the HPVP–CoS–MMT column were very good (Table 5). The model presents a very adequate estimation for simazine concentration in the column effluent; the relative differences between the model predictions and the experimental results are smaller than the estimated analytical method errors (30%). Consequently, the model calculations prove to be reliable for extrapolation of the prediction for different initial concentrations, or for attempting to achieve lower limits of simazine.

Using the model in order to extend the experiment and estimate the volume of water which can be purified below the regulation limit, suggested that another 48 L will emerge from the composite columns at less than 3 μg L^{-1} of simazine. After

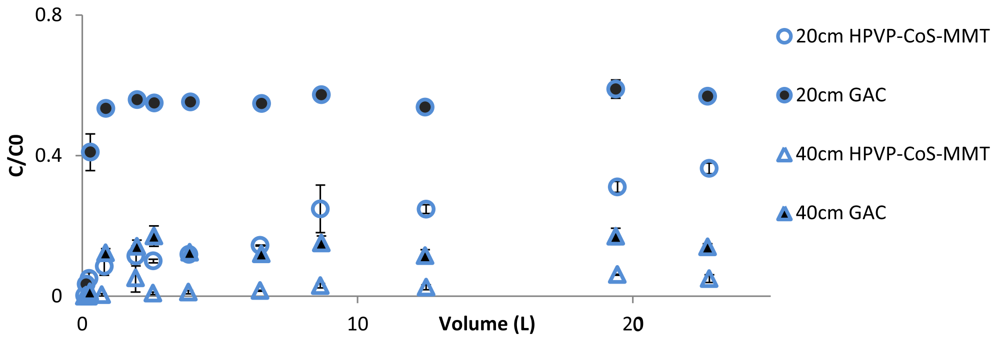


Fig. 5 – Filtration of 1.5 mg L^{-1} simazine by one 20 cm (circles) column or two 20 cm columns in series (triangles) each column included 6 g of HPVP–CoS–MMT [hollow symbols] or GAC [full symbols] mixed with sand at 1:100 (weight ratios). Vertical bars represent the standard deviations of the measured results.

Table 4 – Filtration of simazine (1.5 mg L^{-1}) by 20 and 40 cm filtration columns of HPVP–CoS– MMT mixed with sand (1:100); experimental results (standard deviation mentions in brackets) and model predictions.

Filtrated volume (liter)	20 cm Column (% removed)		40 cm Column (% removed)	
	Experimental (SD)	Calculated	Experimental (SD)	Calculated
0.8	91.5 (2.5)	99.0	99.6 (0.4)	100.0
2.6	90.0 (0.5)	98.2	99.2 (0.4)	100.0
8.7	75.2 (6.7)	93.8	97.0 (0.6)	99.8
12.4	75.2 (1.2)	89.7	97.5 (0.7)	99.6
26.3	60.9 (1.5)	68.3	93.0 (1.3)	97.2
43.1	46.2 (1.7)	37.8	80.9 (1.2)	88.4

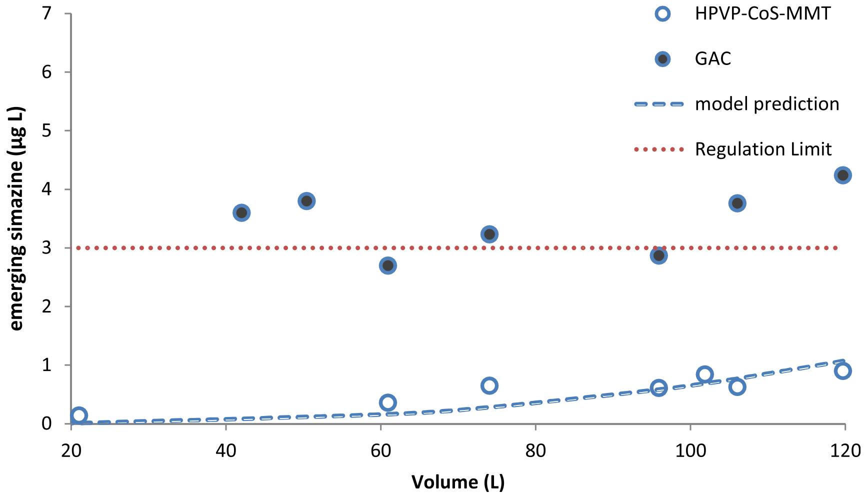


Fig. 6 – Filtration of 10 µg L^{-1} simazine by 40 cm columns, which included 26 g of HPVP–CoS–MMT [hollow symbols] or GAC [full symbols] mixed with sand at 1:40 (weight ratios). Analytical method standard error of 30%. Model predictions for emerging concentration of simazine are marked by dash line and simazine regulations limit (USA) of 3 µg L^{-1} is marked by dotted line.

passing 520 L, the concentration emerging equals the initial concentration, which implies that the use of the column after its breakthrough point as a pre filter, for the remaining 350 L, will be beneficial to extend the capacity of a new filter.

4. Conclusions

Triazine herbicides demonstrated high binding affinity to HPVP–CoS–MMT composite, which was attributed to π-π interaction with the polymer, in addition to hydrogen bonds which have a crucial kinetic effect. Herbicide binding affinity increased with a decrease in herbicide molecular size due to enhanced accessibility of the small herbicide, i.e., simazine, to the binding sites of the polymer. Simazine binding to HPVP–CoS–MMT composite in the presence of terbuthylazine was slower than its binding as a single pollutant whereas binding to GAC was enhanced in the presence of terbuthylazine, but in any case the binding kinetics of simazine to the composite was faster than to GAC. Model calculations adequately predicted simazine filtration by composite columns under a wide range of concentrations as well as environmental ones. At all concentrations tested, simazine filtration was significantly more efficient by the composite columns than by the GAC ones. These findings indicate that treating simazine by filtering with HPVP–CoS–MMT composite columns is a promising approach and that the methodology of modeling is likely to be suitable for upscaling this technology.

Table 5 – Filtration of simazine (10 µg L^{-1}) by 40 cm filtration columns of HPVP–CoS–MMT mixed with sand (1:40); experimental results (Analytical method standard error of 30%) and model predictions.

Filtrated volume (liter)	Simazine (removed %)	
	Experimental	Calculated
21	98.6	99.9
61	96.4	98.4
74	93.5	97.2
96	93.9	94.2
102	91.6	93.1
106	93.7	92.3
120	91.0	89.3

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