Supporting information for:

Using polymer hydrogels for glyphosate sequestration from aqueous solutions: Molecular theory study of adsorption to polyallylamine films

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8 Pages, 7 Figures and 2 Tables.

Additional Results

In the paper, Fig. 6 illustrates the adsorption of glyphosate, as a function of pH, for three polymer network having different polymer density. In that plot, we see that increasing polymer density enhances glyphosate adsorption in the whole pH-range. Figure S1 shows the area density of charge of these networks under the same environmental conditions. We see that increasing the polymer density also increases the area density of negative charge, which enhances network-glyphosate electrostatic attractions and consequently leads to the behavior predicted in Fig. 6.
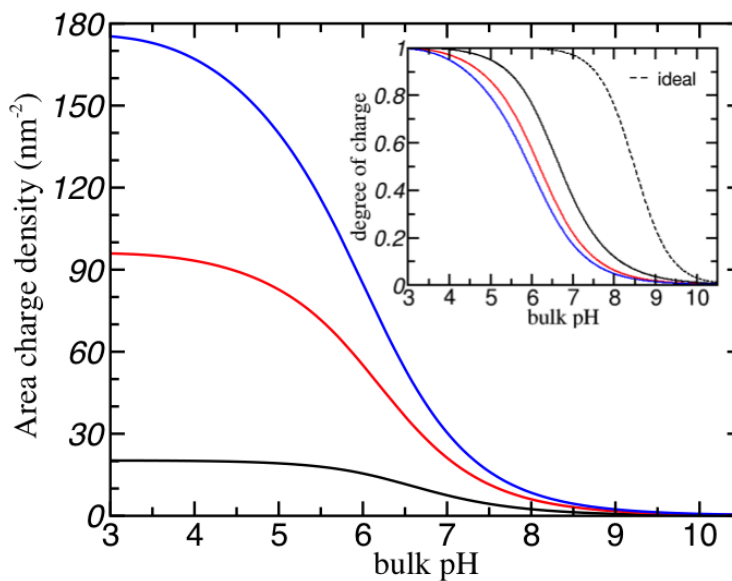

Figure S1: Plot of the area charge density of the polymer network as a function of pH for the three different polymer network of Fig. 6 (paper). The inset shows the average degree of charge/protonation of PAH segments.

Interestingly, the inset in Fig. S1 shows that increasing network density decreases the degree of charge/protonation of PAH segments. Namely, a PAH segment is less likely to be charged as the network density increases. Clearly, this effect of degreasing protonation is overcompensated by the increasing density of PAH units, which results in a higher area density of charge.

To further analyze the behavior described in Fig. 7 (paper), we have considered two

different adsorption models: (a) Langmuir isotherms, with

$$\Gamma = \Gamma_{\max} \frac{b\,[\text{glp}]}{1 + b\,[\text{glp}]} \tag{1}$$

where Γ is the adsorption, b is the affinity constant and $\Gamma_{\max}$ is the maximum adsorption, which corresponds to a complete monolayer coverage; and (b) Freundlich isotherms, with

$$\Gamma = K[\text{glp}]^{1/n} \tag{2}$$

where n is the heterogeneity constant that indicates the type of isothermal adsorption; if $n = 1$ the isotherm is linear; as n increases, the isotherm becomes nonlineal to approach irreversible adsorption at large values of n. The parameters obtained through fitting both models to the isotherms of Fig. 7 are detailed in Table S1 and Table S2, for 1 mM and 10 mM salt concentration, respectively. These fittings are illustrated in Fig. S2 Fig. S3.

For 10 mM salt concentration, this parameterization shows that there are two distinct adsorption regimes: (i) at low glyphosate concentrations, all isotherms fit to the Freundlich model with $n \approx 1$; (ii) at high glyphosate concentrations, on the other hand, the isotherms fit well with the Langmuir model. As the pH increases, $\Gamma_{\max}$ decreases, as does the number of protonated PAH units of the hydrogel. In the case of 1 mM salt concentration, parametrization yields the same adsorption regimes; at low glyphosate concentration, n-values for the Freundlich regime are higher than 1, while the Langmuir model fits the isotherms well at high glyphosate concentrations.

When comparing the values of b and $\Gamma_{\max}$ at the same pH, the Langmuir parameter does not significantly change with salt concentration. This means that, although the adsorbent material regulates charge, the available sites for glyphosate adsorption are essentially the same. However, the values of b are significantly larger as the salt concentration decreases, which is due to the weaker screening of the electrostatic interactions by adsorbed salt ions. Moreover, the analysis $\Gamma_{\max}$ *vs.* pH curves provides an estimation of the degree of protonation

of PAH units (see Fig. S4).

Table S1: Parameters for the Langmuir and Freundlich isotherms at $[\text{salt}] = 1\text{mM}$ obtained fitting the results presented in Fig. 7, panel A.

pH	$\Gamma_{\text{max}} \, (\text{nm}^{-2})$	$b \, (\text{M}^{-1})$	$\ln K$	n
3	81.96	478	10.33	1.075
4	68.96	322	12.76	1.124
5	49.75	43289	11.13	1.482
6	42.55	80306	10.53	1.556
7	37.87	2882	8.77	1.615
8	22.42	306	8.52	1.355

Table S2: Parameters for the Langmuir and Freundlich isotherms at $[\text{salt}] = 10\text{mM}$ obtained fitting the results presented in Fig. 7, panel B.

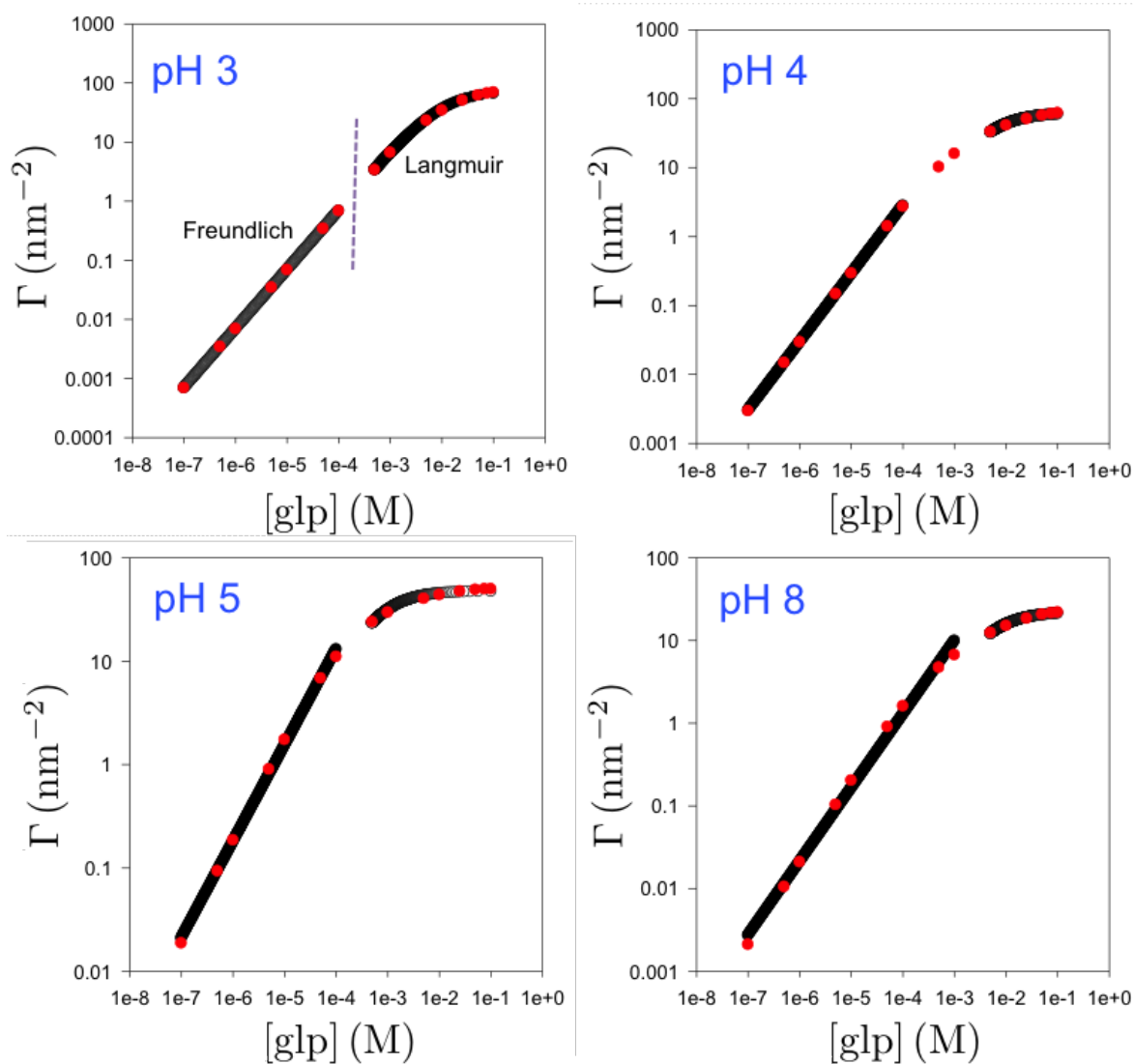| pH	$\Gamma_{\text{max}} \, (\text{nm}^{-2})$	$b \, (\text{M}^{-1})$	$\ln K$	n
3	72.99	97	8.86	1
4	62	220	10.14	1
5	47.61	1913	11.13	1.074
6	40.81	7254	12.38	1.036
7	36.63	1627	10.7	1.087
8	22.07	241	8.44	1.124

Figure S2: Adsorption isotherms at [salt] = 1mM and different pH values. Comparison between the results presented in Fig. 7A (red circles), Freundlich isotherms (black line at low [glp]), and Langmuir isotherms (black line at high [glp]), using the parameters described in Table S1.
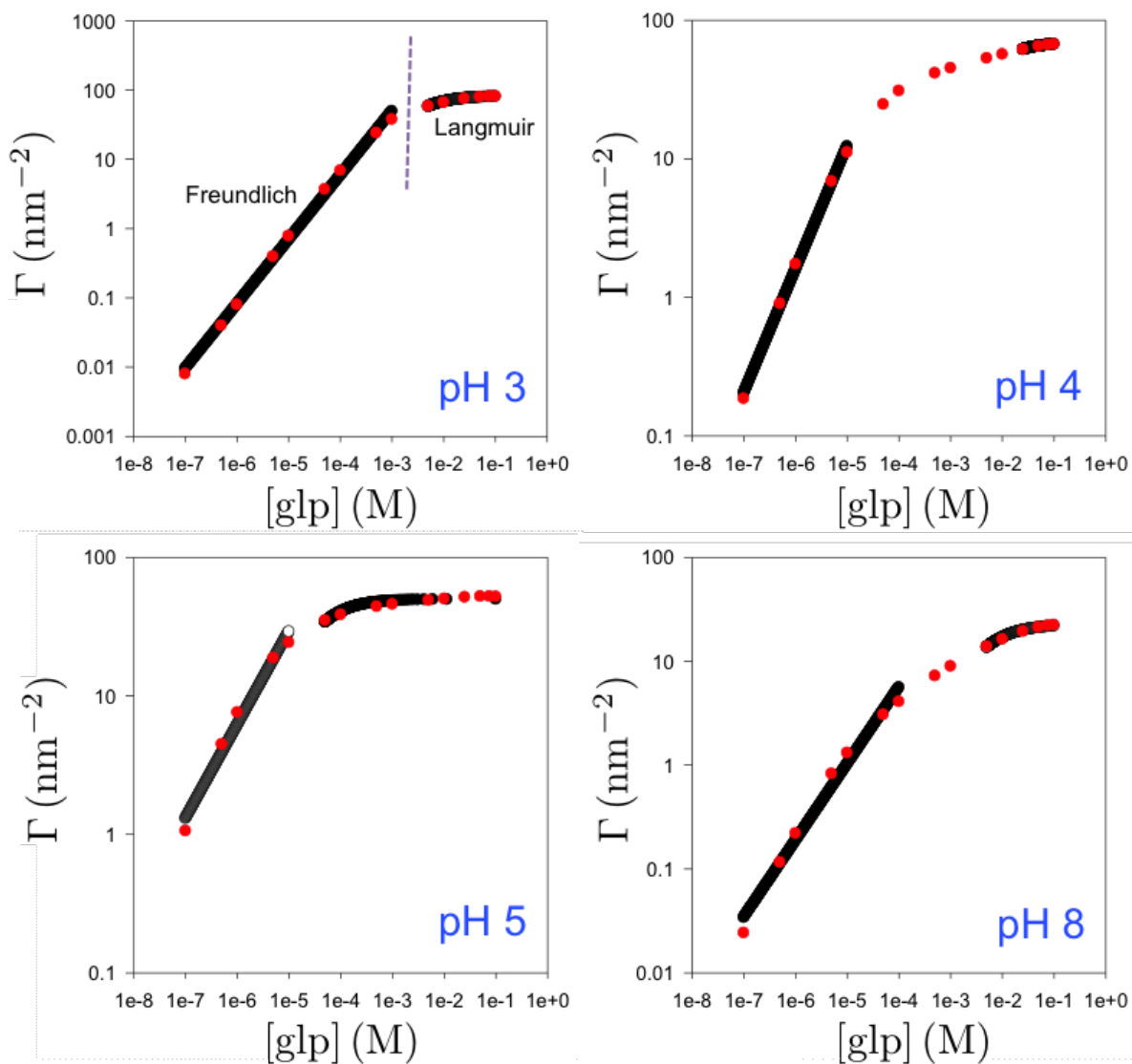
Figure S3: Adsorption isotherms at [salt] = 10mM and different pH values. Comparison between the results presented in Fig. 7B (red circles), Freundlich isotherms (black line at low [glp]), and Langmuir isotherms (black line at high [glp]), using the parameters described in Table S2.
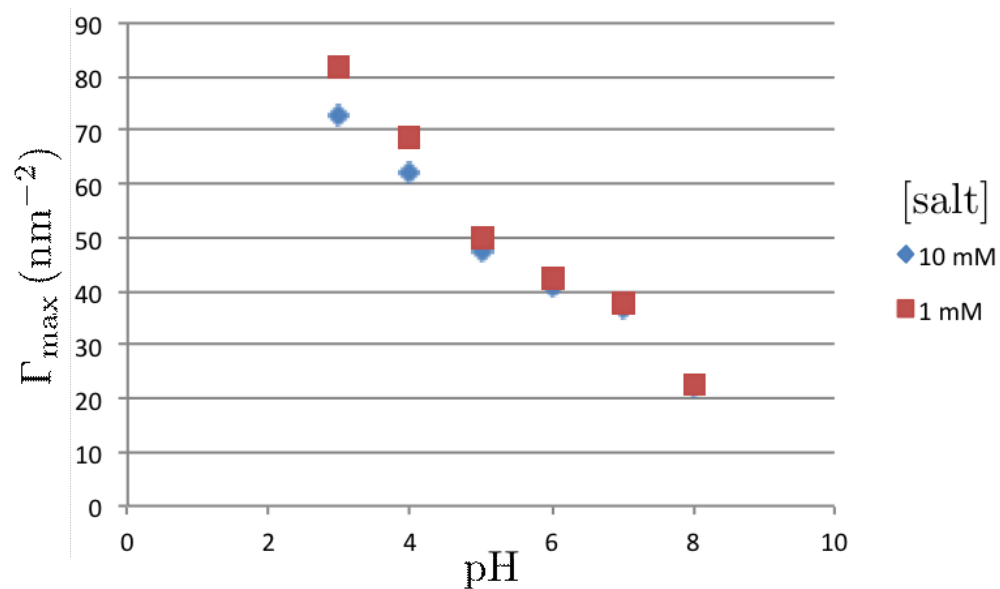
Figure S4: Plot of maximum adsorption in the Langmuir model, Γ_{max}, as a function of the solution pH.
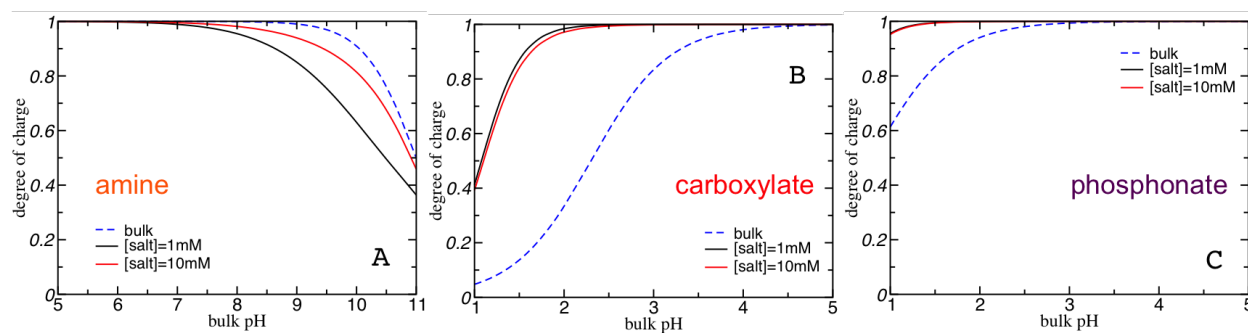

Figure S5: Plot of degree of charge of glyphosate units corresponding to adsorbed molecules. Dashed-line curves represent solution degree of charge.
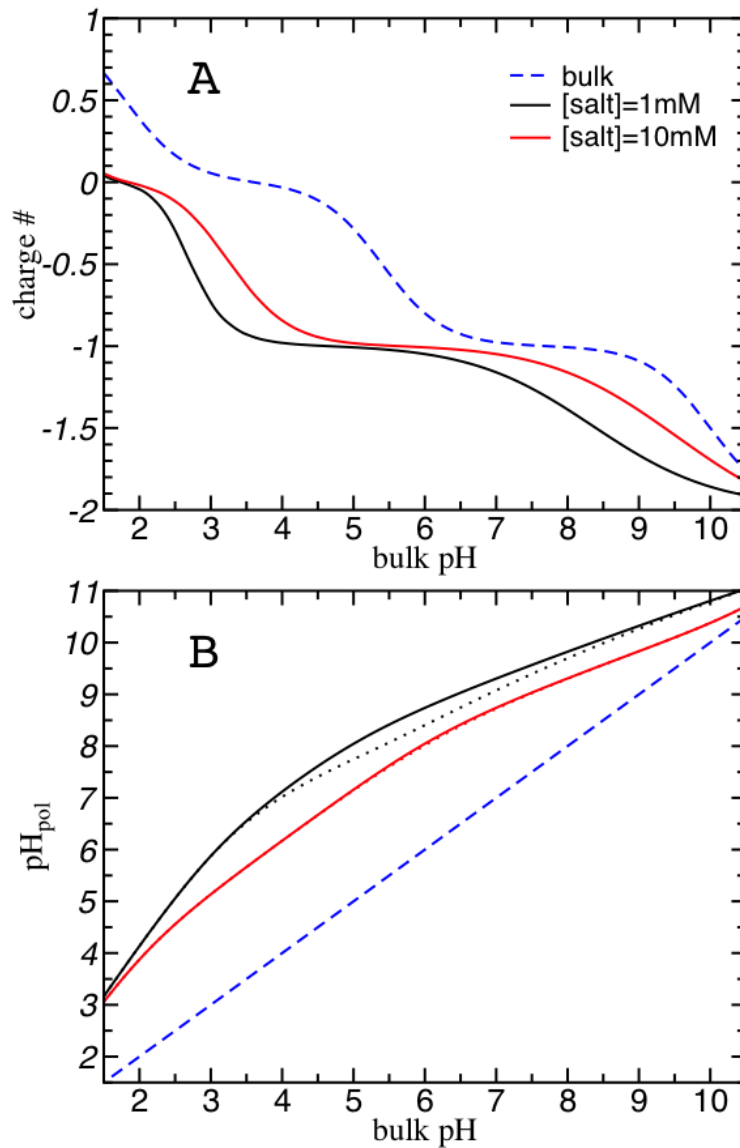
Figure S6: Plots showing the pH-dependence of different quantities at two salt concentrations, $1\,\mathrm{mM}$ (black-line curves) and $10\,\mathrm{mM}$ (red-line curves), and $[\mathrm{ampa}] = 10\,\mu\mathrm{M}$; A: average net charge of adsorbed AMPA molecules (dashed-line curve shows the solution charge); B: average pH inside the film, $\mathrm{pH}_{\mathrm{pol}}$ (dashed-line curve corresponds to $\mathrm{pH}_{\mathrm{pol}} = \mathrm{pH}$).
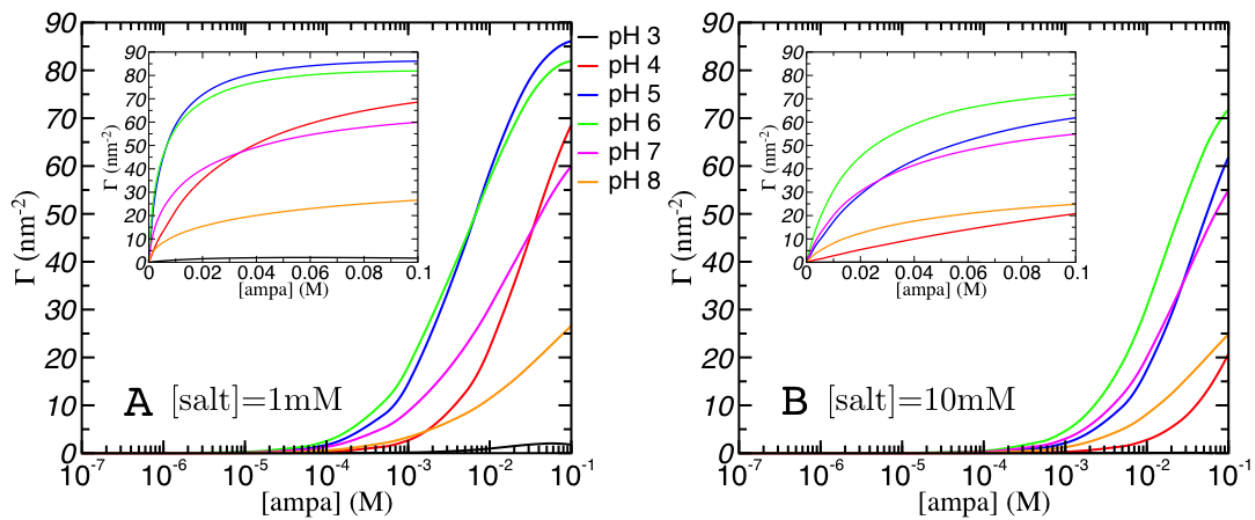
Figure S7: AMPA adsorption isotherms, Γ *vs.* [ampa], for different pH values and [salt] $= 1\,\text{mM}$ (A) and [salt] $= 1\,\text{mM}$ (B).