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# Atrazine removal from water by polycation–clay composites: Effect of dissolved organic matter and comparison to activated carbon

### Dikla Zadaka, Shlomo Nir, Adi Radian, Yael G. Mishael\*

Department of Soil and Water Sciences, Faculty of Agricultural, Food and Environmental Quality Sciences, The Hebrew University of Jerusalem, Rehovot 76100, Israel

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### ABSTRACT

Atrazine removal from water by two polycations pre-adsorbed on montmorillonite was studied. Batch experiments demonstrated that the most suitable composite poly (4vinylpyridine-co-styrene)-montmorillonite (PVP-co-S90%-mont.) removed 90-99% of atrazine (0.5-28 ppm) within 20-40 min at 0.367% w/w. Calculations employing Langmuir's equation could simulate and predict the kinetics and final extents of atrazine adsorption. Column filter experiments (columns  $20 \times 1.6$  cm) which included 2 g of the PVP-co-S90%mont. composite mixed with excess sand removed 93-96% of atrazine (800 ppb) for the first 800 pore volumes, whereas the same amount of granular activated carbon (GAC) removed 83-75%. In the presence of dissolved organic matter (DOM; 3.7 ppm) the efficiency of the GAC filter to remove atrazine decreased significantly (68-52% removal), whereas the corresponding efficiency of the PVP-co-S90%-mont. filter was only slightly influenced by DOM. At lower atrazine concentration (7 ppb) the PVP-co-S90%-mont. filter reduced even after 3000 pore volumes the emerging atrazine concentration below 3 ppb (USEPA standard). In the case of the GAC filter the emerging atrazine concentration was between 2.4 and 5.3  $\mu$ g/L even for the first 100 pore volumes. Thus, the PVP-co-S90%-mont. composite is a new efficient material for the removal of atrazine from water.

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### 1. Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) is currently one of the most widely applied herbicides in the US (Kiely et al., 2004). It has been detected at high concentrations in ground- and surface-waters all over Europe and North America (Graziano et al., 2006; Cerejeira et al., 2003; Papastergiou and Papadopoulou-Mourkidou, 2001; Van Maanen et al., 2001; U.S. Geological Survey, 2003) due to its extensive use, ability to persist in soils, low sediment partitioning, slow rate of degradation and its tendency to travel with water. In the US the upper

\* Corresponding author. Tel.: +972 8 948 9171; fax: +972 8 948 9856. E-mail address: mishael@agri.huji.ac.il (Y.G. Mishael).

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limit for atrazine in drinking water is 3 ppb, whereas the European Union legislation banned its use (since 2003) and fixed a limit of 0.1 ppb (Sass and Colangelo, 2006).

The most commonly used technology for atrazine removal from water is adsorption by granular activated carbon (GAC) (Li et al., 2003; Yue et al., 2006). A study (Jiang and Adams, 2006) comparing a variety of conventional drinking water treatment technologies for the removal of chloro-s-triazines found that ozonation efficiency varied with the water source. Sedimentation with alum and iron salts, excess lime/soda ash softening, and disinfection by free chlorine were all ineffective

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methods, whereas two GACs removed efficiently the chloro-striazines. Although GAC is considered the best alternative for atrazine treatment (Li et al., 2003; Yue et al., 2006) the presence of dissolved organic matter (DOM) reduces its effectiveness (Yue et al., 2006; Guo et al., 2007). Another common method for water treatment employs RO and NF membranes; however, this method is very expensive and numerous studies reported membrane fouling due to accumulation of colloidal particles on the membranes (Bonne et al., 2000; Plakas et al., 2006).

A number of studies explored modifying silicate minerals (clays and zeolites) as adsorbents for atrazine. Lemic et al. (2006) examined removal of atrazine, lindane and diazinone from water by organo-zeolites. However, the adsorption capacity for atrazine was the lowest (2.0 µmol/g). Sanchez-Martin et al. (2006) employed clay minerals modified by a cationic surfactant in batch and column experiments for the adsorption of pesticides. The results showed an increase in the adsorption ability compared to untreated clays, but the adsorption coefficient of atrazine was very low. Borisover et al. (2001) reached high sorption values of atrazine (98% after 18 h) on dye-clay complexes; however, the adsorbent concentration was very high (50 g/L). Modification of the clay minerals vermiculite and montmorillonite by intercalating Fe(III) polymers for the removal of atrazine and its metabolites was examined (Abate and Masini, 2005). Enhancement in the adsorption capacity was observed for both intercalated clays in comparison with the potassium-clays, although, the adsorption time was relatively high (24 h). The studies described above did not include the effect of DOM or a comparison to GAC.

Streat and Sweetland (1998) compared the adsorption of atrazine by Hypersol–Macronet polymer phases and by GAC F-400 and found that the GAC was more effective for the removal of atrazine than the polymer phases.

Only a few studies focused on applying polymer–clay composites as sorbents for organic pollutants (Churchman, 2002; Breen, 1999), e.g., the study of Churchman (2002) on the formation of polycation–clay composites and their use as sorbents for non-ionic and anionic pollutants. Breen (1999) examined the use of polycation–exchanged clays as sorbents for organic pollutants and studied the influence of layer charge on pollutant sorption capacity. Radian and Mishael (2008) studied the binding of an herbicide to polycation–clay composites for the design of controlled release herbicide formulations.

In this study we pioneered the design and testing of the polycation (4-vinylpyridine-co-styrene) (PVP-co-S)-clay (mont-morillonite) composites for the removal of atrazine from water in batch experiments and by filtration. The effect of DOM on atrazine removal by the polymer-clay composite and by GAC is reported.

### 2. Materials and methods

### 2.1. Materials

The clay used was Wyoming Na-montmorillonite SWy-2 obtained from Steetley Bentonite & Absorbents (Nottinghamshire, UK). Quartz sand (grain size 0.8–1.5 mm) was purchased from Shoshani & Weinstein (Israel). Atrazine (purity 98%) was supplied by



Fig. 1 – Chemical structure of (a) atrazine (b) PVP-co-S (m = 0.9, n = 0.1) and (c) PDADMAC.

Agan Makhteshim, Israel. Poly (4-vinylpyridine-co-styrene) (PVPco-S) (MW 105 K) and polydiallyldimethylammonium chloride (PDADMAC) (MW 400–500 K) were purchased from Sigma-Aldrich (Stenheim, Germany). Granular activated carbon Hydraffin 30 N and Hydraffin CC 8x30 were purchased from Benchmark Ltd., (Israel). HPLC grade acetonitrile and double desalinated water (DDW) were purchased from Merck (Darmstadt, Germany). Natural organic matter (NOM) (1R101 N and 1R108 N) was purchased from IHSS (International Humic Substances Society, USA) Structural formulas of polymers and herbicide are shown in Fig. 1.

### 2.2. Methods

## 2.2.1. Polycation adsorption on montmorillonite: composite preparation

The composites were prepared by applying batch experiments using 30 mL polycarbonate Oak Ridge centrifuge tubes. A PDADMAC solution (10 mL) was added to a clay suspension of montmorillonite (5 mL), reaching final concentrations of 0-40 g/L polycation and a suspension of 0.167% clay. The claypolycation suspension was agitated for 2 h (equilibrium reached within 1 h) using a shaker (Radian and Mishael, 2008). To dissolve PVP-co-S it was charged by adding H<sub>2</sub>SO<sub>4</sub> (95%). The co-polymer is composed of 1 styrene monomer for each 9 pyridine monomers. By adding stiochometric concentrations of H<sub>2</sub>SO<sub>4</sub> 45% (0.64 g/L) or 90% (1.28 g/L) of the monomerts (pyridine) were charged. PVP-co-S was mixed with the acid for 1 day to prepare PVP-co-S90% and for 4 days to prepare PVP-co-S45%. The charged PVP-co-S solutions were added (0-2 g/L) to a clay suspension of montmorillonite (1.67 g/L). The claypolycation suspensions were agitated for 24 h. Suspensions were centrifuged (10,000 rpm for 20 min). The precipitates were freeze-dried and the percent of carbon was measured using a CHNSO analyzer (Fisons, EA 1108). The amount of polymer adsorbed was calculated (maximum error +15%) according to the percent of carbon in the composites.

### 2.2.2. Zeta potential

The mobilities (converted to zeta potentials) of PVP-co-S90%, montmorillonite, and PVP-co-S90%-mont. composite (0.2 g polymer/g clay) were measured using a Zetasizer Nanosystem (Malvern Instruments, Southborough, MA). The clay and clay composites were measured in a diluted suspension (~0.05% clay).

### 2.2.3. X-ray diffraction

The basal X-ray diffraction spacings of montmorillonite and PVP-co-S90%-mont. composite (0.2 g polymer/g clay) were

measured. On a round glass slide, 1–2 mL of the suspension were placed and left to sediment (oriented sample) for one day. The basal spacing was measured using an X-ray diffractometer (Philips PW1830/3710/3020) with Cu KR radiation,  $\lambda = 1.526$ .

### 2.2.4. PVP-co-S solution reuse

The preparation of the 0.2 g/g PVP-co-S90%-mont. composite (applied for suspension and filtration experiments) requires a PVP-co-S90% concentration of 2 g/L (added to 1.67 g/L clay). However, only 0.33 g/L adsorb. In order to utilize the remaining PVP-co-S solution and reach an economical process the remaining PVP-co-S solution's concentration was brought back up to 2 g/L and reused to prepare another batch of composite by adding the relevant clay concentrations.

2.2.5. Atrazine binding to composites (batch experiments) Atrazine (25 mg/L) was added to centrifuge tubes containing the PDADMAC-mont., PVP-co-S90%-mont. or PVP-co-S45%mont. composites (0–0.8 g polymer/g clay). The tubes were agitated for 3 days.

For the kinetic and equilibrium experiments a freeze-dried PVP-co-S90%-mont. composite (0.2 g/g) was employed (prepared as described above). The experiments were performed at atrazine concentrations of 0.1–10 mg/L. Atrazine solutions (100 ml) were mixed with polymer–clay composites (reaching 3.67 or 0.367 g composite/L) and kept at  $25 \pm 1 \,^{\circ}$ C under continuous agitation for 5, 10, 20, 40 and 60 min for the high composite concentration (3.67 g/L) and for 24 h for the low composite concentration (0.367 g/L). Supernatants were separated by centrifugation (15000 rpm for 20 min) and prior to HPLC analysis filtered with modified acrylic polypropylene (Acrodisc Syringe Filters with Supor membrane, Pall Corp., Ann Arbor, MI) of 0.2 or 0.45  $\mu$ m pore size. Tests indicated that there was no sorption of atrazine by the filters. The experiments were performed in triplicate.

2.2.6. Modeling atrazine binding to the composites The Langmuir equation was employed as in Nir et al. (2000).

$$(L_0 - L)/L = R_0 k/(1 + k_0 L)$$
(1)

in which  $L_0$  and L denotes the molar concentration of total and free herbicide molecules, respectively.  $R_0$  is the molar concentration of sorbing surface sites, and k, whose unit is  $M^{-1}$ , is the binding coefficient. The equilibrium of adsorption was analyzed by two procedures. In one procedure as in Nir et al. (2000), we employed one parameter, the binding coefficient k, and  $R_0$  was equated to the molar concentration of exchangeable charges from the cation exchange capacity (CEC), i.e., 8e–4 mol/g clay. In another procedure Eq. (1) was used to determine k-values for assumed values of  $R_0$  for given experimental values of adsorbed amounts. The value chosen for  $R_0$  was the one which gave the smallest variation in k. Then in the next stage the value of k was fixed according to the best fit to the experimental data. The kinetics of adsorption was analyzed as follows (Undabeytia et al., 2008):

$$dL_i/dt = -C_iL_i(t)R(t) + D_i(R_0 - R(t))$$
(2)

In Eq. (2) the kinetic parameters  $C_i(M^{-1} \sec^{-1})$  and  $D_i(\sec^{-1})$ 

satisfy the relation  $ki = C_i/D_i$ . R(t) denotes the molar concentration of unoccupied sites of the sorbent. In our case n = i = 1.

# 2.2.7. Effect of DOM on atrazine adsorption by GAC and by the polymer–clay composite

An atrazine solution (0.85 mg/L) or an atrazine and DOM (NOM) solution that was passed through acrodisc filters of 0.45  $\mu$ m pore diameter (0.85 mg/L and 3.7 mg/L final concentration, respectively) were added to 30 mL polycarbonate oak ridge centrifuge tubes containing the GAC (Hydraffin 30 N or Hydraffin CC 8x30) or PVP-co-S90%–clay composite (3.67 g/L). The tubes were agitated for 60 min. The suspensions were passed through acrodisc filters (ISI, Israel) of 0.45  $\mu$ m pore diameter (there was no removal of atrazine by the filters) and analyzed by HPLC.

### 2.3. Column filter experiments

Column filter experiments were performed at two atrazine concentrations, 800  $\mu$ g/L and 7  $\mu$ g/L (trace concentration), in glass columns of 20 cm length and of 1.6 cm diameter. Due to some swelling of the composite, its mixing with a granular substance (e.g., quartz sand) is necessary to enable the flow through the column. Preliminary experiments showed no significant adsorption of atrazine by the quartz sand. For the experiment with 800 µg/L atrazine the columns were filled with 38 g sand mixed with 2 g of composite or with a layer of 2 g of GAC in the middle of the column and the rest of the column filled with 38 g sand. For the experiment with 7  $\mu$ g/L atrazine the filter included 1 g of composite or GAC and 39 g of sand as above. The bottom of the columns was covered by 2 cm layer of quartz sand. Quartz sand was thoroughly washed in distilled water and dried at 105 °C for 24 h. Non woven polypropylene geo textile filters (Markham Culverts Ltd., Papua New Guinea) were placed on both sides of the column to prevent exit of the sand and the composite from the column. Prior to filtration the column was connected to a peristaltic pump and saturated by distilled water from the bottom (2 ml/min). Twenty-five liters of atrazine at a concentration of 800  $\mu$ g/L (for the composite filter a pH of 3  $\pm$  0.3 was adjusted by H<sub>2</sub>SO<sub>4</sub>) with and without DOM (3.7 mg/L) were passed through the composite and GAC columns at a rate of 3.3 mL/min. Fifty liters of atrazine at a concentration of 7  $\mu$ g/L (for the composite filter a pH of  $3 \pm 0.3$  was adjusted by H<sub>2</sub>SO<sub>4</sub>) were passed through the composite and GAC columns at a rate of 3.3 mL/min. The eluate was collected for analysis. One pore volume was 13.8 or 17.6 ml for composite or GAC filters, respectively.

#### 2.4. Atrazine analysis

High atrazine concentrations (mg/L) were analyzed by HPLC and low atrazine concentrations ( $\mu$ g/L) were analyzed by GC– MS. The HPLC (Agilent Technologies 1200 series) was equipped with a diode-array detector. HPLC column was LiChroCART<sup>R</sup> 250-4 Purospher<sup>R</sup> STAR RP-18 (5  $\mu$ m), and the flow rate was 1.0 mL/min<sup>-1</sup>. Measurements were carried out isocratically. A mobile phase of acetonitrile/water (70/30) was used. The concentrations of atrazine were measured at a wavelength of 222 nm. Detection limit was 0.01 ppm.

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For GC–MS analysis, atrazine water samples were extracted based on Method 525.2 "Determination of organic compounds in drinking water by liquid–solid extraction and capillary chromatography/mass spectrometry", U.S. Environmental Protection Agency (Revision 2.0). GC–MS measurements were performed with Finnigan Polaris/GCQ Plus TM fitted with DB-5.MS capillary column, 30 m × 0.25 mm inside diameter of 0.25  $\mu$ m film thickness. The carrier gas was helium (linear velocity was 33 cm/s). Injector temperature was 260 °C. The oven temperature was held at 45 °C for 1 min, then raised at 40 °C/min to 160 °C, followed by 5 °C/min to 295 °C, and finally raised at 40 °C/min up to 315 °C. Phenanthrene  $d_{10}$  was used as the internal standard.

### 3. Results and discussion

### 3.1. Atrazine binding to polymer–clay composites in suspension

### 3.1.1. Polymer-mont. composites

Three polymer–clay composites, PDADMAC-mont., PVP-co-S90%-mont. and PVP-co-S45%-mont. were examined for the removal of atrazine from water. PDADMAC is a widely used polymer in water treatment (Tian et al., 2005; Bendoraitiene et al., 2006). Radian and Mishael (2008) designed PDADMAC-mont. composites to bind an anionic herbicide, imazapyr. PDADMAC adsorption on the clay reached a high loading, which resulted in charge reversal of the clay and promoted imazapyr binding. The composites were characterized by Fourier transform infrared, zeta potential ( $\xi$ ) and X-ray diffraction measurements indicating electrostatic interactions of the polycation with the surface, polycation intercalation in the clay and suggesting a configuration as loops and tails on the surface at high loadings.

In the current study we characterized the PVP-co-S45%and PVP-co-S90%-mont. composites by zeta potential and X-ray diffraction measurements. The measured  $\xi$  of the clay was -50 mV and the  $\xi$  of PVP-co-S90 and of PVP-co-S45 were 53 and 32 mV, respectively. Measurements of  $\xi$  indicate that charge neutralization is reached at a low polymer loading of 0.08 g polymer/g clay for PVP-co-S90 and at a higher loading of 0.3 g/g for PVP-co-S45 due to its lower charge density. Calculated neutralization was based on overall stoichiometric adsorption of the positively charged monomers equivalent to the CEC (Radian and Mishael, 2008). The PVP-co-S90% was employed in the current study at a loading of 0.2 g polymer/g clay. At this loading the composite was positively charged (30 mV).

The XRD patterns of montmorillonite, PVP-co-S45%-mont and of PVP-co-S90%-mont. composite (0.2 g/g) were measured. The d001 spacings were obtained by using the first rational orders corresponding to the 001 reflection. The intercalation of the polycation in the clay interlayers is confirmed by the decrease of  $2\theta$  values as the polymer–clay ratio increases. The air-dried sample of montmorillonite gave the expected basal spacing of 1.25 nm. XRD measurements of both PVP-co-S composites indicated that only one layer of polymer intercalates in the clay (Radian and Mishael, 2008). The 0.2 g PVP-co-S90%/g clay composite gave a basal spacing of 1.48 nm.



Fig. 2 – Atrazine (25 ppm) binding to polymer-clay composites (3.67 gL) as a function of polymer loading.

The design of the PVP-co-S clay composites for atrazine removal from water is based on the hypothesis that "like attracts like" i.e., a structural compatibility between atrazine and the PVP-co-S polymer (see chemical structures in Fig. 1). This structural compatibility between the s-triazine ring of atrazine and the pyridine rings of PVP and the styrene ring will promote atrazine binding by the PVP-co-S composites. The high binding of atrazine to PVP-co-S composites in comparison to its low binding to PDADMAC composites, which have no structural compatibility with atrazine, supports this hypothesis (Fig. 2).

Polycations with a high charge density usually adsorb as trains, whereas polymers with a low charge density may adsorb as loops and tails on a negatively charged surface (Breen, 1999). Such a configuration should produce more hydrophobic areas in the composite available for interactions and therefore increase atrazine binding. However, atrazine binding to a high charge density polymer (PVP-co-S90%) adsorbed on montmorillonite (0.2 g/g) was high (93%) in comparison with its binding to the lower charge density polymer (PVP-co-S45%)-clay composite (0.2 g/g) which only reached 58% binding. The advantage of the PVP-co-S90% composite to bind atrazine correlated with the result that in this case the pH is lower, as will be discussed later. The highest atrazine binding (96%) to PVP-co-S90%-clay composites was achieved at polymer loadings ranging from 0.15 to 0.25 g polymer/g clay (Fig. 2). We further employed the 0.2 g polymer/g clay in this study.

### 3.1.2. Kinetics of atrazine binding

The kinetics of atrazine binding at several initial concentrations (0.2–10 mg/L) to the PVP-co-S90%-mont. composites (3.67 g/L) is shown in Fig. 3. Atrazine removal from water was 90–99% even at its high concentrations. The removal was maximal after 20–40 min. For comparison, 94–98% of atrazine (24.5 mg/L) was bound by dye–clay complexes at a much higher concentration (50 g/L) after 18 h (Borisover et al., 2001); Organovermiculite (10 g/L) bound 50–60% of atrazine (0.25 mg/L) after 24 h (Abate and Masini, 2005); GAC's (from waste charcoal, 20 g/L) bound about 89% of atrazine (5 mg/L) after 2 h (equilibrium time) (Ghosh and Philip, 2005).

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Fig. 3 – Kinetics of atrazine (0.2–10 ppm) binding to PVP-co-S90%-mont. composite (3.67 g/L). Experimental errors 0.1–6%.

### 3.1.3. Modeling of atrazine binding to

#### PVP-co-S90%-mont. composites

In order to have a more reliable estimation of Ro, the concentration of composite sites for atrazine sorption, we considered several concentrations of the composite (0.2 g polymer/g clay), focusing on a smaller concentration, 0.367 g/L, i.e., 0.311 g clay/L. The results of atrazine (0.5 to 28 mg/L) bound at equilibrium to the composite at concentrations of 3.67 and 0.367 g/L are shown in Fig. 4 together with the calculated values. For the high composite concentration (3.67 g/L) the fractions of atrazine bound were 90–99%.

The analysis which fixed the value of  $R_0$  from the CEC of the clay was inadequate, since it yielded serious overestimates for the percents of atrazine adsorption for the relatively large atrazine concentrations and small composite concentrations. The value determined for  $R_0$  for a composite concentration of 0.367 g/L was 3.2E–5 M, whereas fixing the value according to the CEC of the clay would give 2.5E–4 M, i.e., 7.8-fold larger. The value determined for k was 36,000 M<sup>-1</sup>. The value of  $R^2$  was 0.94 and the RMSE (Root mean square error) was 4.1%, i.e., within experimental error. The values of the kinetic



Fig. 4 – Atrazine binding to PVP-co-S90%-mont. composites at equilibrium (24 h for 0.367 g/L composite and 60 min for 3.67 g/L composite).  $C_0$  = initial concentration of atrazine (mg/L).

| Table 1 – Atrazine (0.85 ppm) binding to PVP-co-S90%-  |
|--------------------------------------------------------|
| mont. composite and GAC (3.67 g/L) with or without DOM |

| Adsorbent                                        | DOM<br>(ppm)              | pН                                                                                           | Atrazine<br>bound (%)                                                                       | Atrazine bound<br>(mg/gr adsorbent)                                                                                        |
|--------------------------------------------------|---------------------------|----------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------|
| PVP-co-S90%-<br>mont.<br>GAC<br>(Hydraffin 30 N) | 0<br>3.7<br>0<br>3.7<br>0 | $\begin{array}{c} 3 \pm 0.3 \\ 3 \pm 0.3 \\ 6 \pm 0.3 \\ 6 \pm 0.3 \\ 3 \pm 0.3 \end{array}$ | $\begin{array}{c} 97 \pm 0.5 \\ 96 \pm 0.6 \\ 95 \pm 1 \\ 89 \pm 1 \\ 92 \pm 1 \end{array}$ | $\begin{array}{c} 0.226 \pm 0.001 \\ 0.221 \pm 0.001 \\ 0.219 \pm 0.003 \\ 0.206 \pm 0.002 \\ 0.213 \pm 0.003 \end{array}$ |

parameters, which were employed in fitting the results in Fig. 3 were  $C_1 = 600 \text{ M}^{-1} \text{ min}^{-1}$  and  $D_1 = 0.016 \text{ min}^{-1}$ .

3.1.4. Effect of DOM on atrazine adsorption by GAC and by the PVP-co-S90%-mont. composite

It is well-known that the presence of DOM reduces binding of organic pollutants to adsorbents. We compared the removal of atrazine, with DOM, by the PVP-co-S90%-mont. composite with its removal by two commercially available GACs. The presence of 3.7 ppm DOM, (concentration frequently present in natural waters) resulted in a reduction in atrazine removal as shown in Table 1. The magnitude of this reduction was larger for atrazine binding by GAC; we also considered another type of GAC, Hydraffin CC 8x30, which gave similar results (not shown). Thus the results indicate another advantage of the PVP-co-S90%-mont. composite. A similar trend of the effect of DOM impact will be shown in the filtration experiments. As pointed out the pH of the atrazine solutions was  $3 \pm 0.3$  when the PVP-co-S composite was employed. However, lowering the pH did not improve atrazine removal by GAC (Table 1).

Guo et al. (2007) examined the impact of DOM on the adsorption of atrazine by five GACs and found that all 5 GACs were influenced by DOM (5 or 20 mg/L). The F400He and HD4000ST (carbons with a broader pore size distribution) exhibited a smaller reduction in their adsorption capacities (15–67% depending on the DOM concentration) than the ACF10 and OLC (microporous carbons) (36–99%).

### 3.2. Column filter experiments

In these experiments we considered the initial concentrations of atrazine, 800  $\mu$ g/L (Fig. 5) and 7  $\mu$ g/L, and the effect of DOM was recorded. The flow rate was 3.3 mL/min which corresponds to 1 m/h. In the column filter experiments with the PVP-co-S90%-mont. composite we added H<sub>2</sub>SO<sub>4</sub> to the atrazine solution in order to obtain a pH value of  $3 \pm 0.3$  as in the batch experiments. This low pH value stabilized the PVP-co-S90%mont. composite, i.e., prevented the release of the polymer from the composite. At higher pH release of the polymer from the composite was observed (not shown). It is expected that polymer release reduces the effectiveness of the PVP-co-S90%mont. composite filter to bind atrazine. At neutral and basic pH the polymer has a fewer charges; consequently its binding to the clay is weaker. The results of the batch experiments, which demonstrated higher atrazine removal by employing PVP-co-S90%-mont. (low pH) rather then PVP-co-S45%-mont. (higher pH), support this explanation. The addition of H<sub>2</sub>SO<sub>4</sub> did not improve the binding of the atrazine to GAC (Table 1).



Fig. 5 – Column filter experiments for atrazine (800 ppb) removal by PVP-co-S90%-mont. composite filter and GAC filter (columns  $20 \times 1.6$  cm) in the presence (circles) and absence (triangles) of 3.7 ppm DOM.

The column filter experiments (Fig. 5) which employed equal weights of PVP-co-S90%-mont. composite or GAC (2 gr) show that the PVP-co-S90%-mont. composite filter is more efficient in removing atrazine ( $800 \mu g/L$ ) from water than the GAC filter. For the first 800 pore volumes PVP-co-S90%-mont. composite filter removed 93–96% of atrazine, whereas the GAC filter removed 83–75%. In the presence of DOM the efficiency of the GAC filter to remove atrazine from water decreased significantly (68–52% removal), whereas, the corresponding efficiency of the PVP-co-S90%-mont. composite filter was only slightly influenced by the presence of DOM.

This high efficiency of atrazine removal by the polymerclay composite filter in the presence of DOM is an advantage of this adsorbent versus GAC, which makes this new composite promising for water purification and treatment from atrazine.

Yue et al. (2006) conducted breakthrough tests of chemically activated fiber (CAF) and GAC (F-400) filters with an atrazine solution (100  $\mu$ g/L) with and without humic acid (5 mg/L). The results showed that the GAC filter did not remove atrazine down to 3 ppb in the presence of a high concentration of humic acid, indicating that the presence of humic acid greatly slows down the rate of adsorption of atrazine onto the GAC. Li et al. (2003) reported that natural organic matter adversely affects both the equilibrium and kinetics of atrazine adsorption by activated carbon through two major competitive mechanisms: direct site competition and pore constriction/blockage.

At the lower atrazine concentration (7  $\mu$ g/L) the amount of adsorbing material was lowered to 1 gr. For the 3000 pore volumes PVP-co-S90%-mont. composite filter reduced the

atrazine concentration below  $3 \mu g/L$ , which is the current USEPA standard. In the case of the GAC filter the emerging atrazine concentration was between 2.4 and 5.3  $\mu g/L$  even for the first 100 pore volumes.

The column filter experiments emphasize the higher efficiency and capacity of the polymer–clay filter than that of the GAC one, particularly in the presence of DOM.

### 4. Conclusions

In the current study we designed polymer–clay composites and examined their relative efficiency to remove atrazine from water in comparison with GAC. The removal of atrazine by the PVP-co-S90%- mont. composite was (1) higher than its removal by other substrates examined (including GAC). (2) Insignificantly influenced by the presence of DOM (3.7 mg/L) unlike the reduction in atrazine removal by GAC. (3) Found to be more efficient also in column filtration experiments at relatively high (800 µg/L) and low (7 µg/L) concentrations of atrazine. In addition, the polymer–clay composite filter succeeded in reducing atrazine concentrations below the current USEPA standard.

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