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4 **A CLAY-VESICLE SYSTEM FOR WATER PURIFICATION FROM ORGANIC**
5 **POLLUTANTS**

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7 TOMAS UNDABEYTIA^{*†}, SHLOMO NIR[‡], TRINIDAD SÁNCHEZ-VERDEJO[†],
8 JAIME VILLAVERDE[†], CELIA MAQUEDA[†], ESMERALDA MORILLO[†].

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10 (†). Institute of Natural Resources and Agrobiology, CSIC, Apdo 1052, 41080 Sevilla,
11 Spain.

12 (‡). Faculty of Agricultural, Food and Environmental Quality Sciences, Hebrew
13 University of Jerusalem, Rehovot 76100, Israel.

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16
17
18 *Corresponding author; phone: +34-954624711; fax: +34-954624002, e-mail:

19 undabeyt@irnase.csic.es

Abstract

Vesicle-clay complexes in which positively charged vesicles composed of didodecyldimethylammonium (DDAB) were adsorbed on montmorillonite removed efficiently anionic (sulfentrazone, imazaquin) and neutral (alachlor, atrazine) pollutants from water. These complexes (0.5% w:w) removed 92-100% of sulfentrazone, imazaquin and alachlor and 60% of atrazine from a solution containing 10 mg/L. A synergistic effect on the adsorption of atrazine was observed when all pollutants were present simultaneously (30 mg/L each), its percentage of removal being 85.5. Column filters (18 cm) filled with a mixture of quartz sand and vesicle-clay (100:1, w:w) were tested. For the passage of 1 L (25 pore volumes) of a solution including all the pollutants at 10 mg/L each, removal was complete for sulfentrazone and imazaquin, 94% for alachlor and 53.1% for atrazine, whereas removal was significantly less efficient when using activated carbon. A similar advantage of the vesicle-clay filter was observed for the capacities of removal.

1. Introduction

Water purification procedures have employed flocculation, ion exchange, oxidation/reduction, aeration, chlorination, media filters and activated carbon (Beall, 2003). Activated carbon (AC) has been usually employed in fixed bed columns for wastewater treatment and environmental remediation, which has been efficient in the removal of certain pesticides, surfactants, chlorine (Paune et al., 1998). However, the presence of large molecules, such as humic acids, emulsified oil or grease will reduce the adsorbed amounts because of pore constriction; blockage of the primary micropores; and direct competition for adsorption sites (Pelekani and Snoeyink, 2001).

Natural and modified clay minerals and zeolites are good candidates for improving AC performance, because they have large surface areas for retention of pollutants (Ruzinski et al., 1994; Li et al., 2000; Watanabe et al., 2004). Calcined hydrotalcites can remove very efficiently organic molecules, such as anionic pesticides (Li et al., 2005), or phenols (San Miguel et al., 2003). The hydrophilic surface of montmorillonite can be partially or fully modified to hydrophobic by adsorption of cationic surfactants (Zhang et al., 1993; Smith et al., 1995; Xu et al., 1997; Borisover et al., 2001). Organoclays were shown to compete with AC for retention of a variety of organic contaminants (Beall, 2003; Ake et al., 2003). The use of organoclays to enhance carbon filtration in industrial processes is starting to be implemented (Alther, 2002).

The objective of the current work is to design an efficient technology for water purification from organic pollutants by using a vesicle-clay system. Pollutants will bind to vesicles formed by the cationic double chain surfactant didodecyldimethylammonium bromide (DDAB; Fig.1) which adsorb on the negatively charged platelets of the clay mineral montmorillonite. The formed complex has an advantage as a sorbent of organic pollutants in possessing a large number of hydrophobic sites in the core of vesicular

bilayers. In addition, by preparing the complex with excess of positive charges, it may become an ideal sorbent for anionic organic pollutants. Undabeytia et al. (2003) showed that this vesicle-clay system enhanced the retention of anionic molecules of herbicides compared to organo-montmorillonite where surfactant adsorption as monomers on the clay was occurring. So far, most of the surfactants used in water treatment processes have been of the type of alkylammonium with only one long-alkyl chain (Ake et al., 2003). Recent studies demonstrated an efficient removal of several neutral and anionic pollutants by the micelle-clay system (Polubesova et al., 2005; 2006). The micelle-clay system has some similarity to the vesicle-clay one based on DDAB, since the micelles composed of organic cations with a single alkyl chain have a hydrophobic core and positively charged external surfaces. However, there is critical difference in the concentration of the monomers in solution, which is several orders of magnitude smaller in the case of vesicles in comparison with micelles. This characteristic may have one advantage in reducing the possible concentration of surfactants in solution in the course of the purification of water. Minimizing monomer concentration in solution was solved in Polubesova et al. (2005) by an addition of a layer of clay mixed with sand in the filter whose purpose was to capture the organic cations which might be released from the complex during the process of filtration. The use of vesicle-forming surfactants presents additional sorbents for optimizing interactions with particular pollutants. The selected pollutants studied were widely-used anionic (imazaquin and sulfentrazone) and neutral (alachlor and atrazine) herbicides (Fig.1), which have been reported to cause water contamination (Xue and Xu, 2006).

2. Materials and methods

2.1. Materials.

The clay used was Wyoming Na-montmorillonite SWy-2 obtained from the Source Clays Repository (Clay Minerals Society, Columbia, MO). Quartz sand (grain size ~1-2 mm) was purchased from Panreac SA (Barcelona, Spain). DDAB, AC (2-12 μ m average particle size) and the herbicides alachlor, atrazine and imazaquin (analytical grade) were purchased from Sigma-Aldrich (Sigma Chemical Co., St Louis, MO). Technical sulfentrazone was supplied by Agan Makteshim, Israel. Structural formulas of the surfactant and the herbicides are shown in Figure 1. Dialysis equilibrium bags (MWCO 10000 D) were obtained from Spectrum Laboratories Inc. (Ft. Lauderdale, FL & Savannah, GA U.S.A).

2.2. Adsorption.

Adsorption experiments were performed in triplicate by two procedures. In the first procedure, solutions of pollutants were incubated for 1 h with DDAB vesicles followed by addition of a 5 g/L clay (final) concentration. The vesicle-clay mixtures were shaken for another 1 h, centrifuged at 25000 g and analyzed for the concentration of pollutants in the supernatant. Extended times to 1 day of either incubation of vesicles with pollutants or their adsorption on the clay did not improve the pollutant retention on the clay. Two DDAB concentrations were employed, 3 and 6 mM, so that adsorption of DDAB vesicles on the clay was respectively below and above the CEC of the clay (0.8 mmol/g). Initial concentrations of the herbicides were 10 mg/L with the exception of the less soluble atrazine for which a 8 mg/L concentration was used.

In the second procedure, adsorption experiments employed a dry DDAB-clay complex prepared at the same vesicle-clay ratios as those used in the first procedure. The DDAB-clay complexes were prepared by stirring the suspensions for 24h, then they were centrifuged at 25000 g, the supernatants discarded and the complexes lyophilized. The

organic cation was fully adsorbed on the clay for a 3 mM DDAB solution as determined by CHNSO analysis, whereas a value of 1.114 mmol /g clay was obtained for a 6 mM DDAB solution. These DDAB adsorbed amounts were also obtained in the first procedure where DDAB adsorption was not affected by the presence of herbicide molecules in the solution.

The amount of DDAB-clay complex used for the adsorption experiments of pollutants was determined on the basis of a final 5g/L clay concentration as in the first procedure.

Adsorption and desorption kinetics were determined by using the DDAB-clay prepared from 6 mM and 5 g/L by measuring the amount of herbicide remaining in the supernatant after centrifuging for given time intervals. The DDAB-clay concentration used was 2 g L⁻¹. The desorption step was performed by replacing the whole supernatant with water after 1 h, in which case equilibrium was reached, and equilibrating for certain times proceeding immediately as in the adsorption step.

Adsorption experiments using this DDAB-clay complex in the presence of several electrolytes was also determined. The employed concentrations were 10 mg L⁻¹ for the herbicides and 5g L⁻¹ for the complex.

Adsorption isotherms of the herbicides on the DDAB-clay complex prepared at a 6mM DDAB: 5g/L clay ratio was performed. The concentration of DDAB-clay complex was 1.6 g/L. The concentrations of herbicides ranged from 0 to 50 mg/L for imazaquin and sulfentrazone; from 0 to 25 mg/L for atrazine and from 0 to 175 mg/L for alachlor.

2.3. X-ray Diffraction.

X-ray diffraction of oriented samples of the clay-DDAB complexes on glass slides were measured using a Siemens D-5000 X-ray diffractometer with Ni-filtered CuK α radiation.

2.4. Column filter experiments.

Column filter experiments were performed with 100/1 (w/w) mixture of quartz sand and DDAB-clay complex (18 cm layer) in a column of 24 cm length and 4.5 cm diameter.

The bottom of the column was covered by 3 cm layer of quartz sand, which was previously passed through a 1 mm sieve. The DDAB-clay complex used was prepared from adsorption of 6 mM DDAB on a 5 g/L clay concentration as described earlier. The column was filled with 408.9 g of sand mixed with 4.1 g of DDAB-clay complex, which contained 1.38 g of DDAB (minus the bromide). This mixture was previously shaken for 24 h. A non- woven polypropylene geotextile filter (Markham Culverts Ltd., Papua New Guinea) was placed on the bottom of the column. The same type of column was prepared by mixing 1.38 g of activated carbon with 411.6 g of sand. Polubesova et al.(2006) showed that mixing AC with sand or using AC and sand as two layers gave the same outcome. The pore volume of both column types was 40 mL and the bulk density 1.32 g L^{-1} . The hydraulic conductivities were $2.2 \cdot 10^{-2}$ and $3.5 \cdot 10^{-2} \text{ cm s}^{-1}$ for the AC and clay-DDAB systems, respectively. The column was connected to a peristaltic pump and saturated at a constant flow of 4.6 ml/min. A 1L solution containing simultaneously 10 mg/L of imazaquin, alachlor and sulfentrazone, and 8 mg/L of atrazine was passed through both column types.

In another set of experiments, successive volumes of a 50 mg/L solution of either alachlor or sulfentrazone were passed through both column types and the residual herbicide in the eluates was determined. The total volume of the herbicide solution passed through the column was 5 L.

2.5. Analysis of pollutants.

Solutions were analyzed by using a Shimadzu HPLC equipped with a PDA detector. The reverse phase column used was a 15 cm Kromasil 100 C18. Measurements were performed isocratically. The flow rate was 1.0 mL/min except for imazaquin where a higher rate was used (1.4 mL/min). For neutral herbicides the mobile phases used were acetonitrile/water (60/40) for alachlor, and methanol/water (60/40) for atrazine. For anionic herbicides the mobile phases were binary mixtures of acetonitrile with water acidified to pH 2.58 by phosphoric acid for imazaquin, and to pH 3.25 by trifluoroacetic acid for sulfentrazone. The acetonitrile/water ratios employed were 45/55 for sulfentrazone and 30/70 for imazaquin. The concentrations of pollutants were measured at the following wavelengths: sulfentrazone and alachlor at 220 nm; imazaquin at 240 nm; and atrazine at 230 nm. Retention times were 6.00 min for atrazine; 6.50 min for alachlor; 5.25 min for sulfentrazone and 6.10 min for imazaquin. The presence of DDAB molecules did not interfere in the analytical determination of the herbicides.

2.6. Analysis of adsorption isotherms.

The Langmuir equation was employed as in Nir et al. (2000)

$$(L_0 - L)/L = R_0 \cdot k / (1 + k \cdot L), \quad [1]$$

in which L_0 and L denote 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. As in Nir et al. (2000), we employed one parameter, the binding coefficient k .

The extension of the Langmuir equation to several pollutants, $i=1 \dots n$ considered the kinetics of their adsorption as follows:

$$dLi/dt = -C_i \cdot Li(t) \cdot R(t) + D_i \cdot (R_0 - R(t)) \quad [2]$$

In Eq(2) the kinetic parameters C_i ($M^{-1}Sec^{-1}$), forward constant of adsorption, and D_i (Sec^{-1}), rate constant of dissociation, satisfy the relation $k_i = C_i / D_i$. $R(t)$ denotes the molar concentration of unoccupied sites of the sorbent. This set of equations was solved by a Taylor series as described previously (Nir et al., 1994) up to equilibration. The tests on the Fortran program included a change in the order of pollutants and agreement with Eq(1) for $n=1$.

3. Results and discussion.

3.1. Adsorption of pollutants from single component solutions.

Removal of pollutants by incubation with DDAB vesicles followed by clay addition gave very high percentage of removal for the anionic sulfentrazone and somewhat less for the anionic imazaquin (Table 1). Since both herbicides do not adsorb on the clay per se, the higher sulfentrazone adsorption was due to its higher binding to DDAB vesicles, which were completely adsorbed by the clay (5 g/L) for a 3 mM DDAB concentration. A 2-fold increase in DDAB concentration increased the fraction of imazaquin molecules bound to vesicles in solution, but in this case only 93% of the vesicles adsorbed; consequently the removal efficiency only improved by about 2%. In the case of neutral pollutants, the removal of alachlor from water was highly efficient (94.9%) for the incubation with 3 mM DDAB, but the removal of atrazine was poor, its efficiency increasing only up to 60% when using a 2-fold larger DDAB concentration. It may be noted that atrazine yields lower adsorption despite its low solubility (32 mg/L vs 240 mg/L for alachlor). These results outline the importance of the chemical nature of the herbicide for its incorporation in the vesicle. The larger aromaticity of atrazine

may impede the close approach of this molecule to the non-hydrophobic environment of the vesicle .

The binding of pollutants to cationic vesicles can be by either a partition mechanism inside the core of the vesicles through hydrophobic interactions, or for the anionic herbicides also by electrostatic interactions between the negatively charged moieties of the pollutants with the positively charged headgroups. In addition, aromatic apolar compounds may interact in the palisade (external) region of the vesicle through π -interactions of the rings with the electric field induced by the cationic charge of surfactant groups (Abe and Kondo, 1999).

Imazaquin molecules are mostly negatively charged at the equilibrium pH of the DDAB solutions (pH~4.35), whereas sulfentrazone is mostly in neutral form (pKa=6.56).

However, the high affinity of sulfentrazone for DDAB vesicles suggests an induced dissociation of its molecules in the presence of vesicles, which is enhanced by the stabilization of the anion through the formation of ionic pairs with the positively charged cations forming the vesicle, as was proposed in the case of cationic micelles (Polubesova et al, 2003).

The addition of the clay-vesicle complex to the pollutant solution instead of first incubating the pollutants with the vesicles increased the removal of the herbicides except for the case of alachlor (Table 1). Multiple adsorption mechanisms may be operating in the adsorption of pollutants by the clay-DDAB complex which would be dependent on the configuration of the organic cation within the interlayer space (Sheng et al., 1996a; 1996b). X-ray diffraction results (data not shown) indicate a bilayer arrangement of the organic cation parallel to the basal plane of the clay for a 3 mM DDAB adsorption, whereas a paraffin-type bilayer is obtained for a two-fold higher DDAB concentration. Paraffin configurations will enhance the molecular density of the

bilayers by counteracting the repulsion between the charged headgroups adsorbing onto a small surface area of the clay, and hence the organo-clay will be a more effective partition phase than that of the DDAB vesicles.

In general, the higher adsorption of herbicides by the clay-lipid complex than by first incubating them with the vesicles, is in agreement with previous observations where sorbed surfactants were more effective in partitioning the chemicals than their aggregates in solution (Nayyar et al., 1994; Ko et al., 1998). Chen et al. (2005) obtained carbon-normalized solute distribution coefficients on the uptake of organics by montmorillonite exchanged with myristylpyridinium, which always exceeded the corresponding aqueous micelle-water partition coefficients. In the current study, a similar phenomenon is noted for the adsorption of the herbicides from a 3mM DDAB solution where the removal of the contaminants was usually lower than by the clay treated with the surfactant solution, despite the fact that all the vesicles were adsorbed. It should be recalled that binding of pollutants by the vesicles usually occurs exclusively by the external monolayer, whereas in adsorption by the vesicle-clay complex the inner monolayer is also exposed (Undabeytia et al., 2004). In the case of alachlor it can be speculated that its binding is favored by the vesicular structure, rather than by the modified structure following an interaction with the clay mineral. It should be added that the difference is small and that some additional adsorption of alachlor does occur on montmorillonite alone (Nir et al., 2000).

Table 2 shows the kinetics of adsorption/desorption of the pollutants on the clay-DDAB complex prepared from a 6 mM DDAB-clay solution and 5 g/L clay. The sorbent concentration used in this case was 2.5-fold lower than that used in Table 1; however, the reduction in the adsorbed amounts once the equilibrium was reached was negligible for sulfentrazone and very low for imazaquin, whereas in the case of the neutral

herbicide alachlor adsorption is slightly reduced by 12%, in contrast to the other neutral pollutant, atrazine, which shows very little adsorption. Adsorption of the pollutants was completed in 30 min indicating a very fast process. More than 86% of the adsorbed amounts occurred in the first 10 min, with the exception of alachlor.

Desorption of the pollutants was fully reached in 1 h and presumably in shorter times. The desorbed amounts were very low for the anionic herbicides so that most of the added pollutant is strongly retained by the complex. Alachlor desorption was about 20% of the adsorbed amount and a much higher value was noted for atrazine. This study employed a system with a very dilute clay-DDAB complex (0.2% w:w) which would result in relatively larger removed fractions of pollutants with very low affinity as in the case of atrazine. A higher clay-DDAB complex concentration will provide additional sorbent sites as seen in Table 1, increasing the fraction of pollutant retained. A larger sorbed fraction will also occur by using lower pollutant concentrations. The use of 1 mg L^{-1} amounting to one-order magnitude reduction in the concentrations used in Table 1 under the same experimental conditions, by employing the dry DDAB-clay complex prepared from a 6 mM solution increased the amount retained of the herbicides to 99.7, 93.5 and 75.0 % for alachlor, imazaquin and atrazine, respectively.

The presence of electrolytes in solution within the maximal range of concentrations found in ground waters did not affect appreciably the retention of sulfentrazone, and the neutral pollutants whose adsorption was slightly enhanced (Table 3). However, imazaquin sorption was greatly affected by the presence of other electrolytes. The presence of chloride reduced the retention by 13% independently of the cation; this reduction being more pronounced in the presence of nitrate (~72%). These anions compete with imazaquin for the positive surface charges of the complex and in addition, its adsorption will reduce the positive potential of the surface, both phenomena

amounting to a reduced imazaquin sorption. Polubesova et al. (2002) also observed reduced amounts of imazaquin on a crystal violet-montmorillonite complex prepared at a loading of the organic cation beyond the CEC, in the presence of inorganic anions such as sulfate, phosphate or acetate. These authors noticed competition when added imazaquin to other anions at a molar ratio of 1/100 as in this study, but not at 1/1 ratio. This trend might also occur with the clay-DDAB complex. Consequently the effective competition exerted by other anions on imazaquin adsorption will be lower in natural waters since the electrolyte concentrations employed here are in the upper limit. Other factors that may influence the retention of the organic pollutants by the clay-DDAB complex, such as temperature and pH were also studied. We did not notice any influence on the sorption of pollutants when the temperature was increased from 20 to 35°C or when the equilibrium pH was reduced from 8.6 which was the value recorded in the experiments in Table 1 to 5.0 (data not shown).

Figure 2 shows the removal of the four pollutants from water by means of the clay-DDAB complex. In that figure, the maximal concentrations considered were larger than those used in Table 1, ranging from several mg/L to about 50 mg/L for the anionic herbicides, up to 30 mg/L for atrazine, whereas in the case of alachlor its largest concentration added was 100 mg/L. The adsorption isotherms obtained were of very high affinity or H-type for sulfentrazone, of L-type for imazaquin, which indicates a large affinity of binding of the herbicide molecules to the clay-DDAB complex, and linear for alachlor and atrazine, which might indicate a partition mechanism.

The Langmuir equation was employed for modeling the adsorption isotherms in Figure 2, in which the complex concentration was 1.6 g/L. As explained previously (Nir et al., 2000) the Langmuir equation includes two parameters, the binding constant, k (M^{-1}), and the total number of adsorption sites. However, since a reliable determination of the

total number of adsorption sites requires a very high loading, which is also limited by the solubilities of pollutants, it was preferred to equate it in all cases to the cation exchange capacity of the clay, which amounts to using just a single parameter (k) in all cases. Figure 2 and Table 3 demonstrate that the Langmuir equation yields very good fits, the values of R^2 being close to unity and the values of RMSE being within the experimental errors. Table 1 demonstrates that the Langmuir equation can yield good predictions.

Table 4 shows that the binding constant for sulfentrazone ($k=2.3 \cdot 10^5 \text{ M}^{-1}$) is extremely large, in fact larger by an order of magnitude than k -values in previous studies employing organo-clays (Nir et al., 2000) or micelle-clays (Polubesova et al., 2005), whereas the other k -values fall in the range reported in previous studies. Recently (unpublished) we found a very large k -value also for the interaction of sulfentrazone with the micelle-clay system. The rationalization may be due to a formation of a strong complex between sulfentrazone and the positively charged headgroups of certain organic cations.

3.2. Adsorption of pollutants from solutions of several components.

Removal of pairs of pollutants from water was determined (Table 5). Little effect of competition for adsorption between the herbicides was observed; the removal percentages were similar to those in Table 1. The Langmuir equation yields very good predictions for the removal of pairs of pollutants with the exception of atrazine, whose removal was slightly underestimated in the presence of alachlor. This pattern suggests a synergistic effect of alachlor on the removal of atrazine.

An enhancement of the solubility of hydrophobic chemicals within micelles formed by anionic and non-ionic surfactants has been reported (Nagarajan et al., 1984; Guha et al.,

1998). In the presence of two solutes with different hydrophobicities as in Table 4, the less hydrophobic solute (alachlor) will partition at the core-water interface causing the interfacial tension to decrease, which would enable the core volume to increase, leading to a greater solubility of the more hydrophobic compound, atrazine, which will increase its removal. This was confirmed by a parallel experiment where the amount of atrazine incorporated into the vesicles in the presence of alachlor was determined by equilibrium dialysis experiments as in Undabeytia et al.(2003). In a 6 mM DDAB and 0.3 mM atrazine solution, the percent of atrazine bound to vesicles increased slightly from $39.4 \pm 0.5\%$ to $42.8 \pm 1.1\%$ in the presence of 0.6 mM alachlor. This synergistic effect was also observed when both solutes were added to the clay-DDAB complex. Sheng et al. (1996b) obtained an enhancement of trichloroethylene adsorption on smectite in the presence of either carbon tetrachloride or nitrobenzene. Both cosolutes sorbed through different mechanisms depending on their physical properties and chemical nature. It seems that the addition of aromatic molecules as cosolutes promotes the partition of other solutes into the expanded phase resulting from the reorientation of the long alkyl chains of the surfactant cation, due to strong interaction of the cationic ammonium centers with the delocalized π -bond system of the aromatic compound. In addition to the increase in the solvency of the long alkyl chain for the solute, there is also a larger interaction of the solute with the new exposed hydrophobic mineral surface. This mechanism could also be responsible for the enhancement of atrazine removal in the presence of alachlor. This synergistic effect is clearly illustrated by increasing the herbicide/sorbent ratio as in Table 6.

In Table 6, the simultaneous removal of the four pollutants from a water suspension by DDAB-montmorillonite is compared to the predicted values and to that of removal by AC. The efficiency of the clay-DDAB complex in the removal of these pollutants is

significantly greater than that of AC. The predicted removed amounts of pollutants agree well with the experimental values, with the exception of atrazine, where the experimental percent of removal is 85.5 vs a calculated value of 67.8 (Eq. 2) and a value of 68.8 if competition is ignored. Because the total number of sites was fixed by the cationic exchange capacity of the clay, the application of the Langmuir equation accounts for competitive effects in the simultaneous adsorption of herbicides, which depends on the binding coefficients determined previously. This equation does not account for synergistic effects unless an interaction parameter between herbicide molecules is introduced. However, the comparison between experimental and calculated values elucidates that the presence of alachlor enhances significantly the adsorption of atrazine.

3.3 Column filters.

The results of passing successive volumes of either the anionic herbicide sulfentrazone or the neutral alachlor through the vesicle-clay filter and through the activated carbon filter are shown in Figure 3. In the case of sulfentrazone the DDAB-clay filter yielded an average of 93.4% removal for the first 0.5 L (12.5 pore volumes), whereas the activated carbon filter gave correspondingly just 28.9% removal. The last portion of 0.25 L (from 5 L) yielded 63.3% and 4.3% removal, respectively. The average percentages of removal for 5L (125 pore volumes) were 77% and 9.2% for DDAB-clay and activated carbon filters, respectively. Hence, it is clear that whereas the DDAB-clay filter is quite powerful in removing from water the anionic organic pollutant, sulfentrazone, the activated carbon filter is inadequate. The activated carbon filter performs relatively better in removing from water alachlor, but the DDAB-clay filter is more efficient in this case as well. The advantage of the

DDAB-clay filter is exhibited in particular for passing larger volumes, e.g., after 1.5 L the corresponding percentages of removal are about two-fold larger. Table 7 presents the outcome of filtration of 1 L (25 pore volumes) of a solution including 10 mg/L of each of the three pollutants, sulfentrazone, imazaquin and alachlor and 8 mg/L of atrazine. The DDAB-clay filter removed 100% of the anionic pollutants, vs. 16.7% and 16.2% removal by AC, whereas for the neutral pollutants, alachlor and atrazine the corresponding percentages of removal were about 3-fold higher, respectively.

4. Conclusions

This study presents the vesicle-clay complex as a powerful sorbing material for water purification from organic contaminants both by filtration and sedimentation. A main advantage of the vesicle-clay system stems from providing a relatively large number of highly hydrophobic sites, which yields efficient and large capacity of adsorption for neutral and anionic pollutants. The net positive charge of the complex makes it in particular very efficient for the adsorption of anionic pollutants without impairing the adsorption of neutral ones. Another advantage of the vesicle-clay system arises from the fact that in comparison with other organo-clay complexes it has a very small fraction of organic cations as monomers in solution. Both in the case of single pollutants and for the simultaneous presence of several anionic and neutral ones the vesicle-clay complex yields significantly higher efficiencies and capacities of removal from water in suspension and in a filter than activated carbon.

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1 Table 1. Removal of pollutants from water by a DDAB-clay complex.^{†‡}

Pollutant	DDAB conc. (mM)	Initial herbicide concentration (mg/L)	% removed
Atrazine	3	8	37.3±0.3 (57.4±0.7)
	6	8	56.5±1.0 (59.8±0.1) [59.0]
Alachlor	3	10	94.9±0.8 (85.6±1.0)
	6	10	95.5±0.1 (87.2±0.2) [92.7]
Imazaquin	3	10	73.6±0.4 (92.0±0.3)
	6	10	75.52±0.3 (92.3±1.0) [95.8]
Sulfentrazone	3	10	98.0±1.0 (99.7±0.1)
	6	10	99.7±0.1 (99.7±0.1) [99.9]

2 †. Data in parentheses correspond to the procedure when a dried complex was added to
3 the solution, whereas the other cases correspond to the removal after incubation with
4 DDAB solution followed by clay addition.

5 ‡. Data in brackets are the predicted removals by the Langmuir equation by using the
6 binding coefficients in Table 4.

7

1 Table 2. Kinetics of pollutant adsorption/desorption from the clay-DDAB complex.

2 Concentrations were 10 mg L⁻¹ for each pollutant and 2 g L⁻¹ for the complex.

3

	Adsorption (% of the added)			Desorption (% of the adsorbed)		
	10 min	30 min	1 h	1 h	1 day	7 days
Atrazine	24.29 ±0.77	28.45 ±0.63	28.18 ±0.96	70.03 ±0.37	70.24 ±2.25	72.51 ±3.51
Alachlor	58.83 ±1.56	75.18 ±1.09	75.86 ±0.36	21.25 ±0.18	20.17 ±2.31	21.68 ±0.77
Imazaquin	83.97 ±0.04	87.17 ±0.18	88.52 ±2.28	5.16 ±0.33	4.85 ±0.49	4.67 ±0.59
Sulfentrazone	94.72 ±0.35	96.64 ±0.96	99.47 ±0.01	0	0	0.17 ±0.03

4

5

1 Table 3. Influence of the presence of electrolytes on the removal of pollutants by the
2 DDAB-clay complex. Pollutant concentrations were 10 mg L⁻¹ and 5 g L⁻¹ for the
3 complex.

Pollutant	Electrolyte	Conc. (mM)	Removal (%)
Atrazine	-	-	59.8±0.1
	CaCl ₂	3	63.7±0.3
	Mg (NO ₃) ₂	6	63.7±0.1
	NaCl	3	62.8±0.1
Alachlor	-	-	87.2±0.2
	CaCl ₂	3	90.4±0.1
	Mg (NO ₃) ₂	6	90.5±0.4
	NaCl	3	90.7±0.2
Imazaquin	-	-	92.3±1.0
	CaCl ₂	3	80.0±0.3
	Mg (NO ₃) ₂	6	25.6±0.1
	NaCl	3	83.0±0.3
Sulfentrazone	-	-	99.7±0.1
	CaCl ₂	3	99.1±0.1
	Mg (NO ₃) ₂	6	98.6±0.1
	NaCl	3	99.2±0.1

Table 4. Binding coefficients of the herbicides to the clay-DDAB complex as determined by the Langmuir equation. [†]

Herbicide	k (M ⁻¹)	RMSE (mol g ⁻¹)	R ²
Atrazine	370	6.3 10 ⁻⁷	0.974
Alachlor	3300	3 10 ⁻⁶	0.998
Imazaquin	6000	5 10 ⁻⁷	1.000
Sulfentrazone	2.3x10 ⁵	3 10 ⁻⁸	1.000

[†]. RMSE=[$\sum (y_{iexp}-y_{icalc})^2/(n-1)$]^{0.5}; y_{iexp} and y_{icalc} are experimental and calculated fractions adsorbed; n is the number of data points.

Table 5. Removal of pairs of pollutants from a water suspension by a DDAB-clay complex.^{†‡}

Pollutants (initial conc.)	DDAB conc. (mM)	% Removed	
Atrazine (8 mg/L) +alachlor (10 mg/L)	3	atrazine 44.3±0.5 (59.2±0.1)	alachlor 96.1±0.4 (89.4±0.1)
	6	atrazine 61.7±0.3 (63.1±0.2) [59.3]	alachlor 96.2±0.1 (86.6±0.5) [92.9]
Atrazine (8 mg/L) +imazaquin (10 mg/L)	3	atrazine 42.1±0.2 (56.1±0.1)	imazaquin 70.0±0.3 (91.4±0.3)
	6	atrazine 60.6±1.1 (60.0±0.7) [59.4]	imazaquin 75.0±0.1 (92.9±0.2) [95.9]
Sulfentrazone (10 mg/L) +imazaquin (10 mg/L)	3	sulfentrazone 99.6±0.1 (99.9±0.1)	imazaquin 72.5±0.5 (91.0±0.3)
	6	sulfentrazone 99.7±0.1 (99.9±0.1) [99.9]	imazaquin 75.5±0.7 (90.7±0.8) [95.9]

1 (continuation of Table 5)

Sulfentrazone (10 mg/L) +alachlor (10 mg/L)	3	sulfentrazone 99.5±0.4 (99.7±0.1)	alachlor 96.0±0.1 (89.7±0.2)
	6	sulfentrazone 99.4±0.1 (99.8±0.1) [99.9]	alachlor 96.7±0.4 (90.2±0.2) [92.9]
Atrazine (8 mg/L) + sulfentrazone (10 mg/L)	3	atrazine 38.7±4.5 (57.3±1.7)	sulfentrazone 97.9±3.0 (95.3±0.6)
	6	atrazine 58.5±0.1 (58.7±0.4) [59.4]	sulfentrazone 97.3±0.1 (97.4±0.5) [99.9]
Alachlor (10mg/L) + imazaquin (10 mg/L)	3	alachlor 95.2±0.3 (90.8±1.0)	imazaquin 73.4±0.2 (92.1±0.3)
	6	alachlor 96.0±0.6 (91.7±0.1) [92.8]	imazaquin 74.0±0.2 (93.4±0.2) [95.9]

2

3 †. Data in parentheses correspond to the procedure when a dried complex was added to
4 the solution whereas the other cases correspond to the removal after incubation with
5 DDAB solution followed by clay addition.

6 ‡. Data in brackets are the predicted removal percentages by the Langmuir equation by
7 using the binding coefficients in Table 2.

Table 6. Simultaneous removal of pollutants from a water suspension by a DDAB-clay complex or by an activated carbon. The sorbent concentration was 7.6 g/L, and the concentration of each herbicide was 30 mg/L except 25 mg/L for atrazine.[†]

	% Removal	
	Clay-DDAB complex	Activated carbon
Atrazine	85.5±0.2 [67.8]	69.1±0.5
Alachlor	92.1±1.5 [94.9]	67.6±1.7
Imazaquin	97.1±0.1 [97.2]	70.0±0.7
Sulfentrazone	95.8±0.1 [99.9]	69.8±0.5

[†]. Data in brackets are predicted values by the Langmuir equation.

Table 7. Simultaneous removal of pollutants by a column filter containing DDAB-clay complex or activated carbon. The concentration of each herbicide was 10 mg/L except 8 mg/L for atrazine.

	% Removal	
	Clay-DDAB complex	Activated carbon
Atrazine	53.1	18.2
Alachlor	94.0	31.9
Imazaquin	100	16.7
Sulfentrazone	100	16.2

Figure 1. Molecular structures of the herbicides and DDAB.

Figure 2. Adsorption isotherms of herbicides on the dry clay-DDAB complex prepared from a 6 mM DDAB solution and 5g/L clay. Symbols larger than error bars.

Figure 3. Removal of sulfentrazone and alachlor by column filters based on DDAB-clay or activated carbon (AC). The applied mass of pollutant was 50 and 250 mg L⁻¹ after the seepage of 1 and 5 L, respectively.