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Characterizing and Designing Polycation–Clay Nanocomposites As a Basis for Imazapyr Controlled Release Formulations

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A novel controlled release formulation (CRF) of the herbicide imazapyr (IMP) was designed to reduce its leaching, which causes soil and water contamination. The anionic herbicide IMP was bound to polydiallyldimethylammonium-chloride (PDADMAC)–montmorillonite composites. PDADMAC adsorption reached a high loading of polymer, which resulted in charge reversal of the clay and promoted IMP binding. The composites were characterized by Fourier transform infrared, zeta potential, 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. IMP binding to the composites is affected by polycation loading and flocculation. Upon adding high concentrations of IMP to a composite of 0.16 g/g, we obtained high herbicide loadings (66% active ingredient). IMP release from the CRFs applied on a thin layer of soil was substantially slower than its release from the commercial formulation (Arsenal). Accordingly, soil column bioassays indicated reduced herbicide leaching (nearly 2-fold) upon applying the CRFs while maintaining good herbicidal activity. The new PDADMAC-clay formulations are promising from the environmental and weed control management points of view.

Introduction

The increasing use of agrochemicals such as herbicides poses health and environmental problems due to leaching and surface migration, which can cause surface- and groundwater contamination (*1*). These factors reduce herbicidal efficacy, causing an increase in herbicide frequency and dose application, which further increase the ecological contamination and the cost.

One approach to solve this problem of herbicide leaching and migration is to design controlled release formulations (CRFs), which decrease the rate of active ingredient release. A variety of CRFs have been designed based on lignin (*2*), starch (*3*), organo-clays (*4–7*), liposome–clay (*8*), and micelle–clay complexes (*9, 10*). Efforts to develop CRFs have also focused on encapsulation of herbicides in the natural polymer alginate (*11, 12*) and in a few cases including clay (*13–15*). However, no attempts have been made to design and apply polycation–clay composites for CRFs. In this study, we propose CRFs based on polydiallyldimethylammonium-chloride (PDADMAC)–montmorillonite composites for the anionic herbicide imazapyr (IMP). The leaching and migration of imazapyr in the soil and to water resources has been reported (*16–18*).

The interest in polycation–clay interactions in the last century focused mainly on stabilization and flocculation of clay suspensions (*19*). However, recently, these composites have received attention as potential nanocomposites for surface applications (*20–23*). These few reports on polycation–clay applications include Churchman's (*21*) study on the formation of polycation–clay composites and their use as sorbents for nonionic and anionic pollutants (*21–23*). Breen (*23*) examined the use of polycation-exchanged clays as sorbents for organic pollutants and studied the influence of layer charge on pollutant sorption capacity. Chitosan-clay composites have been relatively well characterized and designed as electrochemical sensors (*22, 24, 25*).

It is well-known that due to the high electrostatic affinity between the polycation and the negatively charged clay surface, polycation adsorption is rapid (*26*), can neutralize the net surface charge, or even result in charge reversal (*23, 27*). Polycation adsorption reaches high loadings on montmorillonite since it intercalates in the clay as indicated by X-ray diffraction (XRD) measurements (*21, 24, 28, 29*). Polycation configuration at the surface, as trains or as loops and tails, is difficult to determine, although polymer configuration plays a main role in binding components to a composite (*30*). The growing interest in polycation–clay composites for various applications emphasizes the need for a better understanding of composites and their ability to bind molecules for optimizing composite performance.

In the current study, we designed, characterized, and developed PDADMAC–montmorillonite (PDADMAC–mont) composites that bind the anionic herbicide imazapyr as a basis for CRFs. The adsorption kinetics and equilibrium of the interaction of PDADMAC with montmorillonite was studied. The PDADMAC–mont composites were characterized by Fourier transform infrared (FTIR), zeta potential, and XRD measurements. These elucidated the electrostatic interaction of the polycation with the surface and the intercalation of the polymer in the clay and suggest the formation of loops and tails on the surface. IMP binding to PDADMAC–mont composites was found to be affected by polymer loading and composite flocculation. The ability of the newly designed formulations to decrease leaching while maintaining good herbicidal activity was demonstrated by applying a soil column bioassay.

Materials and Methods

Materials. Wyoming Na-montmorillonite (SWy-2) was obtained from the Source Clays Repository of the Clay Mineral Society (Columbia, MO), and kaolinite Supreme Kaolinite from the English China Clay. Polydiallyldimethylammonium chloride (PDADMAC) (MW = 400 000–500 000) potassium bromide (IR grade) and sodium chloride were purchased from Sigma-Aldrich (Stenheim, Germany). Imazapyr (IMP) (+2(4, 5 dihdro-4methyl-4 (1methylethyl) 5 (1H imidazol 2-y)-3 pyridine carboxylic acid) and a commercial formulation Arsenal (240 g/L ai liquid) were obtained from Agan Chemicals, Israel. HPLC grade acetonitrile and DDW were purchased from Merck (Darmstadt, Germany). The structural formulas of IMP and of PDADMAC are shown in Figure 1.

Rehovot soil was used for analytical release tests and for plant bioassays. The soil was collected from the top 30 cm of a sandy loam soil at the faculty's experimental farm. The

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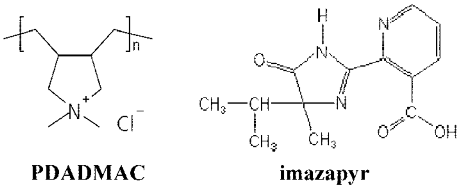

FIGURE 1. Chemical structure of imazapyr and of PDADMAC.

soil was air-dried and sieved through a 2 mm screen. The pH of the soil is 7.5, carbonate content 0.0%, organic matter content 0.2%, sand 95.5%, silt 3.3%, and clay 1.2% (*33*). A sorghum cultivar (*Sorghum bicolor*) was used as a test plant.

Methods. *PDADMAC Adsorption on Clay Minerals: Nanocomposite Preparation.* The nanocomposites 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 or kaolinite (5 mL), reaching final concentrations of 0–40 g/L polycation (to kaolinite only 2 g/L were added) and a suspension of 0.167% clay. Adsorption was also measured in the presence of NaCl (0.001–4M). The clay−polycation suspension was agitated for 2 h (equilibrium reached within 1 h) using a shaker. Suspensions were centrifuged (10000 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 composite.

Imazapyr Binding and Release to/from Nanocomposites. IMP (15 mL of 300 ppm (1.15 mM)) was added to the centrifuge tubes containing the PDADMAC−montmorillonite composites (PDADMAC-mont) (0–0.6 g polymer/g clay). IMP (15 mL of 0–3000 ppm (0–11.5 mM)) was added to the composite (0.16 g /g) with a final concentration of 1.83 g composite/L. The tubes were agitated for 3 days. IMP release was carried out by resuspending the composites for 4 h at the same concentration at which the adsorption experiments were performed. Supernatants were separated by centrifugation (10 000 rpm for 30 min) and prior to analysis filtered with modified acrylic polypropylene (Acrodisc Syringe Filters with Supor membrane, Pall Corp., Ann Arbor, MI) of 0.2 or 0.45 μm pore size. IMP concentration was measured by an HPLC (Merck Hitachi 6200, Tokyo Japan) equipped with a diode array detector set at a wavelength of 254 nm. The reverse phase column was a LiChrospher 100 RP-18 (5 mM) (Merck, Darmstadt, Germany). The mobile phase was 50% acetonitrile and 50% acidified water (with trifluoroacetic acid 40μL/L to reach a pH <3). The flow rate was 1 mL/min, retention time 3 min. The presence of polycation did not cause any interference with IMP detection.

Zeta-Potential. The mobilities/zeta potentials of PDADMAC, montmorillonite, and PDADMAC−mont composites (0–20 g PDADMAC /L added) were measured using a Zetasizer Nanosystem (Malvern Instruments, Southborough, MA). The clay and clay composites were measured in a diluted suspension (~0.05% clay).

X-ray Diffraction. The basal X-ray diffraction spacings of montmorillonite, PDADMAC−mont and the composites with IMP (adding 300 ppm (1.15 mM)) were measured in the same range of polycation added as in the adsorption experiments. On a round glass slide, 1–2 mL of the suspension were placed and left to sediment (oriented sample) for one day or put in an oven at 60 °C for 24 h. The basal spacing was measured using an X-ray diffractometer (Philips PW1830/3710/3020) with Cu Kα radiation, $\lambda = 1.526$.

Fourier Transform Infrared (FTIR). FTIR spectroscopy was used to determine the vibrations of water in montmorillonite and PDADMAC and to examine the interactions of PDADMAC with the montmorillonite surface (0–0.8 g polymer/g clay). Infrared spectra were obtained from composite mixed with KBr pellets, using an FTIR spectrometer (Nicolet Magna-IR-550, Madison, WI). The FTIR spectra were recorded at room temperature in the range of 600–4000 cm^{-1}.

Testing the Mont–PDADMAC–IMP CRFs. The PDADMAC–mont formulations tested were prepared by adding 1000, 2000, or 3000 ppm IMP to composites of 0.16 g polymer/g clay. The suspensions were centrifuged for 20 min at 15 000 g. Herbicide concentration in supernatants was measured by HPLC to determine the percent of active ingredient (ai) in CRFs (i.e., weight percent of herbicide in the CRF). The herbicide−polymer−clay precipitate was freeze-dried and lyophilized. CRFs were denoted comp. 1000, comp. 2000, and comp 3000, respectively. Comp. 1000, comp. 2000, and comp. 3000 contain 13, 21, and 40% active ingredient, respectively, whereas the commercial formulation contains 25%.

Release Studies from a Thin Soil Layer in Funnels: Analytical Test. Commercial and composite formulations were applied on a thin (59 g) Rehovot soil layer deposited on a filter paper in a Buchner funnel (area of 7.85×10^{-3} m^2). Comp. 1000, comp. 3000, and the commercial formulations were sprayed at a rate of 1900 g ai/ha. A control funnel was sprayed with water. The funnels were irrigated 8 times with 40 mL water every 10 min (40 mm water). Leachates were collected after each irrigation; IMP concentration was analyzed by HPLC.

Leaching Studies in Soil Columns: Bioassay. Plastic sleeves, with an upper exposed surface of 78 cm^2 and 20 cm long, were filled with 1600 g sandy Rehovot soil. The column surface was sprayed with water (control), mont–PDADMAC–IMP formulations, and the commercial formulation, at a rate of 500 g ai/ha (four columns for each treatment). The columns were irrigated with 50 mL every 10 min (300 m^3 water/ha) to ensure water movement through the column. The columns were left for 24 h to equilibrate and then sliced along their length and *Sorghum bicolor* seeds were sown. Plant growth was measured after two weeks. The percent of growth inhibition was calculated by comparing the shoot length to that of the control.

Data Analysis. The leaching depths of the commercial and CRF formulations through the soil columns were subjected to a two-way ANOVA model in a "split-plot" design using formulation (CRF vs commercial) and the depth as main effects. Multiple comparisons were done using a *t* test.

Results and Discussion

IMP Binding to a PDADMAC−Mont Composite versus a PDADMAC−Kaolinite Composite. The design of IMP-PDADMAC-clay CRFs is based on the concept that PDADMAC adsorbs electrostatically to the negatively charged clay surface; and that at polymer loadings exceeding the CEC (cation exchange capacity), the composite is positively charged, enabling binding of the negatively charged herbicide IMP (pK_a = 1.9 and 3.6). To efficiently apply CRFs they should have a high percent of a.i. (herbicide/composite w/w%). Therefore, our first goal was to determine which composites based on montmorillonite or on kaolinite would yield higher IMP binding upon adding the same concentration of polymer. PDADMAC (2 g/L) was added to the clays at a concentration that should result in charge reversal (see explanation below), and 300 ppm IMP were added to each composite (Table 1).

As expected, montmorillonite with higher CEC and surface area adsorbed much more polymer than kaolinite (0.15 vs 0.02 polymer g/g clay). However, when normalizing the results by surface area the difference in polymer coverage is emphasized: high on kaolinite (0.47 g/m^2) and lower on montmorillonite (0.2 g/m^2). This higher coverage of polymer on kaolinite and the higher charge reversal (expressed as percent of CEC in Table 1) results in higher IMP binding to

TABLE 1. Effect of Clay Surface Area and CEC on PDADMAC Adsorption and Consequently on IMP Binding

property	montmorillonite	kaolinite
surface area (m^2/g)	760	42
CEC (mmol/g)	0.8	0.065
surface charge density (mmol/g)	0.001	0.0015
PDADMAC ads. (g/g clay)	0.15	0.02
PDADMAC ads. (mg/m^2)	0.20	0.47
PDADMAC ads. (% CEC)	136	224
IMP bound g/g PDADMAC	0.35	1.14
IMP bound mg/g comp.	48	34

PDADMAC adsorbed on kaolinite vs that adsorbed on montmorillonite. In spite of our argument above, IMP binding, per composite weight, is higher on montmorillonite (48 vs 34 IMP mg/g comp) indicating that the large surface area of montmorillonite has a dominant effect. In both cases the percent of a.i. is low; however, since the PDADMAC-mont composite has somewhat of an advantage, we further studied this composite for the design of IMP CRFs, successfully increasing the a.i. substantially (see below).

PDADMAC Adsorption on Montmorillonite. The adsorption isotherm of PDADMAC (0–40 g/L) on montmorillonite and the zeta potential of the composites are shown in Figure 2. The measured zeta potential for PDADMAC was 60 mV. The time dependence (1–24 h) of PDADMAC adsorption (results not shown) indicate that equilibrium was reached within an hour as reported previously (*19, 26, 34*). As expected with Coulombic interactions and as seen by the zeta potential values, adsorption increases steeply at low bulk polymer concentrations up to surface neutralization. Zeta potential measurements indicate that charge neutralization is reached at a loading of 0.03 g polymer/g clay (Figure 2B) which is lower than the calculated loading (0.11 g/g) required to neutralize the clay surface. Calculated neutralization was based on stoichiometric adsorption of the positively charged monomers equivalent to the CEC. This outcome of zeta potential measurements can be explained by the screening of the clay surface by the highly charged polycation even at loadings lower than stoichiometric neutralization. At PDADMAC loadings exceeding surface neutralization, zeta potential and adsorption increased moderately, reaching a high loading of 0.9 g/g that corresponds to nearly 10 times the CEC. An adsorption plateau is not observed, in contrast to several studies on polycation adsorption (*21, 26, 29, 34, 35*). However, these studies concentrated on relatively low polycation concentrations and perhaps observed a pseudoplateau. If higher polymer concentrations had been applied (as in Figure 2A), the continuous moderate increase might have been seen.

The effect of ionic strength (0–4 M NaCl) on PDADMAC adsorption to montmorillonite was studied (Figure S1 in the Supporting Information). PDADMAC adsorption slightly increased with low ionic strength but decreased with a further increase in ionic strength. This maximum is generally accounted for by different behavior in low and high salt regimes. In the first case, corresponding to large Debye lengths, interchain and intrachain repulsions that would tend to reduce coverage are screened by added salt, leading to a slight increase in adsorption. Subsequent increase in salt screens more short-range favorable interactions between polymer segments and the charged surface, and therefore adsorption decreases (see reviews *27, 36*).

The XRD patterns of montmorillonite and of PDADMAC-mont composites (0–0.8 g/g) are shown in Figure 3. The *d*001 spacings are obtained 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 2θ values as the PDADMAC-clay ratio increases. The air-dried sample of montmorillonite gave the expected basal spacing of 1.25 nm. An additional spacing of 10 nm indicated impurity of Illite. Composites of low loading (<0.2 g polymer/g clay) gave a basal spacing of 1.46 nm, which can be related to the intercalation of one polycation layer parallel to the interlayer surface of the clay (Figure 3). A further increase to 1.82 nm at a polymer loading of 0.3 g/g can be explained by the adsorption of two intercalated polymer layers (*24*). At the very high polymer loading of 0.8 g/g clay, two peaks were obtained, corresponding to 1.46 nm and to a large spacing of 6.25 nm. At a polymer loading of 0.8 g/g clay, approximately 170% of the surface is covered (on the basis of clay's surface area and the polymer's area (taking into account bond lengths)). This suggests that the polymer is not only adsorbed as trains (flat) but also in a loop and tail configuration, which is in agreement with the large spacing of 6.25 nm (Figure 3). The basal spacings did not decrease upon heating the composites at 60 °C; the structure does not collapse in the absence of intercalated water.

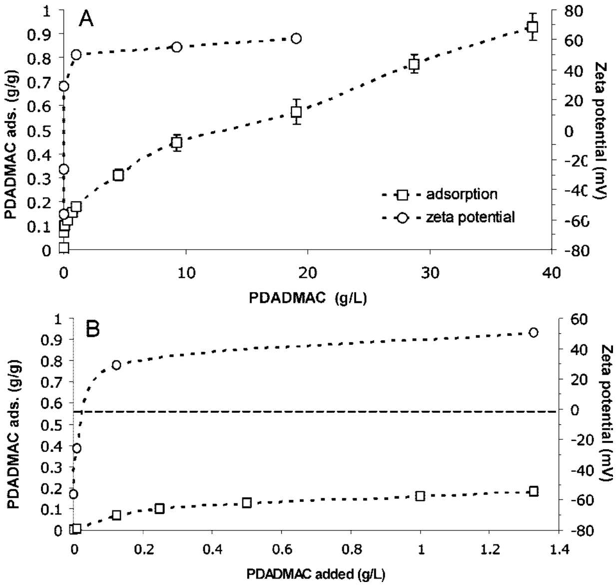

FIGURE 2. (A) Adsorption isotherm of PDADMAC (0–40 g/L) on montmorillonite (1.67 g/L) and zeta potential of the composites. (B) PDADMAC adsorption (low polymer concentration added 0–1.3 g/L) on montmorillonite and zeta potential of the composite as a function of polymer concentration added.

Churchman (*21*) obtained similar basal spacings for PDADMAC–mont composites with low loadings, an increase from 1.49 to 1.9 nm. However, the composite with the highest PDADMAC loading measured in his study was only 0.4 g/g, so the maximum spacing was smaller (2.78 nm) than 6.25 nm. Durand-Piana et al. (*26*) also reported a smaller basal spacing of 3.5 nm.

The addition of the herbicide to the composites had no significant impact on the basal spacing, suggesting that IMP adsorbs on the external composite surface and does not intercalate in the modified clay.

The FTIR spectra of montmorillonite, PDADMAC, and PDADMAC–mont composites (0.16 and 0.8 g/g) in the wavenumber range of 4000–1300 cm^{-1} are shown in Figure 4. The montmorillonite spectrum shows characteristic peaks at 3620 cm^{-1} for O–H stretching, at 3439 cm^{-1} for H–O–H hydrogen-bonded water and at 1647 cm^{-1} for H–O–H deformation (*37*). The 1647 cm^{-1} vibration weakens upon the formation of PDADMAC–clay composites, indicating the release of water from the clay surface upon polymer adsorption. The three characteristic bands of PDADMAC between 2800 and 3000 cm^{-1} and the ones around 1480 cm^{-1} correspond to CH_2 or CH_3 stretching and bending vibrations,

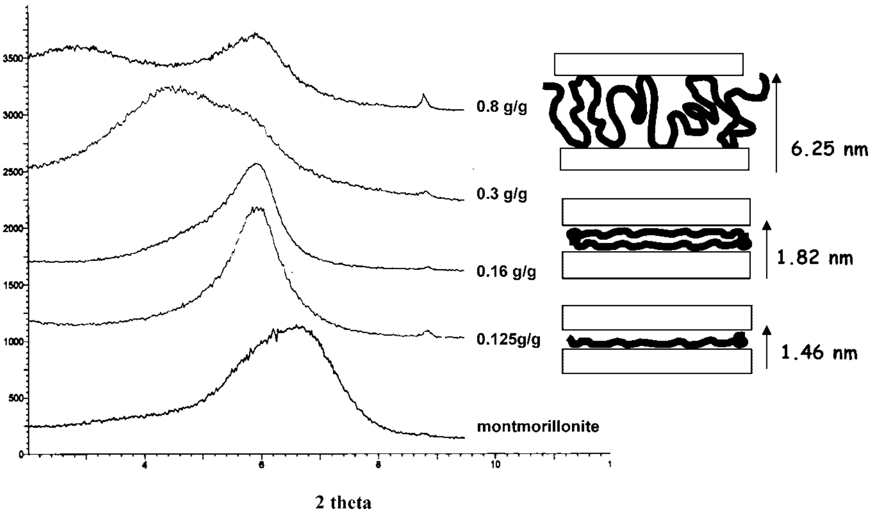

FIGURE 3. XRD of montmorillonite and of PDADMAC−mont composites (0–0.8 g/g).

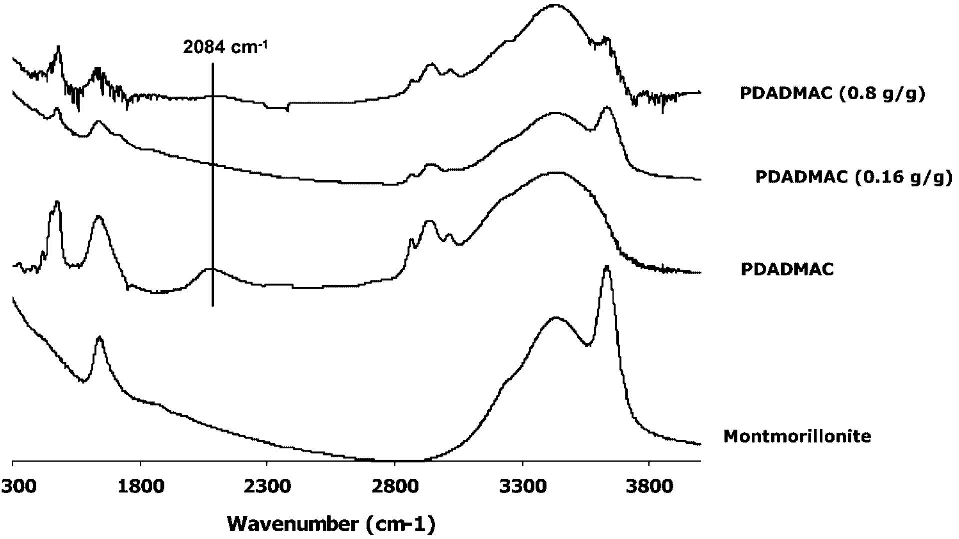

FIGURE 4. FTIR spectra of montmorillonite, PDADMAC, and PDADMAC−mont composites (0.16 and 0.8 g/g) in the 4000–1300 cm^{-1} wavenumber range.

respectively. These vibrations were not altered upon polycation adsorption, validating that these group are not involved in the interactions with the clay.

On the other hand, the PDADMAC spectrum shows a distinctive peak at 2084 cm^{-1}, attributed to the quaternary ammonium chloride bond (*38*) which was not observed for the adsorbed polycation at a loading of 0.16 g/g. The absence of this vibration for the composite confirms the establishment of electrostatic interactions between the quaternary ammonium and the negatively charged clay surface. However, at PDADMAC loadings exceeding charge neutralization, the monomers that do not neutralize the surface may adsorb with their chlorides. Indeed, for the composite with a high loading of 0.8 g polymer/g clay, the vibration at 2084 cm^{-1} appears. This is in agreement with the XRD measurement, suggesting a loops and tails configuration of the polymer in the 0.8 g/g composite.

IMP Binding to PDADMAC−Mont Composites. Based on the XRD measurements (Figure 3) and rough surface coverage calculations, we suggest that polymer adsorbed at high loadings (0.5 g/g) is in a configuration of loops and tails. Such a configuration suggests that the monomers in the loops do not interact electrostatically with the surface (supported by the FTIR measurements) resulting in available positive binding sights enabling enhanced IMP binding. Hence, not only the increase in polymer loading should increase IMP binding (more polymer → more IMP binding) but also the effect of polymer configuration at high loadings should promote its binding. However, IMP binding to PDADMAC-mont composites as a function of polymer loading decreases for composites with polymer loading exceeding 0.18 g poly/g clay (Figure 5).

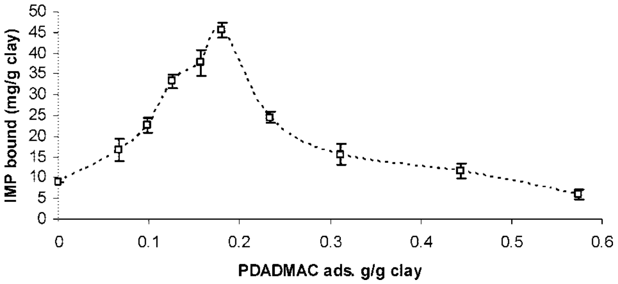

FIGURE 5. IMP (300 ppm) binding to PDADMAC-clay composites as a function of PDADMAC loading.

The surprising decrease may be explained by flocculation. In the case of polyelectrolytes and oppositely charged surfaces, flocculation takes place by charge neutralization. Electrostatic stabilization is achieved when the global charge

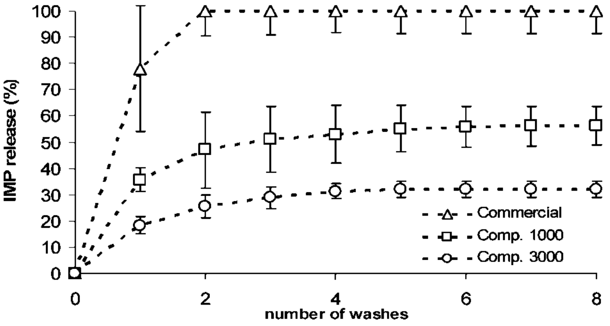

FIGURE 6. IMP release from the commercial and PDADMAC–mont formulations applied on a thin soil layer.

of the particles is reversed, i.e., at higher polymer loadings (*26*). IMP has two negatively charged functional groups, enabling it to bridge positively charged composites. This results in massive flocculation (visually observed). Flocculation reduces available composite surface area which can explain the reduction in IMP binding to highly positively charged composites. Furthermore, when binding toluene (*21*) or sulfentrazone (an anionic herbicide with one negative charge, results not shown), no bridging effect is present and binding does not decrease upon increase in polymer loading. Moreover, reducing flocculation by decreasing (3 times) clay, polymer and IMP concentrations proportionally, IMP binding at high polymer loadings did not decrease in contrast to the results seen in Figure 5.

An efficient application of CRFs implies that they contain a high percent of active ingredient (a.i.). To reach a high percent of a.i., we added IMP at high concentration (up to 3000 ppm) to the composite, which yielded the highest herbicide binding (0.16 g polymer/g clay) (Figure 4). IMP binding to the composite was nearly linear with ~20% binding (Figure S2 in the Supporting Information). When adding 3000 ppm of IMP to the composite, we reached a loading of 760 mg IMP/g clay, corresponding to 66% a.i. (Arsenal is 25%). IMP desorption from the composites (after 4 h) was low (10–30%) and decreased with the increase in IMP loading on the composite. The desorption isotherm (Figure S2 in the Supporting Information) shows hysteresis behavior, i.e., that IMP release is much slower than its binding. The high percentage of a.i. and the slow release are essential for CRF designing.

IMP Release from the Composite and Commercial Formulations in a Thin Soil Layer. IMP release from the commercial and from two PDADMAC-mont formulations was tested by applying the formulations to a thin soil layer, irrigating eight times and measuring IMP concentration in the leachates (Figure 6). After two irrigations (equivalent to 10 mm of rain) 100% of the IMP from the commercial formulation (25% a.i.) leached through the thin soil layer, whereas only 45 and 25% leached from the PDADMAC-mont formulations with 13 (comp. 1000) and 40% (comp. 3000) active ingredient, respectively. The formulation with 40% a.i., comp. 3000, showed less release of IMP than formulation comp. 1000 with 13% a.i., as was observed in batch experiments. These results clearly indicate the potential of the comp.3000 formulation to yield controlled release and reduced leaching.

Bioassay in Soil Columns of the IMP−Composite and Commercial Formulations. Soil columns were sprayed with the mont−PDADMAC−IMP formulations (a mix of comp 3000 and comp 2000), the commercial formulation and water (control) at a rate of 500 g ai/ha (at the low end of the recommended rate). The percentage of plant growth inhibition throughout the columns was calculated to indicate herbicide activity and leaching (Figure 7). Both the commercial and the CRF formulations yielded approximately 80% growth inhibition at the top of the columns indicating good herbicidal activity of the CRF even at relatively low doses. The CRF, however, displayed statistically significantly superior behavior since it reduced leaching at the bottom of the column (15–20 cm) by nearly 2-fold. To conclude, applying the newly designed polycation-clay CRF reduced undesirable IMP leaching while maintaining good herbicidal activity, demonstrating the CRF's environmental and agricultural benefits.

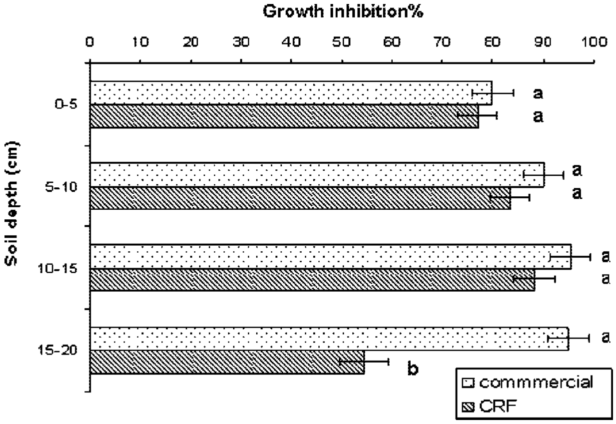

FIGURE 7. Shoot growth inhibition of a test plant as a function of the depth in soil columns sprayed with water (control), commercial formulation (Arsenal), and CRFs (comp. 2000 and comp. 3000).

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Supporting Information Available

Two additional figures on the effect of ionic strength (0–4 M) on PDADMAC adsorption on montmorillonite and IMP binding (0–3000 ppm) and release to/from a PDADMAC−mont composite (0.16 g polymer/g clay). This material is available free of charge via the Internet at http://pubs.acs.org.

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