Journal of Hazardous Materials 209–210 (2012) 67–76

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Montmorillonite–chitosan bionanocomposites as adsorbents of the herbicide clopyralid in aqueous solution and soil/water suspensions

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ARTICLE INFO

Article history:
Received 22 September 2011
Received in revised form 5 December 2011
Accepted 25 December 2011
Available online 9 January 2012

Keywords:
Adsorption
Chitosan
Organoclays
Pesticides
Pollution

ABSTRACT

Montmorillonite (SWy-2)–chitosan bionanocomposites (SW–CH) were prepared following different methodologies, characterized, and assayed as adsorbents of the herbicide clopyralid (3,6-dichloropyridine-2-carboxylic acid) in aqueous solution and soil/water suspensions, to assess the potential of the materials to prevent and remediate soil and water contamination by anionic pesticides. The SW–CH bionanocomposites were good adsorbents for the herbicide at pH levels where both the anionic form of the herbicide ($pK_a = 2.3$) and the cationic form of CH ($pK_a = 6.3$) predominated. The performance of the SW–CH bionanocomposites as adsorbents of clopyralid depended on the amount and arrangement of chitosan in the samples. Clopyralid adsorption was rapid and mostly linear up to herbicide concentrations as high as 0.5 mM. High salt concentrations (0.1 M NaCl) promoted desorption of the adsorbed pesticide from SW–CH, strongly suggesting that adsorption of clopyralid occurred primarily through an ion exchange mechanism on positively charged CH sites at the montmorillonite surface. Amendment of an acidic soil (pH = 4.5) with SW–CH at rates of 5% and 10% led to a significant increase in clopyralid adsorption, whereas this effect was negligible when SW–CH was added to an alkaline soil (pH = 8.0), reflecting the absence of positively charged sites in SW–CH at high pH values. Montmorillonite–CH bionanocomposites can be useful as adsorbents for the removal and/or immobilization of anionic pesticides in soil and water under mild acidic conditions.

1. Introduction

Clay-based nanocomposites and bionanocomposites have become materials of increasing interest due to their nanosized structural and functional properties. Combination at the nanometric scale of the expansive surface areas, anisotropic shape and reactive surfaces of clays with the functional behavior of organic polymers has been pointed out as an attractive way to develop organic–inorganic nanohybrid materials with properties that are inherent to both types of components [1].

Chitosan [poly-β(1,4)-2-amino-2-deoxy-D-glucose], that is, the deacetylated product of chitin [poly-β(1,4)-2-(acetylamino)-2-deoxy-D-glucose], is a cationic biopolymer which has recently gained increased attention for the preparation of clay-based bionanocomposites [1–7]. It has been suggested that both the physical and functional properties of chitosan can be improved when it is adsorbed onto clay minerals [1,3,4,8]. Thus, Darder et al. [1] showed that chitosan can be intercalated into Na^+-saturated montmorillonite providing compact and robust three-dimensional nanocomposites with interesting functional properties. Chitosan chains formed mono- or bilayer structures within the clay mineral interlayer depending on the relative amount of chitosan with respect to the cationic exchange capacity (CEC) of the clay. Subsequent studies have shown that a number of factors, such as pH and temperature, can affect the extent and mode of chitosan adsorption on montmorillonite [3]. For example, given that the pK_a of the primary amine groups in the chitosan structure is 6.3, an increase in pH leads to a decrease in the degree of protonation of the biopolymer, which increases the amount adsorbed on montmorillonite [3].

Adsorption of chitosan on montmorillonite, particularly when in excess of the CEC of the clay mineral, results in structures with good adsorption properties for anions because the $-NH_3^+$ groups not directly involved in the interaction with the clay surfaces can act as anionic exchange sites [1]. Accordingly, montmorillonite–chitosan bionanocomposites have recently been proposed for anion-adsorption related applications, such as the development of potentiometric sensors for anions or the removal of selenate and tannic acid from water [4–6].

Acidic pesticides, which are often in their anionic form at the pH of soil and water environments, display a particularly high risk of ground and surface water contamination, because they are weakly retained by most soil and sediment components [9]. For this reason,

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doi:10.1016/j.jhazmat.2011.12.074

the development of pesticide adsorbents to prevent and remediate environmental contamination by anionic pesticides has become an important research goal [10–18]. Clay minerals are good adsorbents for cationic and very polar pesticides [19,20]. However, they usually display limited affinity for anionic pesticides, as a result of repulsions between the anionic pesticide species and the negatively charged clay surfaces [21]. The interaction of organic cations with clay minerals can reduce such repulsions, changing the nature of the clay mineral surfaces from hydrophilic to hydrophobic or, if adsorbed in excess of the CEC of the clay, even producing charge reversal. Thus, modification with organic cations is a potentially useful strategy to enhance the affinity of clay minerals for anionic pesticides [14,17,21–25].

On the basis of their potential affinity for anionic species, in this work we evaluated the ability of montmorillonite–chitosan bionanocomposites to adsorb the anionic herbicide clopyralid (3,6-dichloropyridine-2-carboxylic acid). Montmorillonite–chitosan bionanocomposites were prepared following different methodologies, characterized, and then assayed as adsorbents of clopyralid in aqueous solution and soil/water suspensions. The objective was to determine the factors controlling clopyralid adsorption by the montmorillonite–chitosan systems and to illustrate the potential usefulness of these systems for the removal and/or immobilization of anionic pesticides present in soil and water.

2. Materials and methods

2.1. Materials

SWy-2 Wyoming montmorillonite was supplied by the Source Clays Repository of the Clay Minerals Society (Purdue University, Indiana). Sodium-saturated SWy-2 (Na-SWy-2) was prepared by three successive treatments of 10 g of SWy-2 with 200 mL of a 1 M NaCl solution. The resulting homoionic clay was repeatedly washed with deionized water until absence of chloride (negative $AgNO_3$ test), lyophilized, and stored at room temperature until used.

Low molecular weight (LMW) and medium molecular weight (MMW) chitosan with a deacetylation degree of ~80% (Fig. 1) were purchased from Sigma–Aldrich (Spain). LMW chitosan (MW = 50,000–190,000 g/mol) contained a number of glucosamine units ranging between 250 and 940, whereas MMW chitosan (MW = 190,000–310,000 g/mol) contained a number of glucosamine units ranging between 940 and 1530.

The herbicide clopyralid used in this study was the pure analytical compound, purity = 99% (Pestanal), supplied by Sigma–Aldrich (Spain). Clopyralid (Fig. 1) is a selective herbicide of the pyridine carboxylic acid family used for control of broadleaf weeds in a range of crops at 50–200 g/ha. It has pK_a = 2.3, MW = 192 g/mol, and water solubility = 1 g/L at 20 °C [26]. Clopyralid is expected to be in its anionic form at the pH of most soil and water environments.

Two soils with markedly different pH values were selected for the experiments. Soil 1 was a sandy loam forest soil of pH = 4.5 with 56% sand, 33% silt, 11% clay, and 5.5% organic carbon. Soil 2 was an agricultural sandy clay loam soil of pH = 8.0 with 63% sand, 16% silt, 21% clay, and 1.4% organic carbon. The soils were sampled from the top 0–20 cm layer, air-dried, passed through a 2-mm aperture sieve, and stored at 4 °C until used.

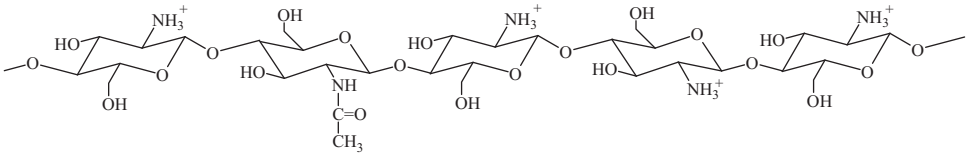
2.2. Synthesis of montmorillonite–chitosan bionanocomposites

Montmorillonite–chitosan (SW–CH) bionanocomposites were prepared following different procedures based on that previously described by Darder et al. [1]. Detailed information on the reagents and synthesis conditions used for the preparation of each sample is given in Table 1. In all cases, 0.8 g of clay (SWy-2 or Na-SWy-2) was added to 200 mL of an aqueous solution containing 650 mg of chitosan at pH = 5.0. Assuming a deacetylation degree for chitosan of ~80%, 650 mg of chitosan contained about 3 mmol of protonable $-NH_2$ groups, which corresponded to 500% of the CEC of 0.8 g of SWy-2 ($CEC_{SWy\text{-}2}$ = 76.4 $cmol_c/kg$).

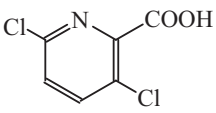
For the preparation of the sample SW–CH-1, 650 mg of LMW chitosan was dissolved in 200 mL of an aqueous solution containing 30 mmol of acetic acid, and after the resulting solution was stirred for 4 h, its pH was adjusted to 5.0 by adding ca. 30 mmol of NaOH. Next, 0.8 g of SWy-2 was added to the chitosan solution, and the resulting suspension was shaken for 24 h at 25 °C. The final pH of the clay–chitosan suspension remained 5.0 after the 24 h-equilibration (Table 1). The suspension was centrifuged, washed five times with 200 mL of deionized water, lyophilized, and the solid stored at room temperature until used.

SW–CH-2 and SW–CH-3 bionanocomposites were prepared following a procedure identical to that described for SW–CH-1, except that the temperature of the synthesis was increased to 60 °C for SW–CH-2, and MMW chitosan was used instead of LMW chitosan for SW–CH-3 (Table 1).

The samples SW–CH-4, SW–CH-5, and SW–CH-6 were prepared reducing the amount of acid used to dissolve the biopolymer. While for the preceding samples (SW–CH-1, SW–CH-2, and SW–CH-3) the amount of acetic acid used to dissolve the polysaccharide (30 mmol) corresponded to 1000% of the amount of protonable $-NH_2$ groups in 650 mg of chitosan (3 mmol) and the exceeding amount was neutralized with NaOH [1], for samples SW–CH-4,



Chitosan



Clopyralid

Fig. 1. Molecular structures of chitosan and clopyralid.

Table 1
Nomenclature and synthesis conditions of montmorillonite–chitosan (SW–CH) bionanocomposites.[a]

Nomenclature	Clay (0.8 g)	Chitosan (CH) solution (650 mg CH dissolved in 200 mL aqueous solution)	T (°C)	$pH_{initial}$	pH_{final}
SW–CH-1	SWy-2	LMW CH + AcOH (30 mmol) + NaOH (30 mmol)	25	5.0	5.0
SW–CH-2	SWy-2	LMW CH + AcOH (30 mmol) + NaOH (30 mmol)	**60**	5.0	5.0
SW–CH-3	SWy-2	**MMW** CH + AcOH (30 mmol) + NaOH (30 mmol)	25	5.0	5.0
SW–CH-4	SWy-2	LMW CH + AcOH (**3 mmol**)	25	5.0	5.0
SW–CH-5	**Na-SWy-2**	LMW CH + AcOH (**3 mmol**)	25	5.0	5.0
SW–CH-6	SWy-2	LMW CH + **HCl (0.3 mmol)**	25	5.0	7.3

[a] SWy-2: raw SWy-2 Wyoming montmorillonite; Na-SWy-2: Na^+-saturated SWy-2 sample; LMW CH: low molecular weight chitosan; MMW CH: medium molecular weight chitosan; AcOH: acetic acid; $pH_{initial}$: pH of the initial aqueous CH solution; pH_{final}: pH of the clay-solution suspension equilibrated for 24 h. The main difference between the preparation procedure for each sample and that for sample SW–CH-1 is indicated in bold.

SW–CH-5, and SW–CH-6 the amount of acid used corresponded to 100% (SW–CH-4 and SW–CH-5) or only 10% (SW–CH-6) of the amount of $–NH_2$ groups present in 650 mg of chitosan. Thus, SW–CH-4 and SW–CH-5 were prepared using 3 mmol of acetic acid and were identical to each other except that the latter was prepared using homoionic (Na-saturated) SWy-2 montmorillonite instead of the raw SWy-2 sample. In both cases, the chitosan solution reached pH = 5.0 without the need for subsequent addition of NaOH, and remained 5.0 after the 24 h-equilibration with the clay (Table 1). SW–CH-6 was prepared using 0.3 mmol of HCl and, due to the low amount of acid used to dissolve the biopolymer, was the only sample for which the final pH of the equilibrated clay–chitosan mixture (pH = 7.3) was considerably greater than the pH of the initial chitosan solution (pH = 5.0) (Table 1).

2.3. Synthesis of montmorillonite control samples

To distinguish the effects produced by the association of chitosan with montmorillonite from potential alterations in the clay produced by the specific preparation procedures conducted for the synthesis of the bionanocomposites, three montmorillonite control samples (SW-BL) were also prepared (Table 2). SW-BL-1 was prepared by treating 0.8 g of SWy-2 with 200 mL of a solution containing 30 mmol of acetic acid neutralized to pH = 5.0 by the addition of 30 mmol of NaOH. SW-BL-2 and SW-BL-3 were prepared by treating 0.8 g of SWy-2 with 200 mL of a solution containing 3 mmol of acetic acid or 0.3 mmol of HCl, respectively, without further addition of NaOH. The resulting suspensions were shaken for 24 h, centrifuged, washed five times with 200 mL of deionized water, and then lyophilized.

2.4. Sample characterization

The resulting SW–CH bionanocomposites and montmorillonite control samples were characterized by elemental analysis, X-ray diffraction, scanning electron microscopy, and Fourier-transform infrared spectroscopy. Elemental analyses were performed using a Perkin-Elmer, model 1106, elemental analyzer. X-ray diffraction patterns were obtained on oriented specimens, both air-dried and heated at 200 °C, using a Siemens D-5000 diffractometer with CuK_α radiation. Scanning electron micrographs were obtained on gold-coated samples using a Hitachi S5200 scanning electron microscope. Fourier-transform infrared (FTIR) spectra were recorded using a Jasco FT/IR 6300 spectrometer (Jasco Europe s.r.l.) directly placing the solid samples in a horizontal trough attenuated total reflectance (ATR) cell.

2.5. Adsorption–desorption of the herbicide clopyralid on SW–CH bionanocomposites

Clopyralid adsorption–desorption on SW–CH bionanocomposites and montmorillonite control samples was determined by the batch equilibration procedure using glass centrifuge tubes lined with screw caps. Aliquots of 20 mg of adsorbent samples were equilibrated by shaking for 24 h at 20 ± 2 °C with 8 mL of clopyralid initial solutions with herbicide concentrations (C_{ini}) ranging between 0.0005 and 0.5 mM. The initial solutions of clopyralid were prepared at pH = 3 (1 mM HCl), since preliminary experiments, conducted under the same experimental conditions but varying the pH of a 0.005 mM initial clopyralid solution between 2.0 and 6.5 indicated that clopyralid adsorption was highest at an initial pH = 3.0. A kinetic experiment was also conducted and revealed that 24 h was sufficient to reach the adsorption equilibrium for clopyralid. After equilibration, the suspensions were centrifuged and 4 mL of the supernatant solutions were removed, filtered and analyzed by high-performance liquid chromatography (HPLC) to determine the herbicide equilibrium concentration, C_e (mmol/L). The amount of clopyralid adsorbed, C_s (mmol/kg), was determined from the difference between the initial and equilibrium solution concentrations. Clopyralid initial solutions without adsorbent were also prepared and served as controls to account for possible losses of herbicide due to processes other than adsorption to the solids. Percentages of clopyralid adsorbed, %Ads, and adsorption distribution coefficients, K_d (L/kg), at a single initial herbicide concentration of 0.005 mM were calculated as $\%Ads = [(C_{ini} - C_e)/C_{ini}] \times 100$ and $K_d = C_s/C_e$, respectively. In addition, adsorption isotherms were fitted to the Freundlich equation: $\log C_s = \log K_f + N_f \log C_e$, where C_s is the amount of clopyralid adsorbed at the equilibrium concentration C_e, and N_f (unitless) and K_f ($mmol^{1-Nf}\,L^{Nf}\,kg^{-1}$) are the empirical Freundlich constants, which can be calculated from the linear plot of $\log C_s$ vs $\log C_e$.

Desorption experiments were conducted from selected samples immediately after measuring adsorption at C_{ini} = 0.01 mM. The 4 mL of supernatant solution removed for the adsorption analysis were replaced with 4 mL of either water or 0.1 M NaCl. The tubes were resuspended, shaken at 20 ± 2 °C for 24 h, centrifuged, and then 4 mL of supernatant were removed, filtered and analyzed

Table 2
Nomenclature and synthesis conditions of montmorillonite control samples without chitosan (SW-BL).[a]

Nomenclature	Clay (0.8 g)	Solution (200 mL aqueous solution)	T (°C)	$pH_{initial}$	pH_{final}
SW-BL-1	SWy-2	AcOH (30 mmol) + NaOH (30 mmol)	25	5.0	5.0
SW-BL-2	SWy-2	AcOH (3 mmol)	25	3.4	3.8
SW-BL-3	SWy-2	HCl (0.3 mmol)	25	2.9	6.4

[a] SWy-2: raw SWy-2 Wyoming montmorillonite; AcOH: acetic acid; $pH_{initial}$: pH of the initial 200 mL-aqueous solution; pH_{final}: pH of the clay-solution suspension equilibrated for 24 h.

Table 3
Results of the elemental analysis of montmorillonite–chitosan (SW–CH) bionanocomposites.

Nomenclature	C (%)	N (%)	Chitosan[a] (%)	Clay[b] (%)	Chitosan[c] ($cmol_c$/kg clay)	Saturation degree[d] (%)
SW–CH-1	3.5	0.58	7.0	93.0	36	47
SW–CH-2	3.6	0.60	7.3	92.7	37	48
SW–CH-3	3.3	0.53	6.4	93.6	32	42
SW–CH-4	5.2	0.90	10.9	89.1	58	76
SW–CH-5	7.0	1.20	14.6	85.4	81	106
SW–CH-6	20.1	3.60	43.6	56.4	365	478

[a] Calculated from the N content of the samples.
[b] Calculated as 100 – %Chitosan.
[c] Calculated from the amount of chitosan in the samples assuming full protonation of the $-NH_2$ groups of the biopolymer.
[d] Percentage of the CEC of the clay compensated by chitosan assuming full protonation of the $-NH_2$ groups of the biopolymer.

by HPLC. This desorption procedure was repeated three times. All adsorption–desorption experiments were conducted in triplicate.

2.6. Adsorption of clopyralid by bionanocomposite-amended soils

Two bionanocomposites with high affinity for clopyralid (SW–CH-5 and SW–CH-6) were selected as soil amendments to determine their effect on clopyralid adsorption by two soils. For this purpose, triplicate 0.5 g of soil samples were amended with SW–CH-5 or SW–CH-6 at different rates (0%, 5%, and 10%), and then equilibrated by shaking for 24 h at 20 ± 2 °C with 8 mL of a 0.005 mM aqueous solution of clopyralid (pH = 6.5). After equilibration, the suspensions were centrifuged, and 4 mL of the supernatant solution were removed, filtered, and analyzed by HPLC. The amount of clopyralid adsorbed (C_s) was determined from the difference between the initial (C_{ini}) and equilibrium (C_e) herbicide concentrations. Percentages of clopyralid adsorbed (%Ads) and distribution coefficients (K_d) were also calculated as described above.

2.7. Herbicide analysis

Clopyralid was analyzed by HPLC using a Waters 1525 chromatograph coupled to a Waters 2996 diode-array detector. The analytical conditions used were: Nova-Pack C18 column (150 mm length × 3.9 mm internal diameter), 91.5/5.0/3.5 water/acetonitrile/acetic acid eluent mixture at a flow rate of 0.7 mL/min, 25 μL injection volume, and UV detection at 280 nm. External calibration curves with standard clopyralid solutions between 0.0005 and 0.01 mM were used in the analyses.

3. Results and discussion

3.1. Characterization of the SW–CH bionanocomposites

3.1.1. Elemental analysis

Results of the elemental analysis of the SW–CH bionanocomposites are summarized in Table 3. The amount of chitosan in the samples prepared in the present study ranged between 6.4%, for SW–CH-3, and 43.6%, for SW–CH-6. Considering the deacetylation degree of chitosan as 80% and assuming full protonation of the $-NH_2$ groups in the biopolymer (Fig. 1), the amount of chitosan present in the samples corresponded to 42–478% of the CEC of the clay (Table 3). The elemental analysis of the montmorillonite control samples, not included in Table 3, revealed C contents < 0.3% and N contents < 0.05% in all cases.

One of the most important factors affecting the amount of chitosan present in the bionanocomposites was the pH of the equilibrated montmorillonite–chitosan suspension (Tables 1 and 3). When the pH of the equilibrated suspension was below the pK_a of chitosan (pK_a = 6.3), the amount of chitosan in the samples rarely exceeded the CEC of the clay (samples SW–CH-1 to SW–CH-5). In fact, for these samples even though chitosan was initially added in an amount corresponding to 500% of the CEC of the clay, the final amounts of biopolymer were often well below the clay CEC (Table 3). In contrast, when the pH of the equilibrated suspension was above the pK_a of chitosan (sample SW–CH-6), the amount of chitosan present in the resulting bionanocomposite greatly exceeded the CEC of the clay mineral (Table 3). These results are in accordance with those previously reported by An and Dultz [3], where pH was found to be a decisive factor in the interaction of chitosan with montmorillonite, because an increase in pH leads to a decrease in the degree of protonation of the biopolymer, increasing the amount adsorbed on the clay.

Considering the sample SW–CH-1 as a reference, an increase in temperature (SW–CH-2) and in the MW of the biopolymer (SW–CH-3) both had little effect on the final amount of chitosan in the sample (Table 3). However, reducing the amount of acetic acid used to dissolve the biopolymer from 30 mmol (SW–CH-1) to 3 mmol (SW–CH-4) led to a significant increase in the amount of chitosan in the sample, and this effect was even more pronounced when montmorillonite was previously Na-saturated (SW–CH-5). Given that the pH of the equilibrated suspensions was 5.0 for all these samples (Table 1), we believe that the high amount of NaOH used to neutralize the polysaccharide solution in SW–CH-1, SW–CH-2, and SW–CH-3 (Table 1) could have resulted in competition between cationic chitosan (3 mmol) and Na^+ (30 mmol) for the cation exchange sites on the clay, thus reducing the amount of chitosan adsorbed. Absence of NaOH in the chitosan solution during the preparation of SW–CH-4 and SW–CH-5 reduced competition and favored the exchange reaction. The homoionic, Na-saturated clay (SW–CH-5) resulted in higher amount of chitosan, most likely because Na^+ in Na-SWy-2 was more easy to replace than the mixture of cations (Na^+ and Ca^{2+}) present in the raw SWy-2 montmorillonite sample [27].

As mentioned above, the only sample where chitosan was present far in excess of the clay CEC was SW–CH-6. This sample was prepared by dissolving chitosan with an amount of HCl (0.3 mmol) corresponding to only 10% of the protonable $-NH_2$ groups present in the biopolymer (Table 1). Due to the low amount of acid added, the pH of the montmorillonite–chitosan suspension increased up to 7.3 after the 24 h-equilibration (Table 1). Taking into account that the pK_a of the primary amine groups of chitosan is 6.3, at pH = 7.3 only 10% of such groups are expected to be in their protonated form, thus explaining the high amount of chitosan associated with the clay [3].

3.1.2. X-ray diffraction and scanning electron microscopy

The X-ray diffraction (XRD) patterns of air-dried oriented specimens of SW–CH bionanocomposites and montmorillonite control samples without chitosan are shown in Fig. 2. The X-ray diffractograms of montmorillonite samples without chitosan (Fig. 2b) gave the expected basal spacing (d_{001}) of 12.5 Å for the Na-saturated clay (Na-SWy-2), consistent with the presence of interlayer Na^+ retaining one layer of hydration water [28,29],

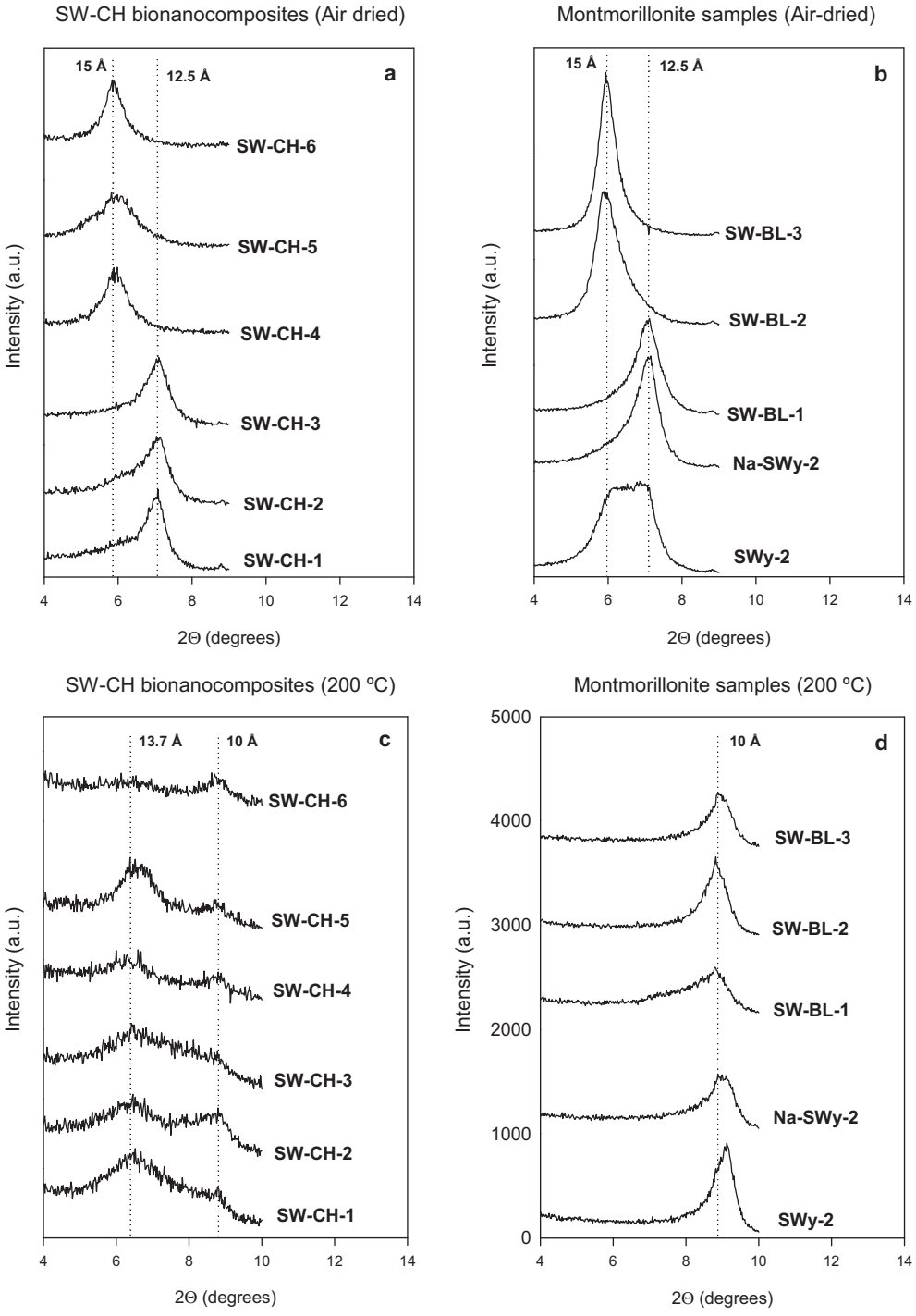


Fig. 2. X-ray diffraction patterns of oriented specimens of SW–CH bionanocomposites and montmorillonite control samples: (a) air-dried SW–CH samples, (b) air-dried montmorillonite samples, (c) SW–CH samples heated at 200 °C, (d) montmorillonite samples heated at 200 °C.

while the presence of different interlayer exchangeable cations (mainly Na^+ and Ca^{2+}) in the raw SWy-2 clay resulted in a poorly defined basal diffraction between 12 and 15 Å (Fig. 2b). SW-BL samples gave basal diffractions of either 12.5 Å, for the sample treated with high acetic acid and NaOH concentrations (SW-BL-1), or 15 Å for the samples treated with lower amounts of acid (SW-BL-2 and SW-BL-3). Therefore, the blank treatments influenced the interlayer hydration of the air-dried clay films. For the SW–CH bionanocomposites (Fig. 2a), the basal diffraction at about 15 Å observed in the SW–CH samples with higher amounts of chitosan (SW–CH-4, SW–CH-5, and SW–CH-6) is consistent with previously reported values for the intercalation of a monolayer of biopolymer within the interlayer space of montmorillonite [1,5,30], although the tailing effect observed for some of the samples (e.g., SW–CH-5) at lower 2θ angles could be indicative of the presence of some bilayer SW–CH structures [1]. In samples SW–CH-1, SW–CH-2, and SW–CH-3, the basal diffraction at 12.5 Å, due to the presence of Na-saturated montmorillonite layers free of chitosan, predominated and partially obscured the reflections corresponding to chitosan-intercalated montmorillonite layers (Fig. 2a).

Because the similarity between the basal spacing of ~15 Å corresponding to montmorillonite intercalated with one monolayer

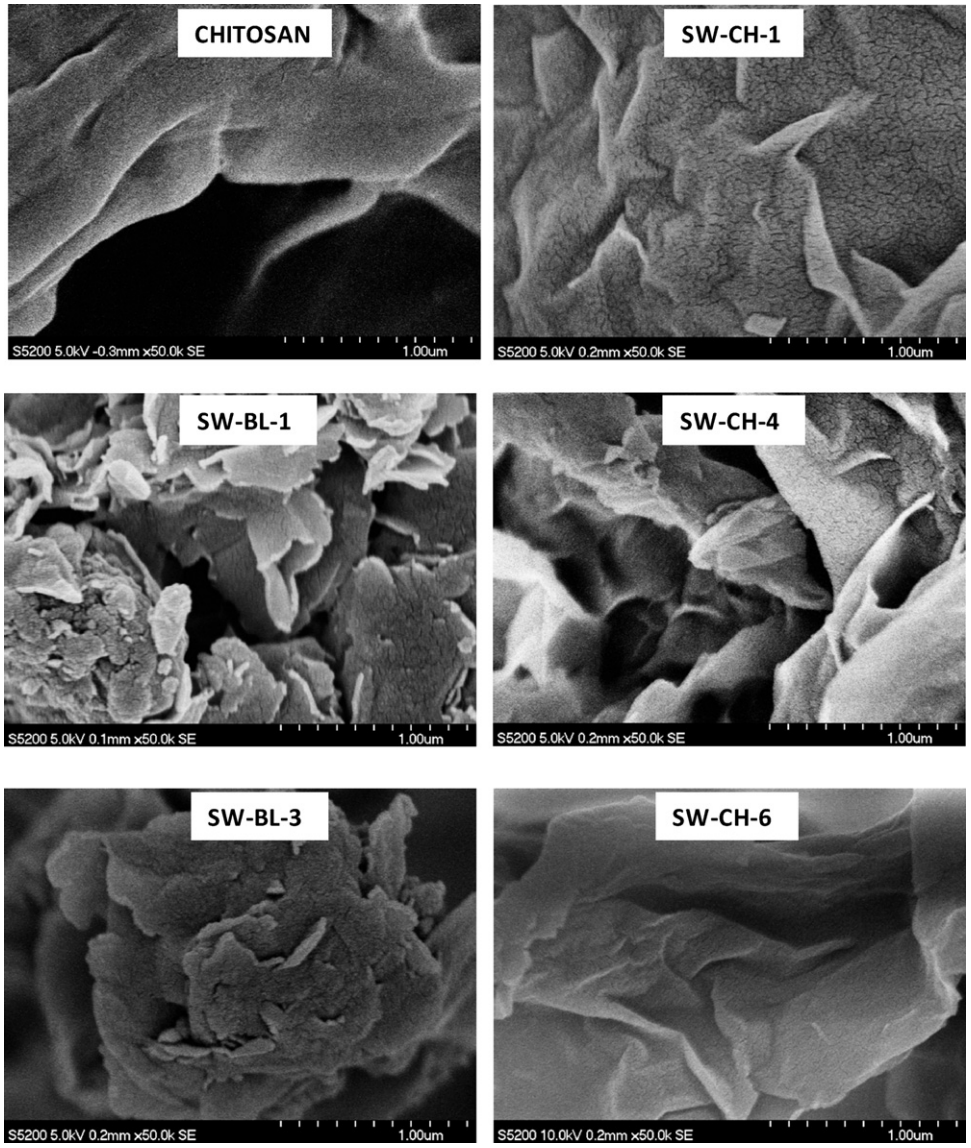


Fig. 3. Scanning electron micrographs of chitosan, montmorillonite control samples (SW-BL) and montmorillonite–chitosan bionanocomposites (SW–CH).

of chitosan and the values corresponding to montmorillonite with interlayer inorganic cations retaining two layers of hydration water, e.g., Ca^{2+}, made the interpretation of XRD patterns of air-dried SW–CH samples difficult, we also obtained the X-ray diffractograms of oriented samples heated at 200 °C (Fig. 2). All montmorillonite samples without chitosan collapsed to a d_{001} value of 9.6–10 Å upon heating (Fig. 2d), whereas the SW–CH bionanocomposites (Fig. 2c) were resistant to collapse, showing a basal diffraction of 13.7 Å. This value corresponds to a clearance space of about 4 Å between the clay sheets, which concords with the presence of a monolayer of chitosan in the dehydrated interlayer region, thus providing strong evidence for the presence of chitosan in the interlayers of montmorillonite. The residual diffraction near 10 Å that can be identified in most SW–CH samples indicated the presence of some unexchanged layers occupied exclusively by inorganic cations and/or illite impurities. The diffraction at 13.7 Å of heated SW–CH samples were, in general, poorly defined, indicating poorly ordered systems or partial intercalation of the polycation, some of which could have remained at the outer surface of the clay. This was particularly evident for the sample SW–CH-6, where the high amount of chitosan (Table 3) most likely resulted in a significant amount of biopolymer at the external clay platelets and in a highly disordered structure upon sample heating, both contributing to the poor definition of the 13.7 Å-diffraction.

Analysis of the bionanocomposites by scanning electron microscopy (SEM) was conducted to get further insight into the sample morphology (Fig. 3). Scanning electron micrographs showed that the presence of chitosan rendered lamellar structures where the clay particles appeared to be enveloped in a biopolymer network (Fig. 3). The final morphology depended on the amount of chitosan, so that as the chitosan content increased from SW–CH-1 to SW–CH-6, the lamellar structures displayed greater definition and size. Compared to SW–CH-1, the sample SW–CH-4 showed a more open structure probably resulting from the presence of chitosan both at internal and external clay surfaces. In SW–CH-6, accumulation of chitosan at the external clay surfaces rendered large lamellae closely resembling the morphology of pure chitosan (Fig. 3).

3.1.3. Fourier-transform infrared spectroscopy

Fig. 4 shows the FT-IR spectra of LMW chitosan, SWy-2 and the SW–CH bionanocomposites containing the highest amounts of biopolymer (SW–CH-4, SW–CH-5, and SW–CH-6). Band assignations were carried out according to Bellamy [31],

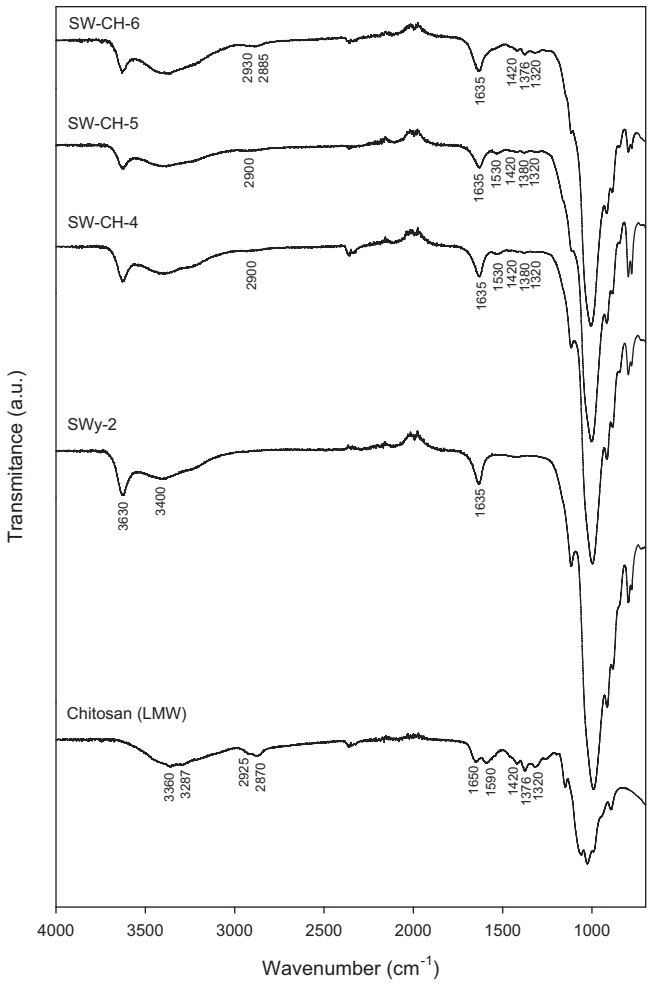


Fig. 4. Fourier-transform infrared spectra of chitosan (LMW), SWy-2 montmorillonite, and selected SW–CH bionanocomposites.

and were in agreement with results previously reported for chitosan–montmorillonite bionanocomposite samples [1,7,32].

In the FT-IR spectrum of pure chitosan, the bands near 3300 cm^{-1} correspond to stretching vibrations of the O—H and N—H groups of the biopolymer, whereas those near 2900 cm^{-1} correspond to aliphatic C—H stretching vibrations. In addition, the chitosan C=O stretching (amide I) and N—H deformation vibrations appear, respectively, at 1650 cm^{-1} and 1590 cm^{-1}, and the bands near 1400 cm^{-1} can be attributed to deformation vibrations of aliphatic C—H groups. In the FT-IR spectrum of SWy-2, the characteristic bands due to structural hydroxyls, (ν_{OH} at 3630 cm^{-1}), hydration water (ν_{OH} at 3400 cm^{-1} and δ_{OH} at 1653 cm^{-1}), and structural Si—O (ν_{SiO} near 1000 cm^{-1}) were identified.

The spectra of SW–CH samples showed the combination of characteristic bands due to chitosan and SWy-2 (Fig. 4). The shifting of the N—H deformation band from 1590 cm^{-1} in pure chitosan to 1530 cm^{-1} in SW–CH-4 and SW–CH-5 indicated interaction of the negatively charged montmorillonite surfaces with the protonated amine groups ($-NH_3^+$) of chitosan [1,32]. Interestingly, this effect was much less evident for the sample SW–CH-6, where according to XRD and SEM results much of the chitosan remained at the external clay surfaces. In this sample only a small fraction of the $-NH_2$ groups of chitosan were expected to be in their protonated form, which should have reduced the intensity of the bands corresponding to the $-NH_3^+$ groups interacting with the clay. Also in SW–CH-6, the intensity of the bands at 3400 and 1635 cm^{-1} indicated a relatively high water content, suggesting that replacement of the original interlayer inorganic cations of the clay and their hydration water with chitosan chains occurred to a very limited extent. In SW–CH-4 and SW–CH-5, the bands corresponding to the C—H deformation modes of chitosan, particularly that at 1376 cm^{-1}, were also shifted upon interaction of the biopolymer with the clay mineral layers (Fig. 4).

3.2. Adsorption–desorption of clopyralid on SW–CH bionanocomposites

A preliminary experiment was conducted to assess the effect of pH and equilibration time on clopyralid adsorption by SW–CH-1 (Fig. 5). In contrast to the negligible adsorption of clopyralid by all SWy-2 montmorillonite control samples without chitosan (not shown), the SW–CH bionanocomposite (SW–CH-1) was found to be a good adsorbent for the herbicide, but only in the range of pH where both the anionic form of the herbicide ($pK_a = 2.1$) and the cationic form of chitosan ($pK_a = 6.3$) predominated. This result strongly indicates that adsorption of the herbicide clopyralid is governed by the presence of positively charged sites at the SW–CH-1 surfaces where, as suggested for other anionic species [4–6,33,34], clopyralid anions can be adsorbed by an anionic exchange mechanism. At low pH levels (e.g., pH < 2), the positive charge of chitosan is expected to be high but predominance of the neutral form of clopyralid results in little adsorption of the herbicide on SW–CH-1 (Fig. 5a). At high pH levels (e.g., pH > 5.5), the anionic form of clopyralid predominates but the positively charged adsorption sites on SW–CH-1 for clopyralid anions are expected to decrease rapidly. It is interesting to note that even though chitosan was present in SW–CH-1 in an amount corresponding to only 47%

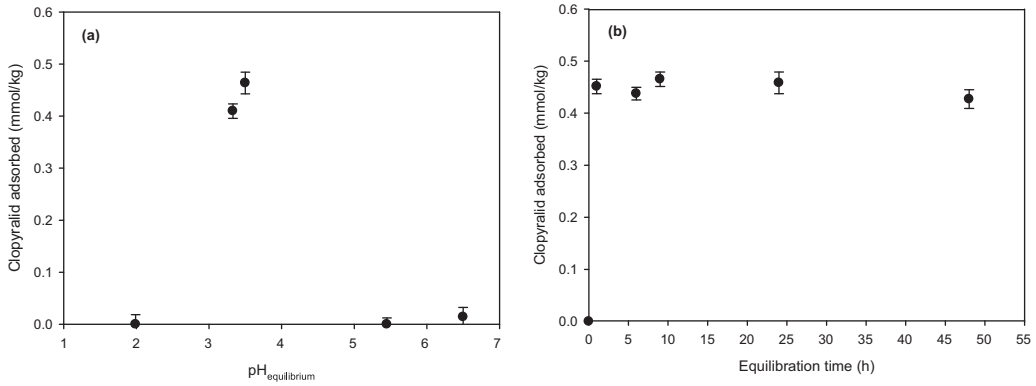


Fig. 5. Effect of pH (a) and equilibration time (b) on clopyralid adsorption by SW–CH-1. The initial concentration of clopyralid in the experiments was 0.005 mM. The pH of the initial clopyralid solution in (b) was 3.0.

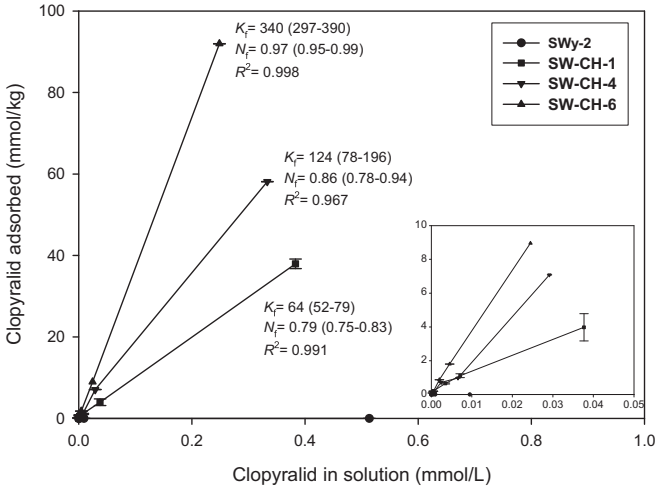


Fig. 6. Clopyralid adsorption isotherms (pH = 3) on SWy-2 and selected SW–CH samples. Adsorption coefficients resulting from fitting the adsorption isotherms to the Freundlich equation are also given. Values in parenthesis correspond to standard errors for the calculated coefficients.

of the CEC of the clay (Table 3), SW–CH-1 appeared to contain some $-NH_3^+$ groups with anionic exchange properties, presumably because they were not directly involved in the interaction with the negatively charged clay mineral surface [1]. According to the adsorption results obtained at different pH levels, the subsequent adsorption experiments were conducted at an initial pH = 3. At this pH, clopyralid adsorption kinetics showed that the adsorption of the pesticide on SW–CH-1 was very fast (Fig. 5b), so that 24 h was assumed to be sufficient to reach the adsorption equilibrium for clopyralid on SW–CH bionanocomposites.

Table 4 shows the coefficients for clopyralid adsorption on the SW–CH samples prepared in this work, obtained at a single initial herbicide concentration of 0.005 mM, and Fig. 6 shows clopyralid adsorption isotherms on selected samples in the range of initial herbicide concentrations 0.0005–0.5 mM. In general, clopyralid adsorption was higher for samples with higher amounts of chitosan (Table 4 and Fig. 6), although the variability of the adsorption distribution coefficients normalized to the chitosan content of the samples, $K_{d\text{-chit}}$ (Table 4), indicated additional factors, such as the equilibrium pH or the accessibility of adsorption sites in the samples, may have also been important in the final amount of clopyralid adsorbed. For example, adsorption of clopyralid on SW–CH-2, which was prepared at 60 °C, was significantly higher than that on SW–CH-1, prepared at 25 °C, even though the final amount of chitosan in both samples was very similar (Tables 3 and 4). Apparently, increasing the temperature for the synthesis of the bionanocomposite did not greatly affect the amount of intercalated chitosan, but could have resulted in a different arrangement of the biopolymer, leading to a structure with enhanced availability of clopyralid adsorption sites. Similarly, for SW–CH-4, SW–CH-5, and SW–CH-6, the adsorption coefficients normalized to the chitosan content of each bionanocomposite, $K_{d\text{-chit}}$, decreased with the amount of biopolymer in the sample (Table 4). As observed for other organo-clay complexes [22], clogging of the interlayer space and/or a reduction in the amount of surface exposed for herbicide adsorption in samples with large chitosan loadings could have reduced the effectiveness of the biopolymer in these samples to adsorb clopyralid. The morphology of the samples, with SW–CH-4 displaying greater porosity and exposed surface compared to SW–CH-6 (Fig. 3), supported the latter assumption.

Adsorption isotherms revealed that clopyralid adsorption by SW–CH samples was mostly linear up to herbicide concentrations as high as 0.5 mM (Fig. 6). Adsorption constants resulting from fitting the adsorption isotherms to the Freundlich equation are included in Fig. 6. The Freundlich K_f values for SW–CH-1, SW–CH-4, and SW–CH-6 (Fig. 6) were somewhat lower than the corresponding K_d values obtained at a single initial herbicide concentration of 0.005 mM (Table 4), but as K_d values, they increased with the amount of chitosan in the bionanocomposites. The linearity of the adsorption isotherms, as indicated by the value of N_f approaching to unity, also increased with the amount of chitosan in the samples. It is also interesting to note that the adsorption coefficients, K_d and K_f, given in Table 4 and Fig. 6 are, in general, greater than those previously reported for the adsorption of anionic pesticides such as imazamox, imazethapyr, 2,4-D, or dicamba by Wyoming montmorillonite exchanged with different natural and synthetic organic cations [15,16,18,35]. Apparently, the combination of the layered structures of montmorillonite and chitosan (Fig. 3) resulted in bionanocomposite morphologies which favored the availability and efficiency of the organic moiety and its $-NH_3^+$ groups for pesticide adsorption.

Fig. 7 shows the desorption behavior of clopyralid from SW–CH-4 and SW–CH-6. Clopyralid desorption with water occurred slowly, particularly from the highly adsorptive bionanocomposite SW–CH-6, where the pesticide seemed to have remained in adsorption sites less accessible for water molecules and hence more resistant to desorption compared to SW–CH-4. In contrast, high salt concentrations (0.1 M NaCl) promoted rapid desorption of the pesticide from both SW–CH-4 and SW–CH-6. This indicated strong competition between herbicide anions and Cl^- for adsorption sites and supported that adsorption of clopyralid occurred primarily through

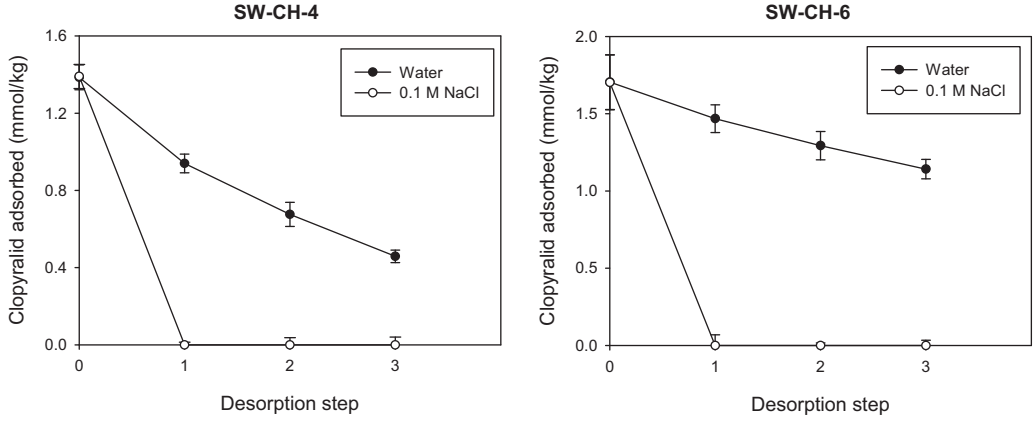


Fig. 7. Clopyralid desorption from SW–CH-4 and SW–CH-6 using water and 0.1 M NaCl.

Table 4
Clopyralid adsorption coefficients on SW–CH bionanocomposites.[a]

Sample	$pH_{initial}$	$pH_{equilibrium}$	%Ads[b]	K_d [c] (L/kg)	$K_{d\text{-}Chit}$ [d] (L/kg)
SW–CH-1	3.0	3.3	15 ± 1[e]	71 ± 7	1014
SW–CH-2	3.0	3.4	20 ± 1	102 ± 2	1397
SW–CH-3	3.0	3.4	12 ± 1	52 ± 3	812
SW–CH-4	3.0	3.7	39 ± 1	252 ± 14	2312
SW–CH-5	3.0	3.9	36 ± 1	214 ± 5	1466
SW–CH-6	3.0	4.5	55 ± 2	501 ± 37	1149

[a] Adsorption was measured at an initial herbicide concentration 0.005 mM.
[b] %Ads: percentage of herbicide adsorbed.
[c] K_d: adsorption distribution coefficient.
[d] $K_{d\text{-}Chit}$: K_d value normalized to the chitosan content of each sample.
[e] Mean ± standard error.

Table 5
Clopyralid adsorption coefficients on unamended and bionanocomposite-amended soils.[a]

Sample	$pH_{initial}$	$pH_{equilibrium}$	%Ads[b]	$K_{d\text{-}exp}$ [c] (L/kg)	$K_{d\text{-}calc}$ [d] (L/kg)
Soil 1	6.5	4.7	5 ± 1[e]	0.67 ± 0.08	0.67
Soil 1 + SW–CH-5 (5%)	6.5	4.8	10 ± 2	1.72 ± 0.27	11.3
Soil 1 + SW–CH-5 (10%)	6.5	4.9	18 ± 1	3.56 ± 0.09	22.0
Soil 1 + SW–CH-6 (5%)	6.5	5.0	26 ± 1	5.62 ± 0.30	25.7
Soil 1 + SW–CH-6 (10%)	6.5	5.1	38 ± 1	10.02 ± 0.21	50.7
Soil 2	6.5	8.0	<5	<0.5	<1
Soil 2 + SW–CH-5 (5%)	6.5	8.0	<5	<0.5	10.7
Soil 2 + SW–CH-5 (10%)	6.5	8.0	<5	<0.5	21.4
Soil 2 + SW–CH-6 (5%)	6.5	8.1	<5	<0.5	25.0
Soil 2 + SW–CH-6 (10%)	6.5	8.1	<5	<0.5	50.1

[a] Adsorption was measured at an initial herbicide concentration 0.005 mM.
[b] %Ads: percentage of herbicide adsorbed.
[c] $K_{d\text{-}exp}$: experimentally measured adsorption distribution coefficient.
[d] $K_{d\text{-}calc}$: expected value of K_d calculated assuming an independent adsorption behavior of the soil and SW–CH in the mixtures.
[e] Mean ± standard error.

a reversible anion exchange mechanism on positively charged chitosan sites at the montmorillonite surface, with ready desorption by formation of the soluble clopyralid salt [36].

3.3. Adsorption of clopyralid by bionanocomposite-amended soils

Two bionanocomposites with high affinity for clopyralid (SW–CH-5 and SW–CH-6) were selected as soil amendments to assess the potential of the materials for the immobilization of this pesticide in two different soils. Amendment of an acidic soil (soil 1) with SW–CH-5 and SW–CH-6 at rates of 5% and 10% led to a significant increase in clopyralid adsorption (Table 5), which can be attributed to the prevalence of cationic exchange sites on SW–CH at the pH of the soil/water suspensions (pH ∼ 5.0). In contrast, the increase in adsorption was negligible when SW–CH was added to an alkaline soil of pH ∼ 8.0 (soil 2), probably reflecting the absence of positively charged sites in SW–CH at such a high pH value [33].

The experimentally measured distribution coefficients, $K_{d\text{-}exp}$, for clopyralid adsorption on the bionanocomposite-amended soils were compared with the expected values, $K_{d\text{-}calc}$, calculated assuming an independent adsorption behavior of the soil and the bionanocomposite in the mixtures (Table 5). Assuming linear adsorption, such expected values can be calculated according to the equation:

$$K_{d-calc} = K_{d-soil} f_{soil} + K_{d-SW-CH} f_{SW-CH} \quad (1)$$

where $K_{d\text{-}soil}$ and $K_{d\text{-}SW\text{-}CH}$ are the individual distribution coefficients for clopyralid adsorption on soil and bionanocomposite, and f_{soil} and f_{SW-CH} are the fraction of soil and bionanocomposite in the mixture, respectively [37,38]. It is worthy to note that, although the bionanocomposites led to a remarkable increase in the adsorption of clopyralid by soil 1, the increase was less than expected from the individual adsorption constants and the fraction of soil and bionanocomposite in the mixtures ($K_{d\text{-}exp} < K_{d\text{-}calc}$). This result revealed that the bionanocomposites were less effective in adsorbing clopyralid in the presence of soil than in the absence of soil, probably because the interaction of soluble soil components with the bionanocomposites resulted in competition for adsorption sites or surface blockage effects which reduced the performance of the bionanocomposite added to the soil in adsorbing clopyralid.

4. Conclusions

The interaction of the biopolymer chitosan with montmorillonite resulted in bionanocomposites with the biopolymer distributed between the internal and external surfaces of the clay depending on the bionanocomposite composition and the preparation procedure. All bionanocomposites showed good adsorption properties for the herbicide clopyralid at pH levels where both the anionic form of the herbicide and the cationic form of chitosan predominated. In general, the removal of clopyralid from aqueous solution was greater for bionanocomposites with higher chitosan contents, although the performance of the biopolymer in adsorbing clopyralid seemed to be affected by its arrangement in each specific sample. Clopyralid adsorption by the montmorillonite–chitosan bionanocomposites was rapid, linear, and high salt concentrations (0.1 M NaCl) promoted the desorption of the adsorbed pesticide, strongly indicating that clopyralid adsorption occurred primarily through an ion exchange mechanism on positively charged chitosan sites at the montmorillonite surface. Addition of montmorillonite–chitosan bionanocomposites to soil was effective in increasing the adsorption of clopyralid, provided the pH of the equilibrated soil suspension remained at slightly acidic levels. These results indicated the potential of the assayed bionanocomposites for different environmental applications such as the removal of anionic pesticides from contaminated water or their immobilization in certain soil environments. The reversibility of the adsorption–desorption process indicates

montmorillonite–chitosan bionanocomposites may be potentially useful biocompatible carriers in the design of pesticide formulations directed to reduce the high mobility of anionic pesticides in the environment and, consequently, ground and surface water contamination risks.

Acknowledgments

This work has been financed by the Spanish Ministry of Science and Innovation (MICINN Projects AGL2008-04031-C02-01 and AGL2011-23779) and Junta de Andalucía (JA Project P07-AGR-03077 and Research Group AGR-264), cofinanced with FEDER-FSE funds through the Operative Program 2007-2013. The authors thank G. Facenda and C. Vaquero for technical assistance. M.A. Adelino also thanks the Spanish MICINN for her FPI fellowship.

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