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Rapid Desorption of Polyelectrolytes from Solid Surfaces Induced by Changes of Aqueous Chemistry

Alberto Tiraferri^{a,*}, Plinio Maroni^b

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^aDepartment of Environment, Land and Infrastructure Engineering, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Turin (Italy)

^bDepartment of Inorganic and Analytical Chemistry, University of Geneva, Sciences II, Quai Ernest-Ansermet 30, 1205 Geneva, Switzerland

**Corresponding author e-mail address: alberto.tiraferri@polito.it, phone: +39 011 090 7628*

Abstract

The short-term desorption induced by changes of aqueous chemistry of pre-deposited polyelectrolyte layers on solid surfaces was studied with reflectometry. The behavior of a strong polycation, polydiallyldimethylammonium chloride (PDADMAC), interacting with flat silica was investigated in detail. Results showed that partial desorption of pre-adsorbed polymer chains can be quickly triggered by changes in ionic strength and pH. When lowering these parameters in the PDADMAC-silica system, the increased lateral repulsive potential of neighboring chains drove the desorption of some of the polymer. Furthermore, layer desorption was favored when electrostatic interactions between a polyelectrolyte and the underlying surface became less attractive or switched to repulsive. At the investigated timescales (< 1 h), adlayer desorption was always partial and often incomplete. When initiating desorption from a condition of large adsorbed mass, desorption effects did not result in the plateau mass obtained by adsorption on a clean surface: an excess mass remained deposited. The results thus suggest that a relatively large energy barrier needs to be overcome to induce re-dissolution of pre-deposited chains and that this barrier may be function of the number of polymer-surface interactions, which are in turn correlated with polymer molecular mass. These mechanisms have important implications for environmental processes and colloidal systems because they imply that, once adsorbed, polymeric chains may be re-dissolved but only to a limited degree at typical engineering timescales.

INTRODUCTION

Polyelectrolytes are ubiquitous and their adsorption on and modification of surfaces govern a plethora of environmental and engineering processes.¹ For example, natural sorption on mineral surfaces influences bacterial adhesion, biomineralization, and the fate and distribution of pollutants. Layers of polyelectrolytes are also exploited in a variety of engineering systems,² e.g., for the nanoremediation of contaminated aquifers^{3, 4, 5} and in the biomedical field to enhance drug delivery and to create protein resistant surfaces⁶. Cationic polymers, such as poly(diallyldimethylammonium chloride), are extensively used in water treatment plants to induce the flocculation of suspended solids and remove turbidity.⁷ On the other hand, undesirable adsorption of organic macromolecules on engineered surface, referred to as fouling, negatively affects the functionality of these systems.⁸ One prominent example is membrane-based water treatment: there, fouling must be reduced or its effect minimized by appropriate membrane cleaning, which entails the desorption of the organic foulants.⁹

The adsorption of polyelectrolytes on different surfaces has been widely studied.^{1, 10, 11} On the contrary, the reversibility of adsorption and the desorption of adlayers are less understood, although these phenomena are as important as adsorption to govern the behavior of surfaces. The existing literature on the mechanisms of layer desorption is limited and has focused on the effects observed upon dilution, change in pH or ionic strength, displacement with other polymers, molecules, or solvents, and interaction with surfactants. Previous research has established that the adsorption of polyelectrolytes is mostly irreversible upon dilution.^{1, 12, 13} This process is kinetically blocked as the activation energy to peel off all the polymer segments from a surface is high. Some desorption may be initially observed when the adlayer comes in contact with the pure electrolyte but this phenomenon quickly slows down as the mass transfer becomes rate-limiting,^{14, 15, 16, 17} the layer undergoes conformational changes that increase the total attraction energy to the underlying surface,¹⁸ or when all

the more loosely bound chains have already returned into solution. A hysteresis has been thus reported during cycles of adsorption and desorption.^{19, 20} More substantial desorption of pre-deposited chains has been observed due to the replacement with other molecules, originally free in solution.^{21, 22} The ability of displacement was correlated with the homogeneity of the pre-adsorbed layer and to the relative affinity of the different competing molecules.²¹ Several recent studies have also discussed the effect of sodium dodecyl sulfate or other surfactants to desorb pre-adsorbed layers of polyelectrolytes from various surfaces.^{23, 24, 25, 26, 27, 28} Others have underlined the effect on polymer desorption of the introduction of different solvents²⁹ in the system and that of competition between solid surfaces of different chemistry to act as adsorbent in a polymeric solution³⁰.

Studies focusing on desorption upon changes in aqueous chemistry are also directly relevant for environmental and biomedical applications. Examples include the potential instability of adlayers when modified drug carriers encounter aqueous environments with varying composition within the body. Also, changes in aquifer properties following drainage, percolation of substances, and intrusion of low or high salinity streams. The mechanisms discussed in previous reports may be summarized with rapid desorption observed in the cases when the changes in aqueous chemistry result in (i) increased chain-chain repulsion and (ii) decreased surface-chain attraction.^{25, 31, 32} However, in numerous cases, desorption phenomena led to adsorbed amounts that did not coincide with the corresponding plateau of adsorption, which was explained by a number of different mechanisms, including surface heterogeneities,³³ heterogeneity in the chemistry of the polymeric chains, thus in their interaction with the surface,¹³ the existence of multiple binding between the adsorbed molecules and the substrate,¹² the concomitance of forces acting at different distance range,^{19, 34} as well as surface fractionation^{17, 35} and conformational re-arrangement.¹⁸ These different reports are evidence of the uncertainty still existing around the topic of layer desorption.

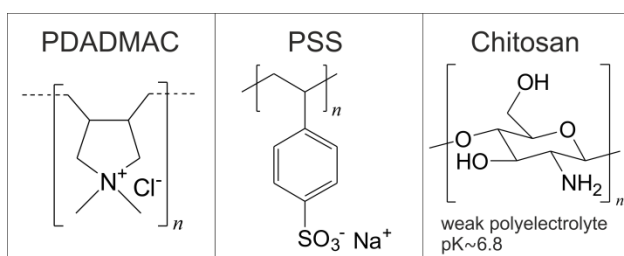
This study seeks to provide a rational investigation of the effect of changes in pH and/or ionic strength on the rapid desorption of pre-adsorbed polyelectrolyte layers on solid substrates. Flat surfaces are used in reflectometry and the study is conducted under flow conditions by observation of the adsorbed amounts in the correspondence of a stagnation point. A specific system is first examined in detail, consisting of PDADMAC interacting with silica. Its desorption behavior is discussed following changes of a single parameter, pH or ionic strength, and of both aqueous properties simultaneously. Then, the results obtained with systems comprising a variety of polyelectrolytes and substrates are presented. Other questions of this study concern the influence of polymer molecular mass and the difference in adsorbed amounts obtained upon desorption and upon adsorption under the same aqueous condition.

EXPERIMENTAL SECTION

Substrates and polymers. Quartz crystal microbalance sensors coated with a gold layer were purchased from Q-Sense (QSX 301, Gothenburg, Sweden). Following deposition of a middle adhesion layer of titanium, the crystals were sputter coated with a silica layer. The thickness of the uppermost silica layer was 260 ± 1 nm and its RMS roughness 2.0 ± 0.1 nm. Before each experiment, this surface was cleaned in an ozone-rich atmosphere for 20 min and activated by placing a droplet of a piranha solution (3:1 volume mixture of H₂SO₄ 98% and H₂O₂ 30%) on top of the silica for 10 min. The substrates used to produce SAMs consisted instead of an underlying layer of silicon, a 2.5 nm-thick middle adhesion layer of titanium, and an uppermost sputter coated layer of gold with a thickness of 8.5 nm and a RMS roughness of roughly 0.5 nm. Film thickness and roughness were determined, respectively, by scanning angle null ellipsometry (Multiskop, Optrel, Berlin, Germany) and by atomic force microscopy using a Cypher AFM (Asylum research, Santa Barbara, CA) in amplitude modulated mode. Prior to fabrication of SAMs, gold surfaces were treated using an oxygen-enriched UV-ozone

cleaner for 20 min followed by rinse with ethanol. The alkanethiol assemblies were spontaneously adsorbed on these surfaces by immersing them overnight (> 10 h) into an ethanolic solution of 0.5 mM 11-mercaptopundecanoic acid with 2% (v/v) CF_3COOH to form COOH SAMs, or 0.5 mM 11-amino-1-undecanethiol hydrochloride with 3% (v/v) $\text{N}(\text{CH}_2\text{CH}_3)_3$ to fabricate NH_2 SAMs. These films were rinsed sequentially with ethanol, an ethanolic solution of 10% (v/v) NH_4OH for carboxyl terminated films or 10% (v/v) CH_3COOH for amine terminated films, and again ethanol.

Sodium poly(styrene sulfonate) (PSS, molar mass 30 kg/mol), poly(diallyldimethyl ammonium chloride) (PDADMAC, molar mass < 100 kg/mol), and chitosan (molar mass 140-220 kg/mol) were employed as polyelectrolytes; see Scheme 1. All polymers were purchased from Sigma-Aldrich, Switzerland, and dissolved in Milli-Q (Millipore) water to obtain stock solutions. The solutions for experiments were obtained by dilution of these stocks with Milli-Q water, their pH adjusted with HCl or NaOH, and their ionic strength corrected using NaCl. All the solutions of pH 6 or higher were kept under nitrogen atmosphere during the entire duration of the tests, to prevent the dissolution of carbon dioxide from the lab atmosphere. The refractive index increment, dn/dc , of the polymers was determined using a refractometer (Abbemat, Anton Paar, Austria), at a wavelength of 532 nm. For the three polymers, the following values of dn/dc were measured: 0.15613 mL/g for PSS, 0.23640 mL/g for PDADMAC, and 0.14985 mL/g for chitosan.



Scheme 1. Formula of the three polymers used in this study. Poly(diallyldimethylammonium chloride) and sodium polystyrene sulfonate are strong polyelectrolytes. Chitosan is a weak polyelectrolyte: the pK of its amine group is roughly 6.8.

Reflectometry. A reflectometer was used to measure the dry mass of adsorbed polymers per unit area. The substrate was installed in an impinging jet cell into which the solution was injected through a 0.5 mm radius hole in a capped prism, thus forming a stagnation point in the center of the adsorbing surface. A polarized green diode laser with a wavelength of 532 nm was projected into this stagnation point with a final angle of incidence on the surface of roughly 71°. The light beam was reflected from the adsorbing surface and split into its parallel and perpendicular components, whose intensities are proportional to the respective reflectances, R_p and R_s . From the ratio between these components, $R(t)$, the adsorbed dry mass, Γ , was calculated as:

$$\Gamma(t) = A \cdot \frac{R(t) - R(0)}{R(0)} \quad (1)$$

where A is a sensitivity constant and $R(0)$ is the initial ratio between the parallel and perpendicular reflectance. The sensitivity factors were calculated for each polymer/substrate combination from a five-slab model, in which the upper slab corresponded to the adsorbed layer, and using the appropriate refractive indexes. For further information on the reflectometry setup and on these calculations please refer to our previous publications.^{36, 37, 38}

Adsorption and desorption test protocol. Figure 1 exemplifies the typical experimental protocol followed in this study. Initially, a background solution of the desired aqueous chemistry was pumped onto the surface until attainment of a baseline signal; step A. Subsequently (step B), the same solution that would be later used to induce desorption was introduced, resulting in a signal change due to the different refractive index compared to the background solution. Re-injection of this latter solution in step C caused a reversal of the signal back to the baseline value. These three steps were performed to ensure the possibility to return to the baseline value upon the sequential change in pure electrolytes of different composition. Upon attainment of a stable baseline, adsorption was then initiated in step D by

injecting a polymer solution at a concentration of 10 mg/L, having the same aqueous chemistry of the background solution. When the adsorption reached saturation, as evidenced by a plateau in the signal, the solution was again substituted with a polymer-free solution of the same composition (step E). At this point, desorption was induced by pumping a polymer-free desorption solution in step F (the same solution used in step B) until the signal showed negligible shifts. To quantify the amount of polymer still adsorbed on the surface, the last step G comprised the final introduction of the background solution. All experiments were conducted at room temperature (21 ± 2 °C).

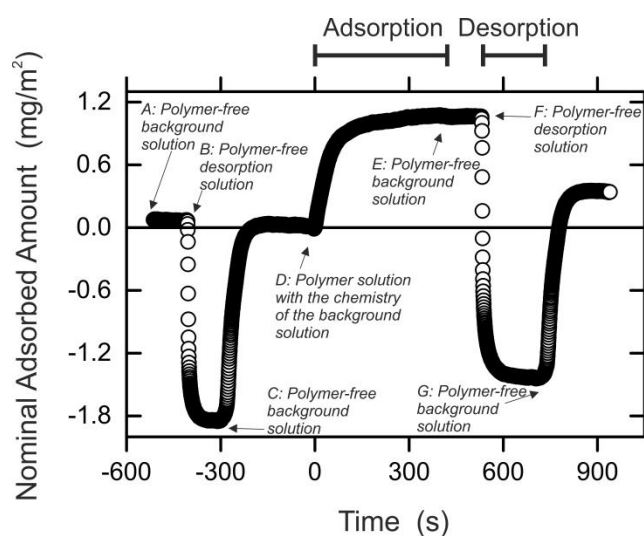


Figure 1. Representative experimental trace to assess the desorption of a layer of polyelectrolyte from a solid surface. The protocol consisted of seven stages, each carried out until a negligible change in signal was observed over time.

The refractive index of the solution introduced onto the stagnation point changed based on its chemistry. Therefore, the sensitivity constant, A , was not constant throughout the test exemplified in Figure 1. The signal conversion into adsorbed amount was straightforward and was achieved using the sensitivity constant associated with the background solution. Only the values computed during injection of this background were used for further calculations. For example, the relative amount of

desorption was obtained by dividing the mass related to the stable signal in step G and that in step E. However, for the same reason the calculation of the initial kinetics of desorption was not possible. Therefore, this work focuses only on the adsorbed and desorbed amounts. Also, the various steps indicated in Figure 1 were prolonged until negligible change in signal was observed. These time steps were relatively short, usually between few minutes to one hour. As such, this work investigates the rapid desorption occurring in such timescales, which are typical of engineering applications.

RESULTS AND DISCUSSION

Adsorbed amount of PDADMAC on silica. We present first the adsorbed mass of PDADMAC on silica surface at saturation, which may be used as a comparative value for subsequent desorption results. The amount of deposited PDADMAC increased with increasing pH and ionic strength (IS) in solution; see Figure 2 and Table S1 of the Supporting Information. This mechanism was due to a generally large ion concentration in solution or to an increase in the magnitude of the diffuse-layer negative potential of the silica substrate at higher pH values.^{1, 36, 39} A larger negatively charged potential increases the likelihood of adsorption of oppositely charged molecules and it recalls a high concentration of ions at the solid/water interface. Therefore, both in the case of larger bulk ionic strength and higher pH, the local ionic strength near the surface increased, allowing for a denser packing of charged PDADMAC molecules on the silica substrate. The largest adsorbed mass of 1.2 mg/m² was obtained by inducing adsorption in a solution of 250 mM NaCl at pH 10. The lowest mass of roughly 0.2 mg/m² was recorded at pH 2.5, conditions under which the silica surface is weakly charged and ionic strength is approximately 3 mM.

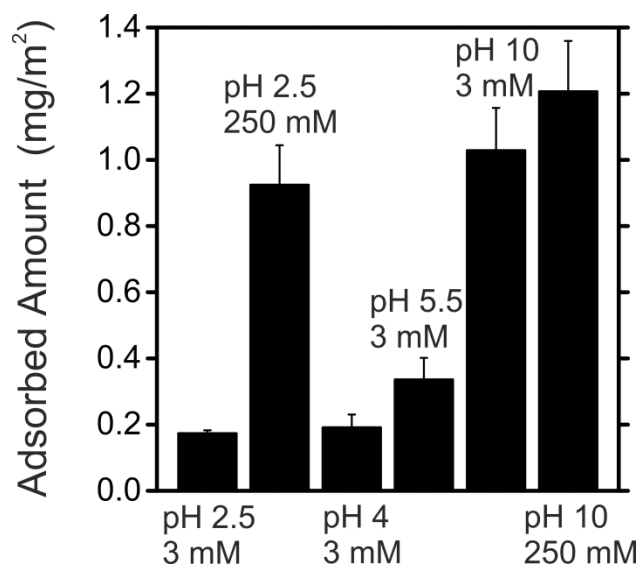


Figure 2. Adsorbed mass for saturated layers of PDADMAC on silica as a function of solution chemistry, indicated near each bar. Data points are the average of at least duplicate experiments. All experiments were performed with 10 mg/L PDADMAC at room temperature.

Effect of pH changes and pathway of change on desorption. A first set of desorption tests aimed to understand the effect of pH changes on the re-dissolution of pre-deposited layers of PDADMAC on silica. In Figure 3, all the data were normalized by the adsorbed amount at saturation obtained on a clean surface with 10 mg/L PDADMAC at pH 10 in 3 mM NaCl. This amount is related to the solid bar and corresponded to 1.03 ± 0.13 mg/m². The absolute values of the data displayed in Figure 3 are tabulated in Table S2 of the Supporting Information. The results indicate that a decrease of pH induced the desorption of part of the polymeric layer. This effect was more pronounced as the aqueous chemistry changed to lower pH values; see Figure 3a. This effect is rationalized with protonation of the substrate silanol groups in more acidic environments, which caused a reduction of the concentration of ions at the solid/water interface, thus an increase of the magnitude of the overlapping electric potential of pre-deposited chains. Following this effect, the surface became oversaturated with PDADMAC molecules because of increased chain-chain repulsion. Also, the polymer-surface

electrostatic attraction decreased as the surface charge was reduced. This phenomenon also increased the likelihood of chain desorption, as a lower anchoring energy was present. Therefore, some of the chains re-dissolved, consistently with data discussed in previous studies.^{17, 19, 27, 31}

The data in Figure 3 also suggest that the pathway taken to reach the final pH value was not important and that the final conditions governed the extent of rapid desorption. Specifically, the final layers of PDADMAC upon desorption induced by changes to pH 2.5 from 3 mM NaCl pH 10 had similar dry mass regardless of whether this change was obtained in one step, multiple steps through intermediate pH values, or by continuous addition of small quantities of HCl into solution (Figure 3b). The same effect was registered when lowering the pH to a value of 4 via two different pathways (Figure 3a).

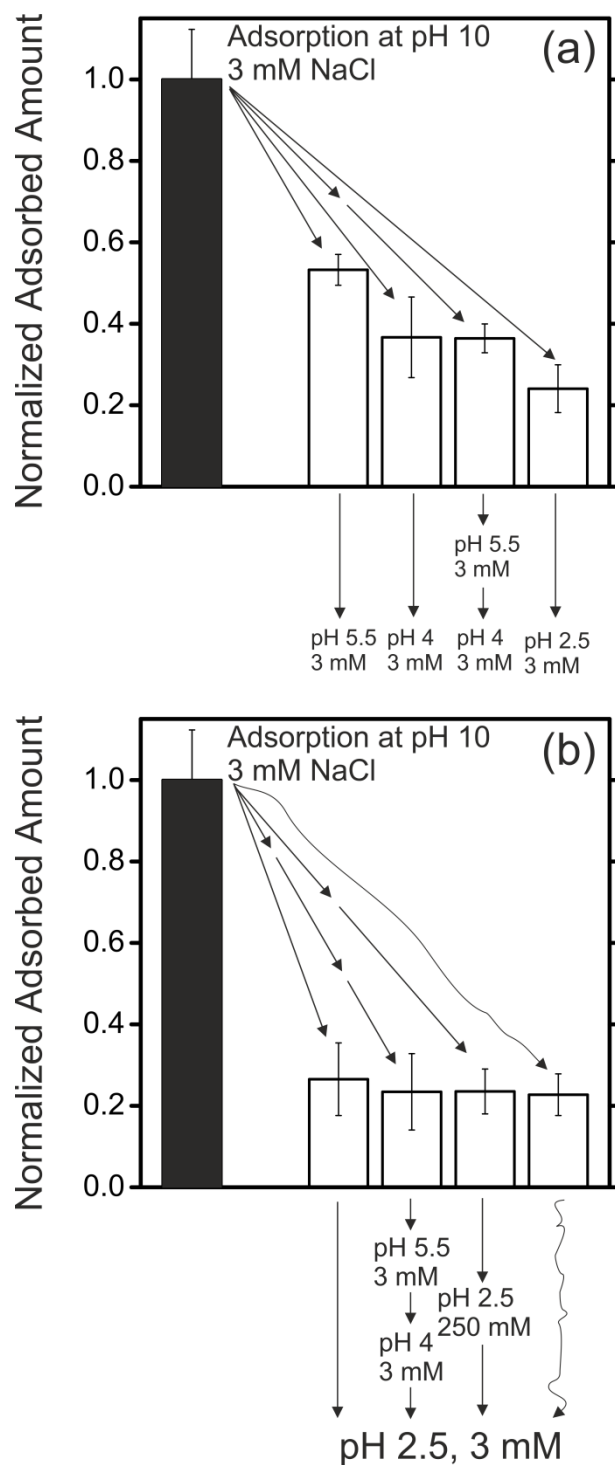


Figure 3. Desorption of PDADMAC from pre-adsorbed layers on silica induced by pH changes. (a) Desorption induced by changes of pH, achieved in diverse pathways and ending with different pH values indicated below each empty bar. (b) Desorption induced by changes of pH, achieved via different pathways indicated below each bar and all ending with a final pH of 2.5.

Effect of changes in ionic strength, with or without pH change, on desorption. The next hypothesis to be tested concerned the possible desorption of PDADMAC adlayers upon reductions of solution ionic strength. Results of the related tests are summarized in Figure 4 where, as was the case in Figure 3, all the data were normalized by the adsorbed amount at saturation obtained at pH 10 in 3 mM NaCl. The absolute values of data from Figure 4 are tabulated in Table S3 of the Supporting Information. Indeed, when the aqueous chemistry changed to comprise a lower amount of dissolved ions, part of the pre-deposited layers of PDADMAC desorbed from the silica surface. A small desorption was induced by lowering the IS from 250 mM to 3 mM at pH 10, while more pronounced chain detachment was observed for the identical reduction of salinity but induced at pH 2.5. The same mechanism explains the desorption induced by a decrease of pH and that prompted by a reduction of ionic strength, i.e., increased chain-chain repulsion due to a change in local ionic concentration at the solid/water interface. Indeed, when both parameters were changed in the system toward the same direction, i.e., both pH and IS decreased, the observed desorption was enhanced compared to the case in which only one of the two parameters was adjusted. Interestingly, when these changes had opposite direction, desorption was thwarted compared to the case in which only the pH value was decreased. In particular, changing the pH from 10 to 2.5 with also the addition of 250 mM NaCl resulted in a final layer comprising 60% of the mass at the original condition. The final PDADMAC layer had instead 20% the mass of the initial layer for the same pH change if the salinity was kept at a value of 3 mM. Overall, it seems that pH changes can cause a more significant rapid desorption compared to changes in ionic strength, at least for the system investigated here. While both shifts in aqueous chemistry induce a change in the local ionic concentration at the solid/water interface, a pH reduction also prompts protonation of the surface moieties and a lower PDADMAC-silica attraction, thus decreasing the density of anchoring points and enhancing the likelihood of chain desorption. This phenomenon does

not occur when only bulk ionic strength changes and it might partly explain the larger effect of pH on the magnitude of desorption.

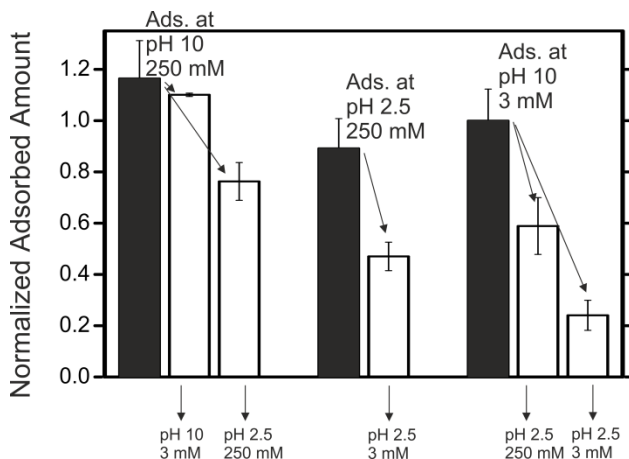


Figure 4. Desorption of PDADMAC from pre-adsorbed layers on silica induced by solutions characterized by different pH and/or ionic strength values. Solid bars summarize the adsorbed amount following adsorption under different conditions indicated near the top of each solid bar. Empty bars summarize the adsorbed amounts following desorption induced by solution with composition indicated below each empty bar.

Literature reports showed desorption of pre-adsorbed polyelectrolyte chains on an oppositely charged surface upon an increase in ionic strength, rather than a decrease.^{25, 32, 40} The desorption caused by an increase of ions in solution is due to screening of the electrostatic attraction between the charge polymer and the oppositely charged substrate and was usually observed for salt concentrations in the order of 1 M or higher. Also, the magnitude of ionic strength needed to induce desorption has been correlated with the polyelectrolyte charge density and molecular mass. In this study, however, the driving force for desorption was mostly the lateral repulsion of pre-adsorbed chains, hence its occurrence when lowering the ionic strength. That being said, there could be a contrasting effect of such a change in aqueous chemistry, causing an increase in chain-chain repulsion and simultaneously a larger polymer-surface attraction potential. This result may be a second reason why a pH reduction

seemed more effective than a IS reduction to induce desorption for the specific PDADMAC-silica system.

Excess sorbed mass upon desorption. One of the main questions that this study attempts to address is whether the polyelectrolyte mass adsorbed under a certain condition is the same or different in the case that this condition is reached upon desorption of some pre-deposited layer due to a change in solution chemistry and in the case that this condition is the one under which adsorption originally occurs. Or, further, if the starting pre-deposition condition influences the adsorbed amount upon a change in aqueous chemistry. Figure 5 summarizes most of the results presented earlier, together with additional data, plotted in a way to attempt answering such questions; please see Table S4 of the Supporting Information for the same tabulated data. In Figure 5a, the five chemical conditions indicated below the abscissa axis are those that induced desorption, i.e., the final conditions. The different bars represent the adsorbed amounts upon rapid desorption when the polymer was pre-adsorbed in different solution chemistries, indicated above each bar. As such, the solid bars represent adsorption and desorption under the same condition, i.e., no desorption, and are the benchmarks for comparison.

In almost all the cases, the adsorbed amounts observed upon desorption were larger than the mass measured by directly adsorbing the polyelectrolyte layer on a clean surface under the final condition. For example, the mass of PDADMAC adsorbed onto clean silica in a solution at pH 2.5 was just under 0.2 mg/m^2 . When a polymer layer was pre-deposited in a 250 mM NaCl solution at pH 2.5 and then made to desorb in a solution at pH 2.5, the final observed amount at steady-state was much larger and almost equal to 0.5 mg/m^2 . Only if the relative desorption stimulus was sufficiently strong, the mass went back to the “expected” value, e.g., from pH 5.5 to 2.5. This example, similarly to other results presented in Figure 5, implies that rapid desorption phenomena did not detach all the required PDADMAC chains to reach the same mass observed following adsorption onto clean silica, but in most

of the experiments an *excess* mass remained deposited. This discussion is not valid for the case displayed at the far right of Figure 5a related to desorptions induced in a 250 mM solution at pH 2.5. Specifically, by pre-depositing a PDADMAC layer at pH 10 and then drastically reducing the pH, a very large desorption was induced, even when ionic strength was increased to counteract this effect. The final adsorbed amounts were smaller than that adsorbed directly in a solution of 250 mM NaCl at pH 2.5. This observation corroborates the hypothesis that changes in pH were more capable of inducing extensive desorption than changes in ionic strength and that there may be a complementary effect of higher ionic strength to induce desorption due to lower PDAMAC-silica attraction potential or due to an exchange with the co-ions competing for the same sorption sites with the polyelectrolyte.

Two experimental traces related to the example discussed in the previous paragraph are presented in Figure 5b and 5c. The first graph is related to the adsorbed amount represented by the leftmost solid bar in Figure 5a, while the second graph to one of the associated empty bars. Here, it is possible to more visibly appreciate the difference in adsorbed mass, i.e., the *excess* mass, between the final data recorded in the two experiments. It could be argued that these observations were due to very slow kinetics of desorption and that the system would have reached the same final condition had sufficient time passed.³¹ However, this study focuses on relevant timescales of many engineering applications of adlayer systems; during this time, the final data were recorded when no further or negligible change in signal was detected. We surmise that all these observations may be reasonably generalized, at least for the interaction of strong polyelectrolytes with oppositely charged surfaces. They may be rationalized considering the large number of chain-substrate electrostatic interaction points, roughly correlated with (i) the charge density of both the polymer and the substrate, (ii) the molecular mass of the polymer, (iii) the degree of dissociation of its moieties, and (iv) the conformation of the molecules on the surface. According to the multiple binding hypothesis, while the repulsion between pre-deposited chains may be strong following changes in the solution chemistry, once the polymer chains are adsorbed on the

surface, the system needs to overcome a significantly higher energy barrier related to numerous chain-surface attractions.^{12, 41} The desorption is thus incomplete or significantly slowed and some of the pre-deposited chains tend to remain sorbed in the solid phase. Also, the presence of the polymer layer may affect the charging of the surface, compared to a clean condition.

Other studies also discussed the existence of an adsorption/desorption hysteresis for highly charged polyelectrolytes.¹⁹ This effect was explained not only with an incomplete desorption, but with the thwarted deposition on a clean surface due to the pronounced electrostatic adsorption barrier provided by previously deposited chains. In fact, the hysteresis disappeared in high ionic strengths. This rationalization underlines the role of long range electrostatic repulsion and short range attraction, which may be both electrostatic and non-electrostatic. Therefore, while approaching molecules may not be able to adsorb due to chain-chain repulsion, pre-adsorbed chain will desorb only if lateral repulsion is stronger than both the short- and long-range anchoring energy formed upon layer formation.

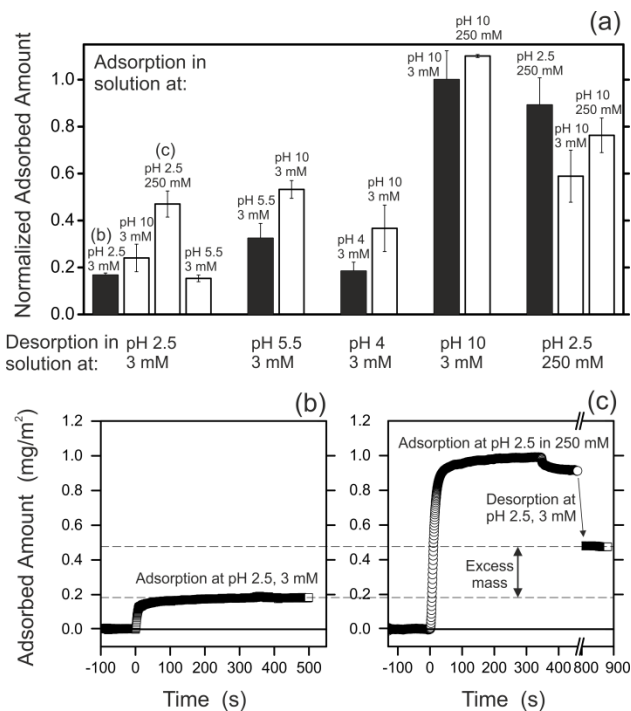


Figure 5. Desorption of PDADMAC from layers pre-adsorbed on silica in solutions characterized by different pH and/or ionic strength values. In (a), the adsorption conditions are indicated near the top of each bar; the desorption conditions are indicated below each group of bars. Solid bars represent experiments in which desorption was assessed in the same background solution used for previous adsorption, i.e., no desorption recorded. (b) and (c) present exemplificative adsorption and desorption traces relative to data of two bars indicated in (a) and specifying the excess mass of PDADMAC following desorption.

Other examples and hints on the influence of polymer molecular mass. Figure 6 presents experimental traces of adsorbed mass measured with diverse polymer-substrate systems. In some instances, the same experiment was performed with polymers of the same nature but different molecular masses. In general, the data confirmed all the trends discussed so far for the specific PDADMAC-silica system. The effect of both pH and IS changes were corroborated. Therefore, partial or complete desorption of a pre-adsorbed layer was observed when the electrostatic repulsion between adsorbed chains was increased. Also, chain detachment was registered when the polyelectrolyte-surface electrostatic attraction was reduced due to protonation of the surface moieties or when this electrostatic interaction became repulsive owing to a switch in the sign of the charge of either of the two players. A qualitative representation of the sign and density of such charges is depicted on the graphs for each aqueous condition.

If the rationalization of the previous chapter is correct, there should be an effect of polymer molecular mass and polydispersity on the extent of desorption. In particular, the larger the molecular mass the higher will be the density of interactions with the surface; a higher density of binding would increase the energy barrier to desorption and thus thwart the re-dissolution of pre-adsorbed chains. In other words, for the longest macromolecules the barrier may be too high to allow them to re-dissolve. Indeed, the data in Figure 6a-e seem to strengthen this hypothesis. This observation is in accordance

with data from several previous studies discussing the thwarted desorption of pre-deposited chains of larger molecular mass.^{16, 17, 18} Few accounts explained this mechanism kinetically, with the desorption rate depending mainly on the number of bonds and the strength of these bonds.^{16, 17, 34} Other studies proposed the presence of both reversible and irreversible adsorption sites on the surface,³³ or the concomitant presence of heterogeneous molecules that may adsorb reversibly or irreversibly.¹³ Non-electrostatic attraction between the adsorbed chains and the surface would further increase the barrier of desorption.^{34, 40}

We surmise that, even for purely electrostatic interactions, the different chain length of a homogeneous polymer plays an important role in the extent of desorption at least in short-term observations. Conformational changes also affect the number of contact points with the surface, with macromolecular spreading and flattening causing reduced desorption.¹⁸ Indeed, it has been noted that both the rigidity of a polymer backbone and its flat adsorption thwart desorption of pre-adsorbed chains.⁴² If a polymer is flexible, detachment may instead occur easily segment by segment. This phenomenon will eventually result in the formation of a thin flat layer rather than one consisting of loops and tails. In any case, all these mechanisms indicate a strong history dependence on adsorption and desorption effects. Factors related to such history are the sequence of earlier aqueous chemistries prevalent in the system, previous adsorption and desorption cycles, surface residence times of the adsorbed chains, and progressive fractionation resulting in longer molecules remaining attached to the substrate.^{31, 32} With respect to fractionation, previous studies relevantly observed that in the case of widely polydisperse polymers, while short chains may preferentially adsorb on a substrate in the initial times of contact because of their higher diffusion rate, an exchange process occurs as the short chains desorb and longer chains take their place.^{35, 43} This phenomenon should be more pronounced when polyelectrolytes are not highly charged and can easily approach pre-deposited layers that would otherwise repel them electrostatically, when polymer concentration is high, polydispersity is low, or

when the molecular mass is distributed mostly within a range of large values. In all cases, these effects lead to a gradual accumulation of more or more firmly bound chains onto the surface, thus a progressively more difficult rapid desorption.

It is possible that this phenomenon is one of the mechanisms underlying the shift between kinetically-driven systems, associated with more or less irreversible adsorption, and equilibrium-driven systems, in which the aqueous compound in the liquid phase undergoes unceasing exchanges with the solid phase. Dissolved low molecular mass compounds interacting with a solid surface are often subject to phase partitioning governed by equilibrium, while larger compounds of similar chemical nature adsorb until saturation and tend to remain deposited even when a compound-free solution is in contact with the pre-deposited layer. In this sense, it would be interesting to study the behavior of oligomers, which may lie in the transition region between these two regimes of phase interchange.

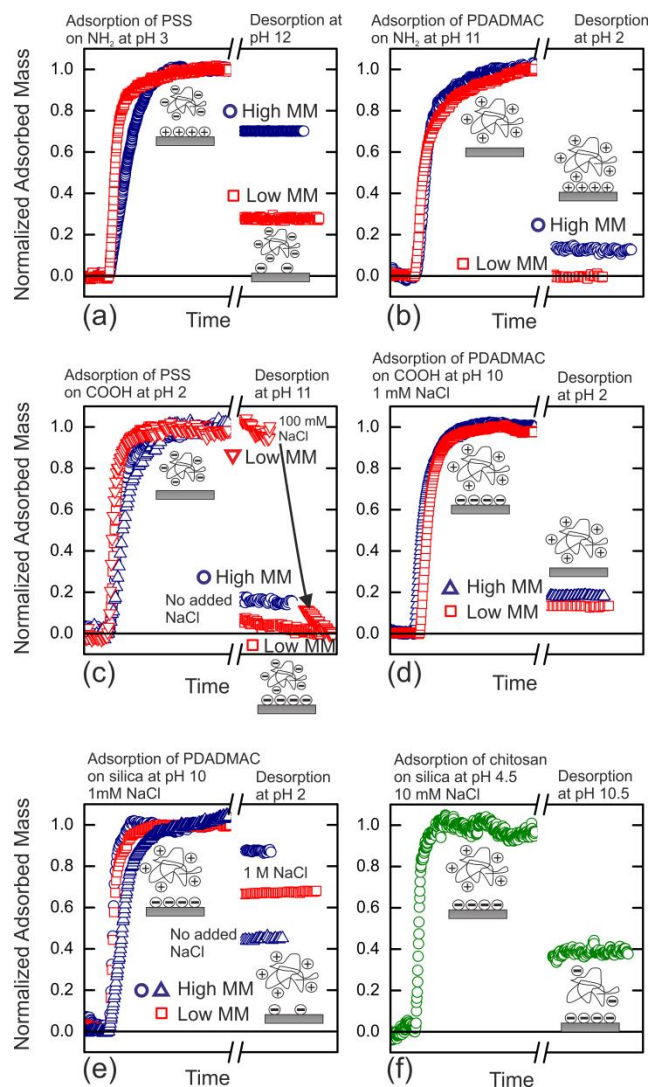


Figure 6. Traces of adsorption and desorption of different polyelectrolytes onto and from different surfaces. Only the significant time ranges are presented and the data were normalized by the mass adsorbed at saturation. Results were obtained with (a) PSS or (b) PDADMAC on amine-functionalized SAMs; (c) PSS or (d) PDADMAC on carboxyl-functionalized SAMs; (d) PDADMAC or (f) chitosan on silica. Traces depicted as blue squares or triangles were obtained with polyelectrolytes of higher molecular mass; the data presented as red squares from experiments using lower molecular mass chains. The aqueous conditions during the steps of adsorption and desorption are indicated at the top of each graph. One experiment in (c) involved two desorption steps in series induced by different solutions, the first of higher ionic strength.

CONCLUSIONS

Partial desorption of pre-adsorbed layers of PDADMAC on silica was observed in short-term experiments when the system was immersed in a solution with lower ionic strength (IS) and/or pH compared to adsorption conditions. A similar behavior was observed in preliminary experiments with other weak and strong polyelectrolytes interacting with surfaces of varying chemistry and charge. Changes of solution chemistry altered the charge sign or density of polyelectrolytes and of the surfaces, and they affected directly or indirectly the diffuse-layer potentials. Therefore, layer desorption was generally caused by increased lateral repulsion between deposited chains or to a reduced favorable electrostatic interaction between the charged polymer and the underlying substrate. Under the new conditions, some of the chains tended to return into solution to minimize the energy of the system.

The experimental results suggested that pH changes were more effective to promote desorption with respect to changes in IS, and concurrent changes in both parameters could either enhance or thwart desorption. Interestingly, the adsorbed mass at steady-state achieved by adsorbing PDADMAC under one condition was always lower than the mass achieved under the same condition but upon a desorption process starting from an adlayer of larger mass. Therefore, desorption seemed to occur only if an energy barrier was overcome, likely due to the large density of both short- and large-range interactions between the pre-adsorbed polyelectrolyte chains and the surface. This result implies that the barrier for desorption was relatively high and that significant changes of solution chemistry were needed to trigger re-dissolution of previously deposited chains. Generally, a lower extent of desorption was observed for polyelectrolytes of larger molecular mass, strengthening the hypothesis about the influence of the number of polymer-surface interactions on the extent of rapid desorption. At the same time, the experimental results suggested that the final aqueous chemistry is the governing parameter influencing the extent of desorption, while the pathway followed to achieve this final chemical

condition was not important. These seemingly contradictory results imply that a number of unanswered questions remain about the mechanism of desorption. Finally, results suggest that a system undergoing adsorption/desorption cycles will eventually favor the formation of an increasingly flatter layer comprising chains of larger molecular mass, especially for highly polydispersed polyelectrolyte system.

The results discussed in this study have implications for a number of environmental and engineering processes. They suggest that the introduction of low ionic strength solutions in a system may trigger the partial desorption of polyelectrolytes previously adsorbed on oppositely charged surfaces. This is the case of floods or rain infiltration into soils. On the other hand, the opposite mechanism, i.e., saline intrusion, may induce the large adsorption of polyelectrolytes that would be later only incompletely desorb when standard conditions are restored. To generalize, a process that aims at maximizing the mass of adsorbed polyelectrolyte on a surface could be accomplished under conditions in which adsorption is more favorable compared to the actual process conditions, as only a partial amount of polyelectrolyte would desorb upon the following change in chemistry. Specifically, PDADMAC is one of the most common polyelectrolytes deployed to promote colloidal flocculation in surface water treatment. The dosing amount and protocol may thus be tailored based on the mechanisms discussed here to maximize the removal of aqueous turbidity while minimizing the amount of added polymer.

AUTHOR INFORMATION

Corresponding Author

*E-mail: alberto.tiraferri@polito.it. Tel.: +39-011-090-7628

ORCID

Alberto Tiraferri: 0000-0001-9859-1328

Notes

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