Electronic Supplementary Material (ESI) for Soft Matter.

Fluorescence Spectroscopy Analysis of Fly Ash Removal from Aqueous System: Adsorption of Alginate to Silica and Alumina

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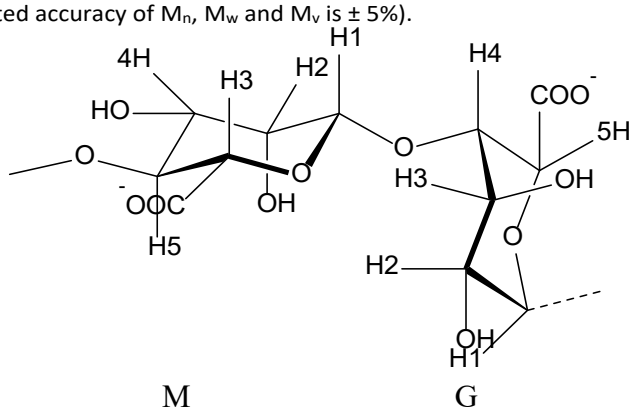
Electronic Supporting Information

Contents

1. Additional Experimental Data

Alginic acid (Yield ~90 %) ^{1}H NMR (400 MHz, DEUTERIUM OXIDE) δ ppm 2.74 (s, 1 H, C**H-3** of M) 3.62 (br. s., 1 H, C**H-4** of M) 3.77 (br. s., 1 H, C**H-5** of M) 3.89 (br. s., 1 H, C**H-2** of M) 3.98 (br. s., 1 H, C**H-2** of G) 4.04 (br. s., 1 H, C**H-3** of G) 4.31 (br. s., 1 H, C**H-4** of G) 4.50 (br. s., 1 H, C**H-5** of G) 4.85 (br. s., 1 H, C**H-1** of M) 4.90 (br. s., 1 H, C**H-1** of G) [M = mannuronate; G = guluronate]. FTIR spectrum (KBr, cm^{-1}): 3446 (-OH, hydrogen bonded), 12260 (CC); 2929 (CH), 1740 (COOH), 905 (CO). GPC(RI): M_n = 38782 g/mol, M_w = 66480 g/mol, M_v = 62212 g/mol. Viscometry: M_v = 61294 g/mol. (The estimated accuracy of M_n, M_w and M_v is ± 5%).



Scheme SI1.1 - Alginate structure, shows *G* and *M* protons.

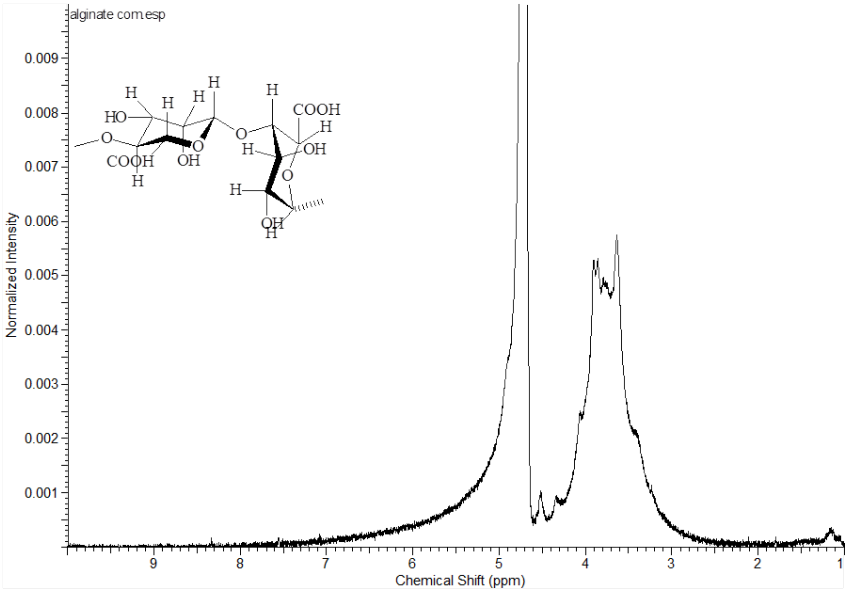


Figure SI1.1 – ^{1}H NMR of unpurified commercial alginate

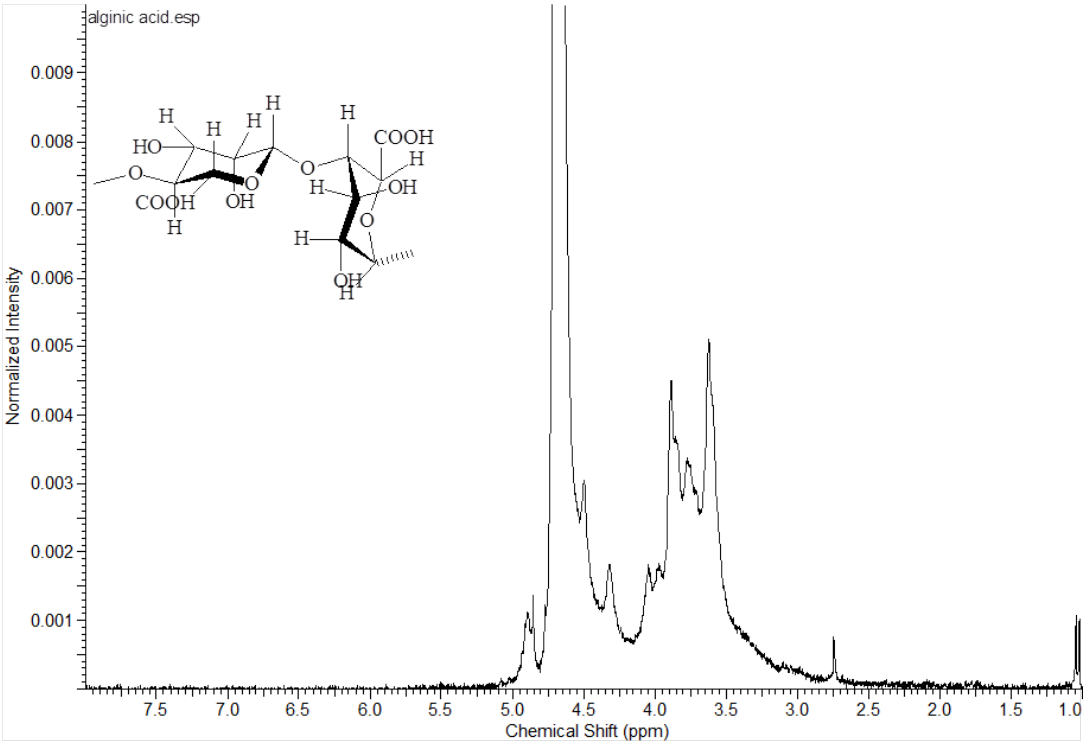


Figure SI1.2 – ^{1}H NMR of purified commercial alginate

AmNS-alginate (Yield ~89 %) ^{1}H NMR (400 MHz, DEUTERIUM OXIDE) spectra of the product was indistinguishable from the spectra of the unlabelled alginate due to the low content of fluorophore. FTIR spectra of (KBr, cm^{-1}): were indistinguishable from the spectra of alginic acid due to the low loading of the fluorophore. Fluorescent label content: $(mol\ \%)_{AmNS}$ = 0.96 mol%. GPC (RI): M_n = 20965 g/mol, M_w = 31733 g/mol, M_v = 29870 g/mol. Viscometry: M_v = 29507 g/mol. (The estimated accuracy of M_n, M_w and M_v is ± 5%).

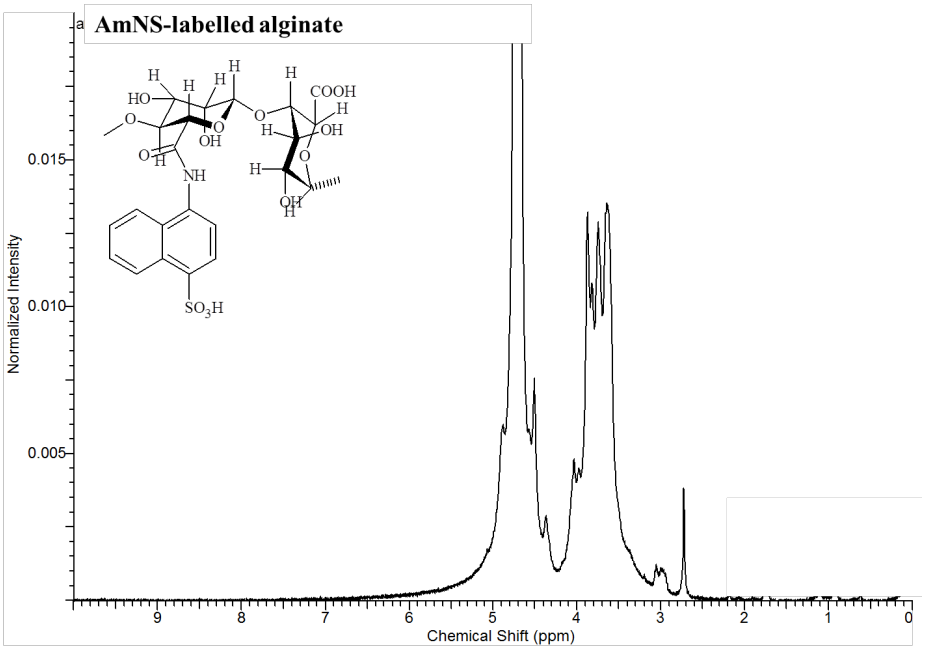


Figure SI1.3 – ^{1}H NMR of purified commercial alginate

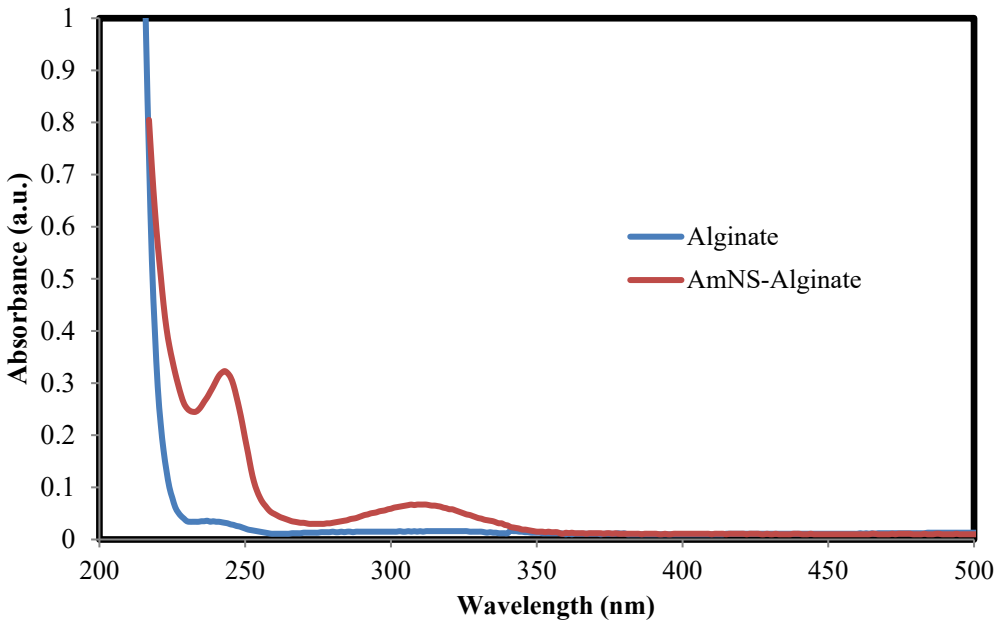


Figure SI1.4 UV-Absorption spectra of 0.1 g/L AmNS-labelled alginate and alginate.

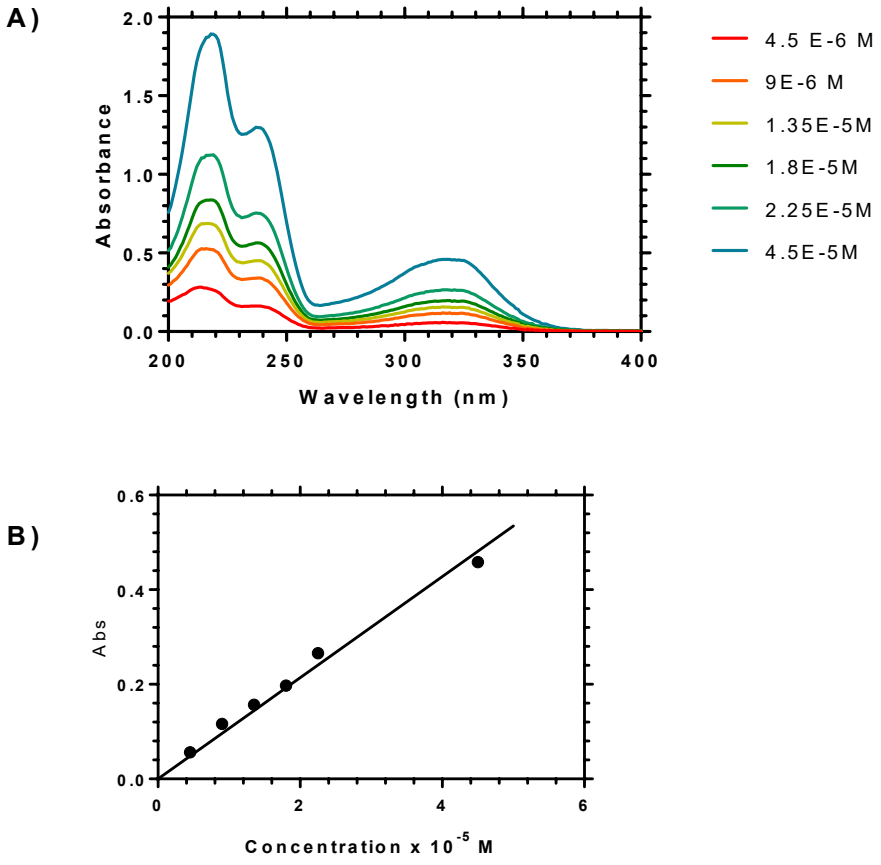


Figure SI1.5 A) UV-Absorption spectra of AmNS dilute solutions in water B) λ_{max} peak (320 nm) of AmNS with varying molar concentration in water.

2. Fluorescent Properties of AmNS

Fluorescent Properties of AmNS

UV-vis absorption of dilute aqueous solutions of AmNS (10^{-5} M in deionised water) showed that the peak λ_{abs} ~320 nm (see Figure SI1). Excitation at this wavelength lead to emission with a peak λ_{em} 420 nm (Figure 1A), matching prior studies of the AmNS fluorophore.[1] Although λ_{em} is pH independent the intensity was observed to decrease in acidic solutions (pH 3), below the pKa of the AmNS moiety (≈4.2).[2] The Excited state lifetime of the Alginate* was measured to interrogate the effect of pH on the Alginate* and the excited state decay was successfully resolved for all samples with a single exponential model decay function (see ESI). At pH 3 a relatively short-duration decay was obtained (τ_f = ~6 ns) compared with the values obtained at pH 7 and 11 where the decay time value was doubled (τ_f = ~11 ns) (Figure 1B). Time resolved anisotropy measurements showed that the free dye has an extremely short rotational correlation time (~0.1 ns) that is not affected by the pH (Figure 1C). We can therefore conclude that although quenching in the excited state lifetime occurred in the acidic media due to the binding of the amino group for AmNS with H^+ ion it does not affect the dynamic behaviour of the fluorophore.

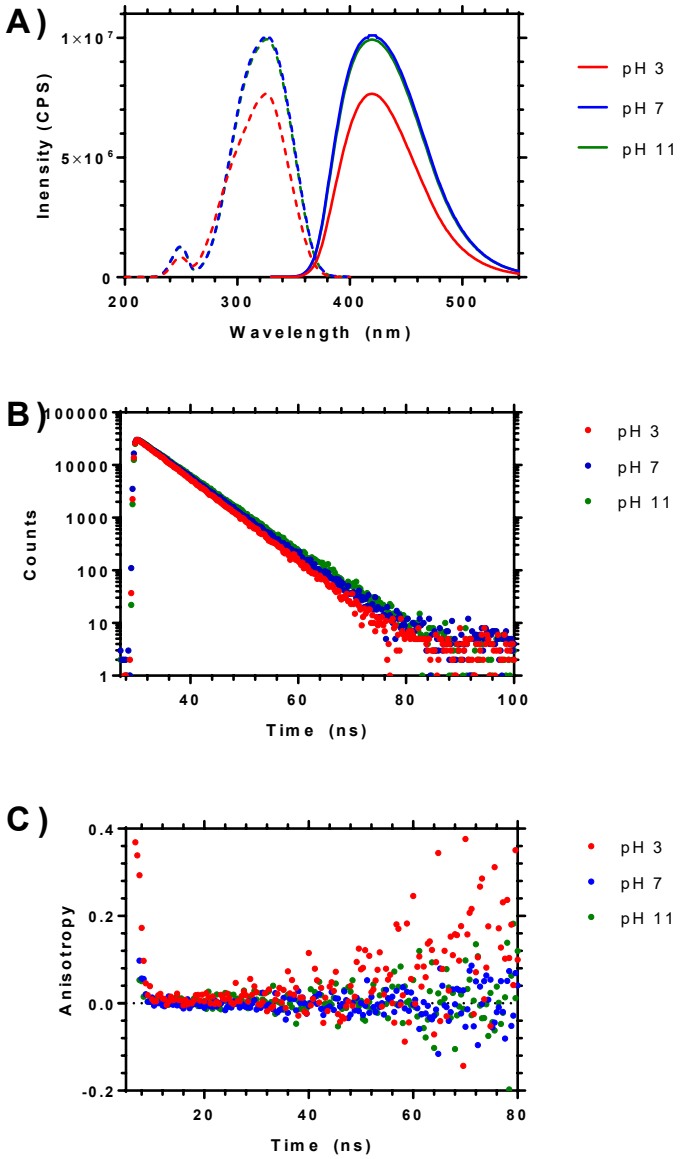


Figure SI2.1. A) Fluorescence emission spectra for 10^{-5} M AmNS in aqueous solution at varied pH values, excitation (λ_{em}= 415 nm) dashed and emission (λ_{ex}= 320 nm) as solid line. B) Fluorescence excited state lifetime decays of 10^{-5} M AmNS in water at varied pH values. C) Anisotropy decays of 10^{-5} M AmNS in water at different pH values.

3.Interactions of AmNS with Silica and Alumina particles

Figure SI3.1 show the fluorescence steady-state spectra of 10^{-5} M AmNS in 1 wt % silica solution at pH 3 and 11 before and after separation of the solid components by centrifugation. At both pH values, it was found that the fluorescence intensity before separation was indistinguishable from that after separation. This is evidence that the free AmNS remains dispersed in the bulk solution and does not interact with silica.

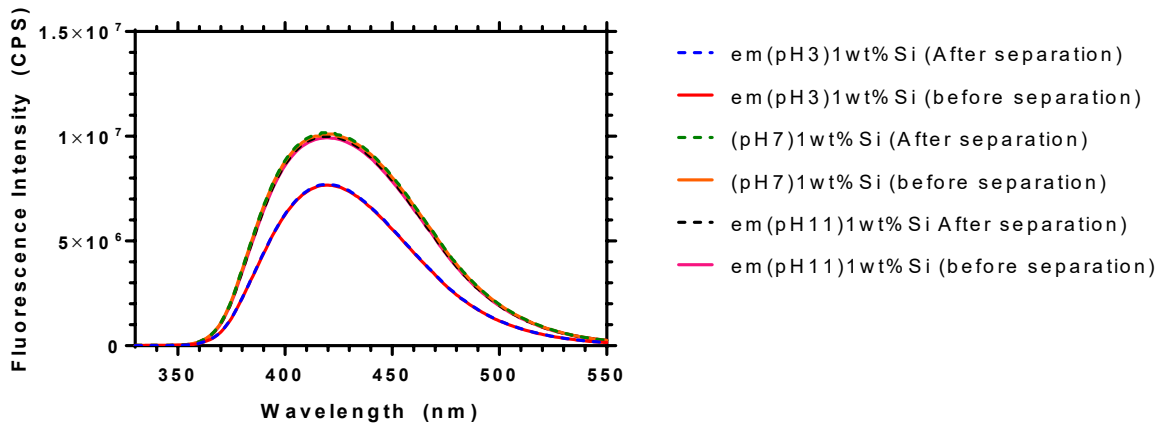


Figure SI3.1. Emission scan in a range equal to 330-550 nm at fixed excitation λex= 320 nm for AmNS (10^{-5} M in 1wt % Silica), before and after separation at pH 3, 7 and 11.

The anisotropy decays of AmNS in silica (Figure SI3.2) confirm that the free fluorophore is not absorbed to the silica surface. This can be concluded from the value obtained for the duration of fluorescence anisotropy decays, which are like that of AmNS in water at pH values 3, 7 and 11. If the AmNS fluorophore was attached to the silica surface, an increase in the correlation time should have occurred. However, this increase was not observed during the anisotropy analysis.

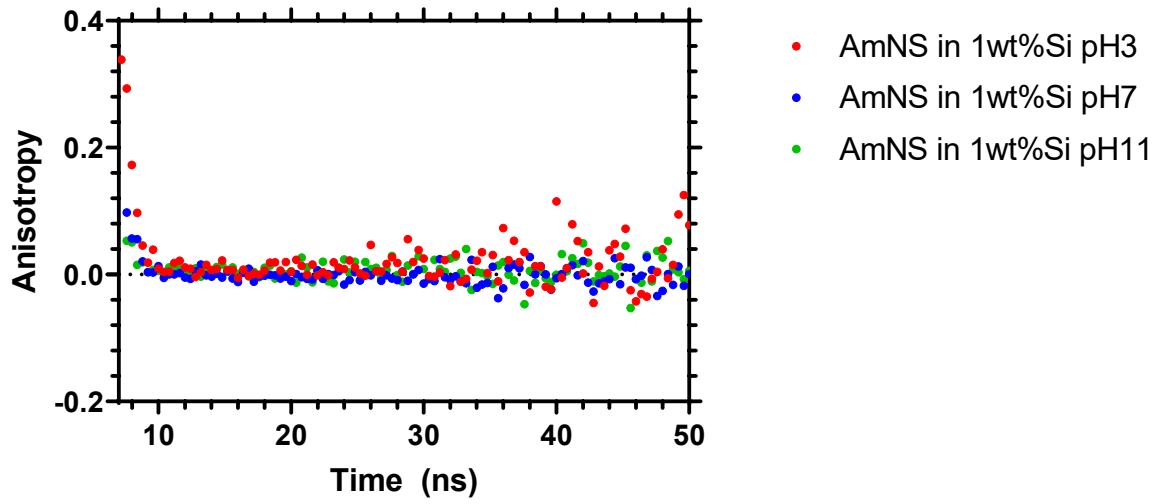


Figure SI3.2. Anisotropy decays of 10^{-5} M AmNS in 1 wt % Silica at different pH values.

In order to further confirm the argument that any attachment between the AmNS-alginate and the alumina surface is independent of any interference from the AmNS label. The free AmNS was dispersed into the alumina solution in order to determine whether any adsorption at the surface happens.

Figures 7 and 8 display the fluorescence steady-state spectra of 10^{-5} M AmNS in 1 wt% alumina solution at pH 3 and pH 11 before and after separation. The results show that the fluorescence intensity values obtained before separation by centrifugation is identical to that obtained after separation. This could be attributed to the fact that the free AmNS remains dispersed in the bulk solution and is not attached on the surface of alumina.

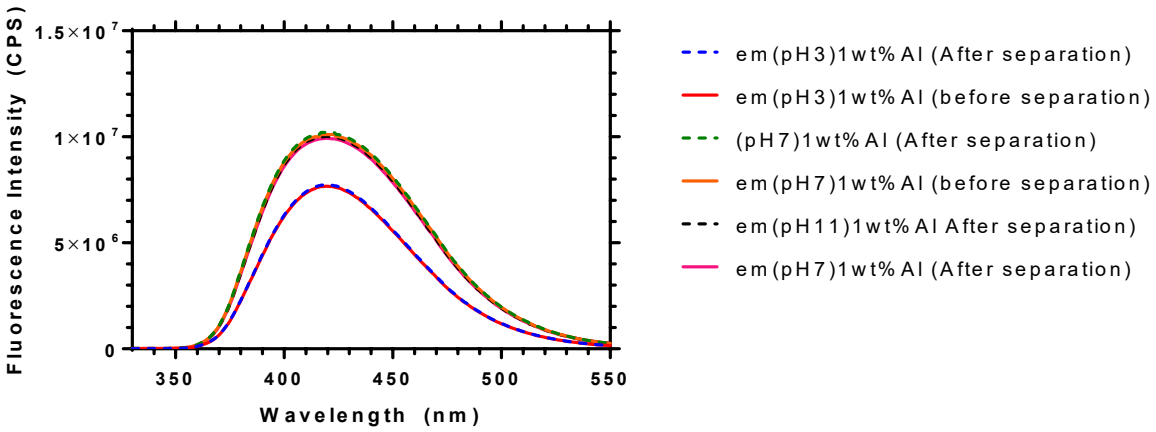


Figure SI3.3. Emission scan in a range equal to 330-550 nm at fixed excitation λ_{ex}= 320 nm for AmNS (10^{-5} M in 1wt % Alumina), before and after separation at pH 3, 7 and 11.

The anisotropy decays of AmNS in the presence of an alumina surface are shown in Figure 9, The shape of the decays at in presence of alumina indicate that the free AmNS does not adsorb onto the mineral surface. This can be observed from the duration of fluorescence anisotropy decays, which are analogous to that of AmNS in water at pH 3, 7 and 11, see Figure 3. Furthermore, no change in the correlation times of AmNS was recorded from the anisotropy analysis. All these results confirm that AmNS remains free in solution and does not interact with the alumina surface.

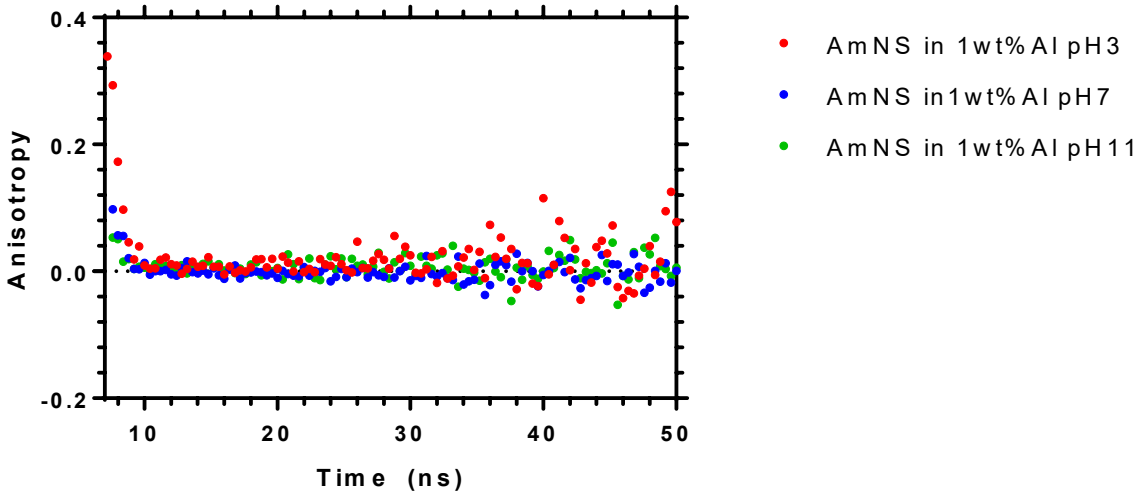


Figure SI3.4. Anisotropy decays of 10^{-5} M AmNS in 1 wt % alumina at different pH values.

4. Additional Analysis of Alginate* Solution Fluorescence

The gradual decrease of the fluorescence intensity at extremely high pH (11 and 12) has been observed before and is suggested to be due to dynamic quenching by OH^- ions.[3]

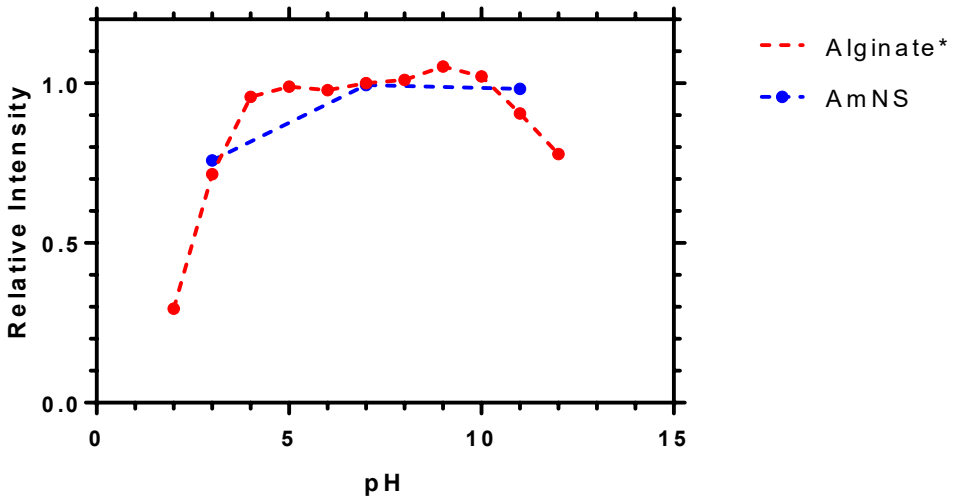


Figure ESI4.1. Comparison of relative % fluorescence intensity of 1 wt% solutions compared to neutral (pH 7) intensity of solutions (n = 3)

5. Interactions of Alginate* with Salts

Conformational Behaviour of AmNS-Alginate and Its Interaction with Sodium Ions

The interaction of alginate with monovalent cations such as Na^+ was investigated in order to evaluate their effect on the anionic polyelectrolyte conformations. The fluorescence steady state and TRAMS data were collected for the AmNS-labelled-alginate as a function of sodium chloride concentration. Fluorescence studies enabled the observation of changes in the alginate conformation, aggregation and expansion. The results of the TRAMS provides a better understanding of conformational changes in the presence of multivalent cations.

Fluorescence steady state spectra of AmNS-alginate as a function of NaCl concentration

The steady-state fluorescence emission plots collected at pH 9 in water and in presence of NaCl concentrations ranging from 1 M to 5 M, are shown in Figure ESI 5.1. The fluorescence intensity of aqueous AmNS-labelled-alginate is gradually quenched by increasing the NaCl concentration. Since the control experiment does not show any possibility that, the fluorescence of the free AmNS is quenched by the presence of NaCl (Figure 15), the observation suggests that the decrease in the fluorescence intensity for high salt concentrations results from the collapse of the biopolymer chain. This could be attributed to the decrease of the electrostatic repulsion between the ionized carboxylic groups and alcoholic moieties because of the sodium ions since screening of the negatively charged alginate chain by Na cations cause a transition of the open form to the partly coiled shape.[4,5]

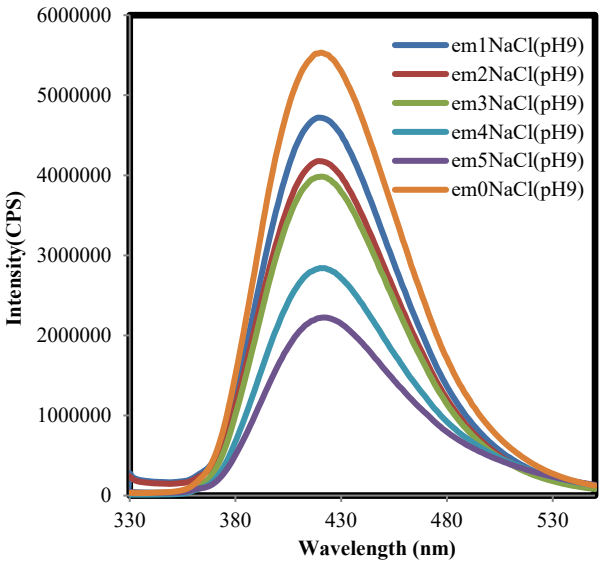


Figure ESI5.1. Fluorescence emission spectra for 10^{-1}w%AmNs-alginate in water as a function of NaCl concentration ranging from 1 M to 5 M at pH=9, λ_{ex}= 320nm.

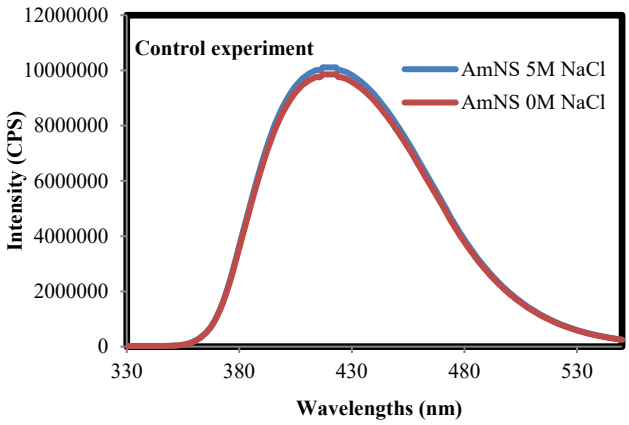
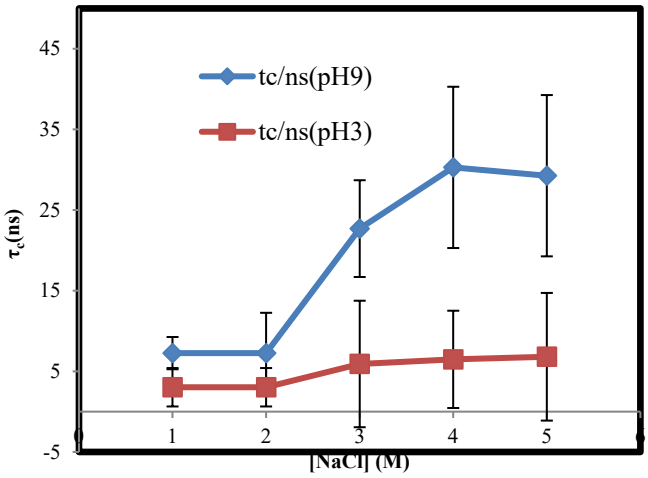


Figure ESI5.2. Fluorescence emission spectra for 10^{-5} M AmNS in water and in 5 M NaCl at pH=9, λex= 320nm.

Fluorescence time-resolved anisotropy measurements (TRAMS) of AmNS-alginate as a function of NaCl concentration

Figure 6 presents the plots of τ_c with respect to the concentration of NaCl added to the AmNS-alginate solutions at pH 3 and 9. A marked increase of correlation times (ca.~7 to ~ 29 ns) with increasing concentration of NaCl was recorded at pH 9, whereas a much smaller increase was noted at pH3. However, over the entire concentration range the increment in correlation time values at pH 9 is higher than in those at pH 3. The Figure also illustrates that τ_c is independent of the NaCl concentration up to 2 M at both pH values. The possible effect of Na^+ cations at pH 9 is a shielding effect on the electrostatic repulsions between the anionic COO^- groups and C-O^- moieties in polyelectrolytes [4,5]. This may lead to the screening of the electrostatic repulsion in the entire alginate chain. As a result, the collapsed biopolymer chains move slower than the expanded coils. This has been previously observed in relation to changes in viscosity of a polysaccharide solution. It has been reported that the intrinsic viscosity for polysaccharides solution decreases with an increasing concentration of salt in basic medium, which indicates that the electrolyte polysaccharide chains assume coiled conformations at high salt concentration. [6]



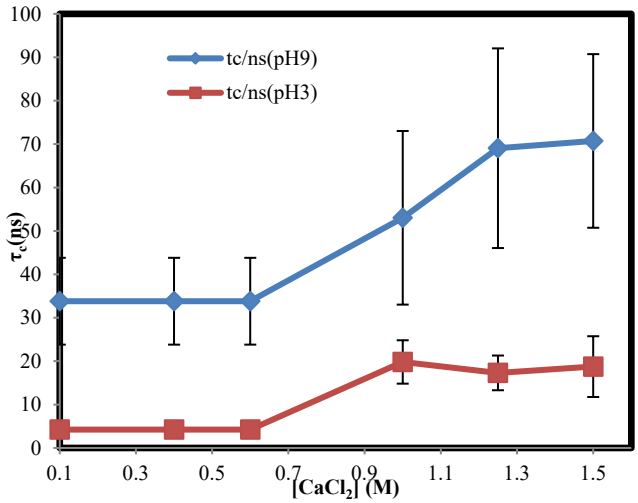


Figure ESI5.3 Correlation times (τ_c) for molecular segmental motion of 10^{-1} wt% Alginate* in aqueous solution in different A) NaCl B) $CaCL_2$ concentration(M) at pH9 (blue curve) and pH 3 (red curve). (λ_{ex}=370nm, λ_{em}=450nm).

Conformational Behaviour of AmNS-Alginate and Its Interaction with Calcium Ions

The influence of cations in solution may be different between monovalent and divalent. It is expected that divalent ions will have a higher attractive interaction with deprotonated carboxylate groups due to higher charge. This may lead to a change in conformation that would be related to the charge of the cation. A better understanding of the conformational changes exhibited by the alginate interaction with Ca^{2+} ions in dilute aqueous solution can be investigated by the fluorescence technique. The fluorescence steady-state and time resolved anisotropy records were collected for the AmNS-labelled alginate as a function of calcium chloride concentration.

Fluorescence steady state spectra of AmNS-alginate as a function of $CaCl_2$ concentration

Figure 17 shows the steady-state fluorescence emission plots versus the $CaCl_2$ concentration at pH 9, with calcium chloride concentration ranging from 0.1 M to 1.5 M. Below 0.1 M no important effect of Ca^{2+} ions were observed (data are not presented), and above 1.5 M is the solubility limit of $CaCl_2$ in water. The spectra indicate the gradual decrease of the fluorescence intensity of aqueous AmNS-labelled-alginate by increasing the $CaCl_2$ concentration. Since the control experiment does not show any possibility that, the fluorescence of the free AmNS is quenched by the presence of $CaCl_2$ (Figure 18). The observation suggests that the decrease in the fluorescence intensity for high salt concentrations results from the collapse of the biopolymer chain. This could be attributed to the neutralising of COO^- and $C\text{-}O^-$ groups by linking with Ca^{2+} ions. Which leads to the aggregation of the anionic biopolymer chain [4,5,7], and hence the hydrophilic AmNS becomes sparingly soluble in a hydrophobic environment. This leads to quenching of the fluorescence intensity.

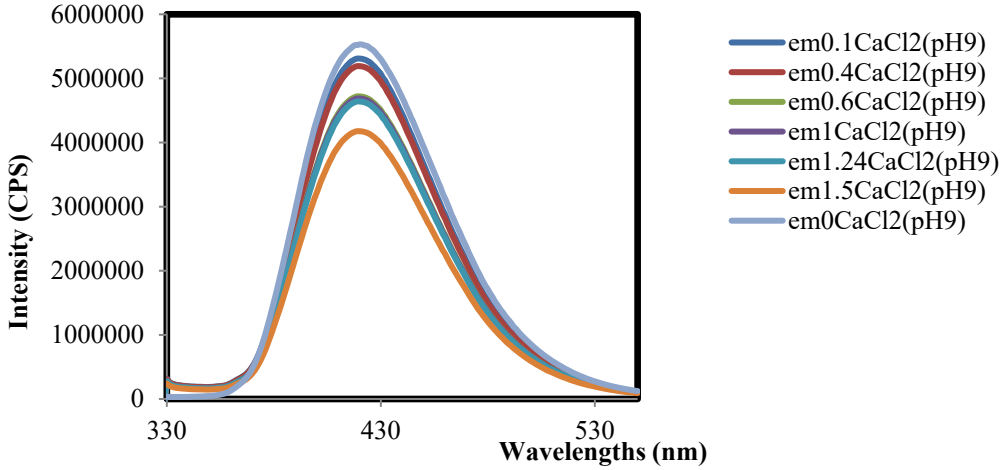


Figure ESI5.4 Fluorescence emission spectra for 10^{-1}w% AmNS-Alginate in water as a function of $CaCl_2$ concentration ranging from 0.1 M to 1.5 M at pH=9, λ_{ex}= 320 nm.

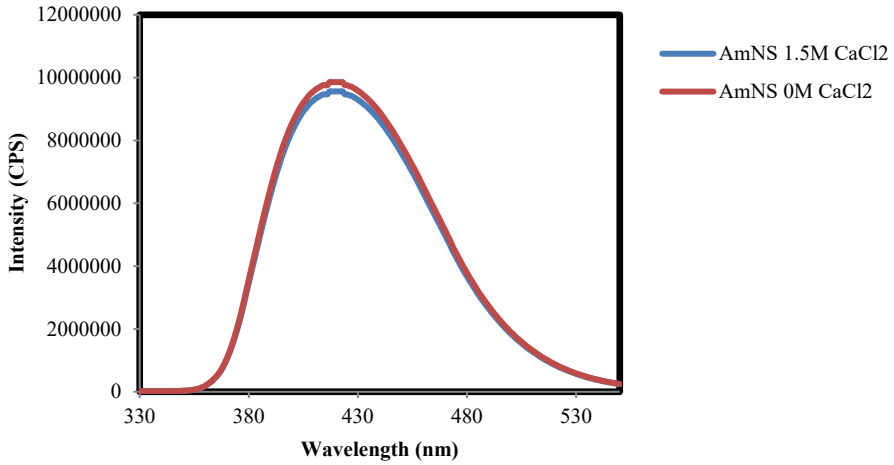


Figure ESI5.5. Fluorescence emission spectra for 10^{-5} M AmNS in water and in 1.5 M $CaCl_2$ at pH=9, λex= 320nm.

Fluorescence time-resolved anisotropy measurements (TRAMS) of AmNS-alginate as a function of $CaCl_2$ concentration

The cross-linking of alginic acid chain, which is induced by the interaction of Ca^{2+} ions with the carboxylate and C-O^- anions groups, was also examined by measuring the correlation times as a function of calcium chloride concentration at pH 3 and 9, respectively, see Figure 19. A marked increase in correlation times (from 34 to 71 ns) with increasing concentration of $CaCl_2$ was recorded at pH 9, while a small increase was demonstrated at pH3 (from 4 to 18 ns). However, over the entire concentration range the rate of increment in τ_c values at pH 9 is more than in those at pH 3. The increase can be attributed to the interaction between Ca^{2+} ions and COO^- and C-O^- groups of alginic acid.[4,5,7] Since the COOH and C-OH groups are deprotonated at pH9 compared to neutral groups present at pH 3, the interaction with Ca^{2+} ions is favoured. However, this interaction screens the carboxylate and alkoxy groups charge and leads to the collapse of the natural polyelectrolyte chain, which in turn inhibits the motion of the AmNS-alginate chain. The chelation of calcium cations by COO^- groups of alginate has been examined by atomic force microscopy (AFM) [8]. It was found that the addition of Ca^{2+} ions transformed the alginate solution into a thin gel, which indicates that the anionic polysaccharide chains assume coiled conformations in the

presence of $CaCl_2$ salt. In other studies FTIR has shown that both COOH and C-OH functional groups in alginate are involved in the metal binding.[7]

6. Interactions of Alginate* with Silica Particles

Figure 21 shows the fluorescence time-resolved decays of AmNS-labelled alginate (10^{-1} wt %). Parallel and perpendicular fluorescence intensities are plotted logarithmically against time on the nanosecond time range. Shortly after excitation, the two polarized fluorescence decays were separated from each other for long time, when the biopolymer was adsorbed onto the silica.

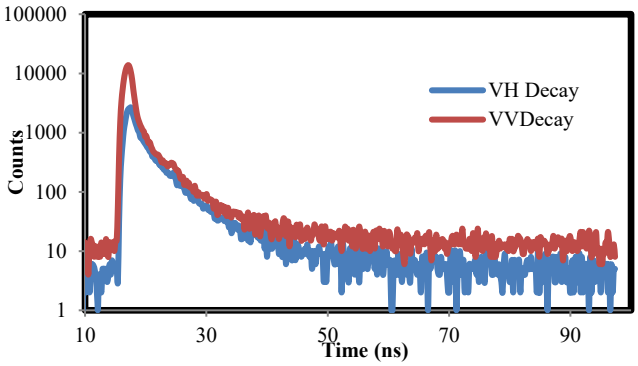


Figure ESI 6.1. Parallel (red curve) and perpendicular (blue curve) fluorescence intensity decay curves following excitation with vertically polarized light (λ_{ex}= 370 nm) analysed at 450 nm from 10^{-1} wt% AmNS-labelled alginate aqueous solution in 10w% silica at pH = 2.

Figure 22 compares the fluorescence anisotropy decays of AmNS-labelled-alginate in water in the absence and presence of silica and shows that the anisotropy decays rapidly to zero in the absence of silica. Conversely, in the presence of silica, the anisotropy does not decay to zero for a longer time. This photophysical behaviour can be clarified as follows. Since the AmNS label was randomly attached to the biopolymer backbone. As chains require physical contact with the solid surface, and the control experiments proved that AmNS alone did not adsorb onto silica, this indicates that the biopolymer chain attaches to silica suspension. This in turn, leads to the restriction of the segmental motion of fluorescently labelled biopolymer and longer anisotropy decay is observed accordingly.

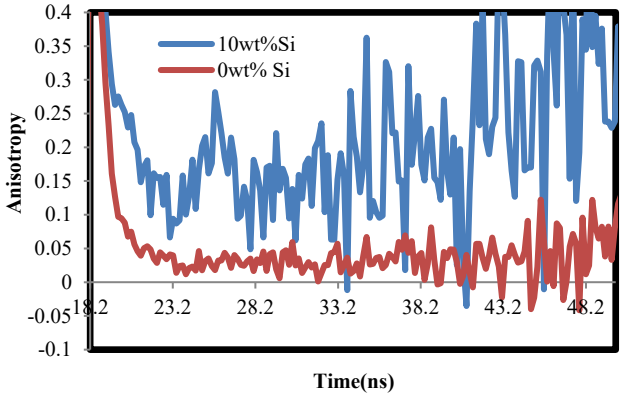


Figure ESI6.2. Fluorescence time resolved anisotropy data of aqueous AmNS-labelled alginate solution (10^{-1} wt %) in the absence of silica(red curve) and at the silica concentration of 10wt%(blue curve). λ_{ex}= 370 nm and λ_{em}= 450 nm.

Likewise, the anisotropy decay of the biopolymer in the presence of silica was found to be pH dependent. Figure 23 displays the anisotropy decays of alginate in the presence of 10 wt % silica at pH 2 and 11, respectively. It was found that the anisotropy decays rapidly to zero at pH11, whereas at pH 2 the anisotropy stays relatively higher than zero for a longer period.

The correlation times derived from mathematical analysis of anisotropy decays of AmNS-labelled-alginate (10^{-1} wt%) were plotted against the silica content at different pH values, as presented in Figure 4.26. When the concentration of added silica is low (10^{-4}, 10^{-3} and 10^{-2} wt%) no important adsorption occurs and the AmNS label exists in a homogeneous environment. In these cases, a single exponential function (Equation 1.21) could be used to calculate the correlation times in nanoseconds. When the concentration of colloid is increased to 10 wt%, absorption begins while some of polymer remains in the bulk solution. In this complex situation a double exponential fit (Equation 1.22) presented the best results which indicates that different environments around the polymer chain might exist (adsorbed vs. free) affecting the motion of the polymer backbone.

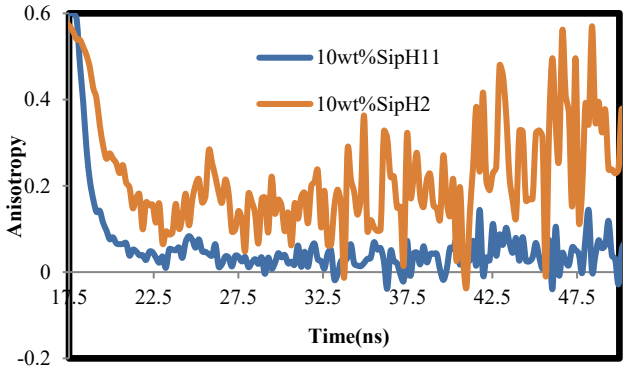


Figure ESI6.3. Fluorescence time resolved anisotropy data of aqueous AmNS-labelled alginate solution (10^{-1} wt%) at the silica concentration of 10wt%, pH 11(blue curve) and pH2(orange curve). (λ_{ex}= 370 nm and λ_{em}= 450 nm).

7. Interactions of Alginate* with Alumina Particles

Fluorescence steady state spectra of AmNS-alginate at alumina surface as a function of pH

The fluorescence emission spectra of 0.1 wt % of AmNS-alginate at pH 3 and 11 in 10 wt% alumina are displayed in Figure 25 and 26. As mentioned before in the experimental part of the adsorption experiment the fluorescence intensities were recorded before and after separation. The results showed that the fluorescence intensity of the supernatant is importantly reduced at pH 3 compared to a minor reduction at pH11, suggesting that, a large quantity of biopolymer attaches to alumina at pH3 while a smaller quantity is adsorbed at pH 11.

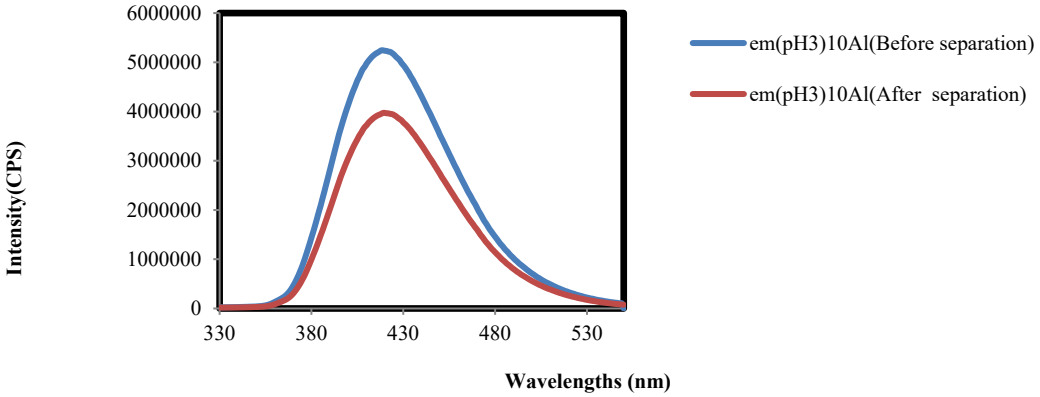


Figure ESI7.1. Steady state fluorescence emission spectra of aqueous AmNS-labelled alginate (10^{-1} wt%) and alumina (10 wt%) solutions before and after the separation at pH3, λ_{ex}= 320 nm.

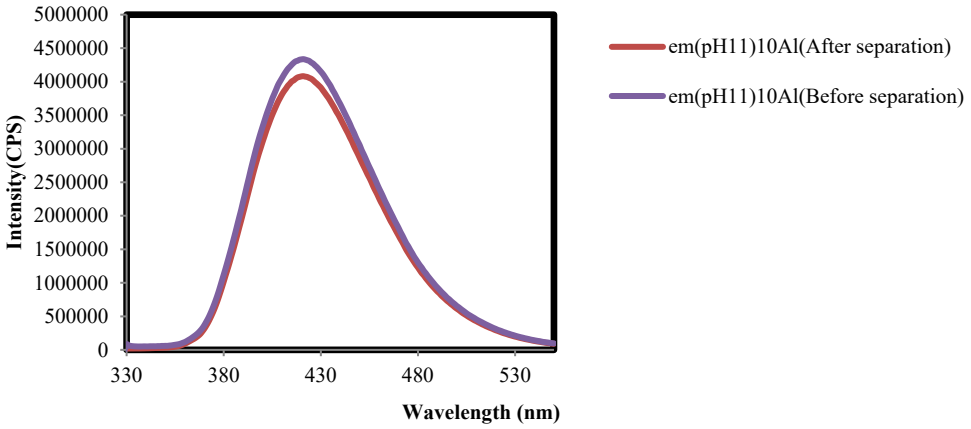


Figure ESI7.2. Steady state fluorescence emission spectra of aqueous AmNS-labelled alginate (10^{-1} wt %) and alumina (10 wt %) solutions before and after the separation at pH11, λ_{ex}= 320 nm.

Fluorescence time-resolved anisotropy measurements (TRAMS) of AmNS-alginate at alumina surface as a function of pH

Figure 28. matches the fluorescence anisotropy decays of AmNS-labelled-alginate in 0.0001 and 10 wt% of alumina, respectively. It was found that the anisotropy quickly drops to zero in the presence of 0.0001 wt% alumina, this proposes that an extremely dilute concentration from Al_2O_3 particles is not enough to be attached with alginate chain, accordingly cannot

alter the macromolecule dynamic. When 10 wt% of alumina was added, the anisotropy did not decay entirely to zero. This result suggets that the macromolecule chain adsorbs onto the alumina particles, which in turn slows down the segmental motion of fluorescently labelled biopolymer; hence a long anisotropy decay is observed in the presence of high concentration from alumina.

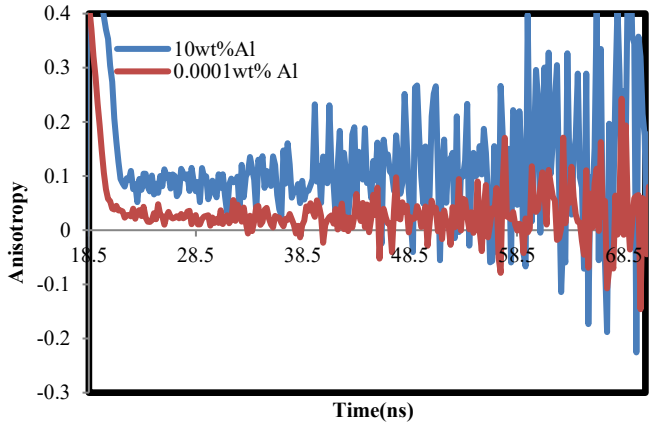


Figure ESI7.3. Fluorescence time resolved anisotropy data of aqueous AmNS-labelled alginate solution (10^{-1} wt%) at the alumina concentration of 0.0001wt%(red curve) and at the alumina concentration of 10wt%(blue curve). (λ_{ex}= 370 nm and λem= 450 nm).

Similarly, the anisotropy decay of the biopolymer in the presence of alumina was found to be pH dependent. Figure 29 displays the anisotropy decays of alginate in the presence of 10 wt % alumina at pH 2 and pH 11, respectively. It was found that the anisotropy decays rapidly to zero at pH 11, whereas at pH 2 the anisotropy stays for a longer period. This confirms the suggestion that the collapsed alginate chains adsorb more than the expanded coils.

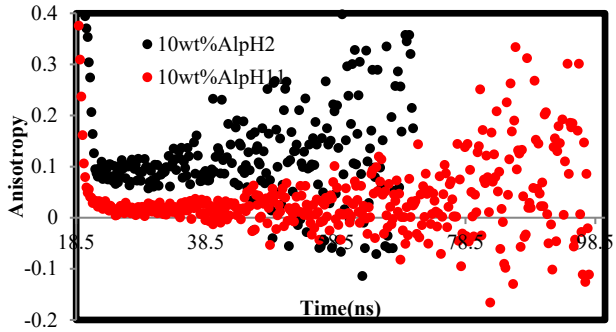


Figure ESI7.4. Fluorescence time resolved anisotropy decays of aqueous AmNS-labelled alginate solution (10^{-1} wt%) at the alumina concentration of 10wt%, pH 11(red curve) and pH2(black curve). (λ_{ex}= 370 nm and λ_{em}= 450 nm).

8. Computational Analysis of Alginate and Polyacrylic acid Monomers

Calculations on molecular structures were carried out comparing neutral monomers (or dimers / trimers of acrylic acid) using a method previously used to explain the interpolymer complexation of acrylate polymers with polyacrylic acid.[9] Each molecule was initially structurally optimised by DFT methods (PBE-D3/TZV(2d) non H atoms, TZV(p) H atoms) in both the gas, aqeous and octanol solution phases. The thermodynamic properties at 298.15 K of the optimised structures were then evaluated at the B3LYP-D3/def2-TZVPPD level45 in both the gas, aqueous and octanol solution using the COSMO methodology. All calculations were carried out in the program orca.

Table ESI8. The electronic enthalpies and entropies of solvation

System	Electronic Energy /Ha	Enthalpy /Ha	T*Entropy kcal/mol	T*Entropy /Ha	Free Energy /Ha	Direct Free Energy	ΔGsol /Ha	ΔGsol /kJ/mol	Log P
acrylic acid monomer									
AAM (Gas)	-347.23	-347.08	30.85	0.05	-347.13	-347.12			
AAM (Water)	-347.24	-347.09	31.09	0.05	-347.14	-347.13	-0.011	-28.121	
AAM (Octanol)	-347.24	-347.09	9.09	0.01	-347.10	-347.13	-0.010	-25.321	0.49054
acrylic acid dimer									
AAD (Gas)	-614.59	-614.36	30.85	0.05	-614.4068	-614.4106			
AAD (Water)	-614.61	-614.38	31.09	0.05	-614.43	-614.43	-0.020	-52.013	
AAD (Octanol)	-614.60	-614.38	9.09	0.01	-614.39	-614.43	-0.018	-46.535	0.95954
acrylic acid trimer									
AAT (Gas)	-881.94	-881.64	30.85	0.05	-881.69	-881.70			
AAT (Water)	-881.97	-881.67	31.09	0.05	-881.72	-881.73	-0.030	-79.898	
AAT (Octanol)	-881.97	-881.67	9.09	0.01	-881.68	-881.73	-0.027	-71.886	1.40339
G monomer									
Algul (Gas)	-839.77	-839.54	30.85	0.05	-839.587	-839.593			
Algul (Water)	-839.87	-839.64	31.09	0.05	-839.689	-839.692	-0.099	-260.363	
Algul (Octanol)	-839.86	-839.63	9.09	0.01	-839.644	-839.684	-0.091	-238.102	3.89916
M monomer									
BDMan (Gas)	-839.77	-839.54	30.85	0.05	-839.59	-839.594			
BDMan(Water)	-839.87	-839.64	31.09	0.05	-839.69	-839.697	-0.103	-269.542	
BDMan (Octanol)	-839.86	-839.63	9.09	0.01	-839.65	-839.688	-0.094	-246.346	4.06308

This showed that the alginate monomers, both B and M form, have a far greater degree of solvation (both by the ΔG of solvation and Log P) than the polyacrylic acid segment.

9. Henry Isotherm Comparisons

Henry Isotherms from this study were compared with data previously published to compare the efficiency of alginate to remove alumina and silica particles from solution.

Table ESI 9 – Absorption isotherm data

	PAA - Alumina		PAA - Silica	
pH	Kh	R2	Kh	R2
2	0.9097	0.9999	0.336	0.9995
3	0.6145	0.9998	0.2006	0.9876
5	0.2875	0.9796	0.1813	0.9951
7	0.2663	0.9953	0.0566	0.8891
9	0.2296	0.9993	0.0468	0.9956
11	0.2289	0.9999	0.0432	0.9737
	Alginate - Alumina		Alginate - Silica	
pH	Kh	R2	Kh	R2
2	0.58	0.9999	0.14	0.99
3	0.59	0.9998	0.10	0.96
5	0.29	0.9977	0.08	0.95
7	0.29	0.9954	0.00	0.97
9	0.00	0.9999	0.00	0.97
11	0.00	0.9993	0.00	0.99
	LPS - Alumina		LPS - Silica	
pH	Kh	R2	Kh	R2
2	0.57	0.9999	0.09	0.9571
3	0.59	0.9998	0.09	0.9613
5	0.29	0.9977	0.06	0.9613
7	0.29	0.9977	0.01	0.9601
9	0.03	0.9999	0.00	0.9969
11	0.04	0.9993	0.00	0.9968

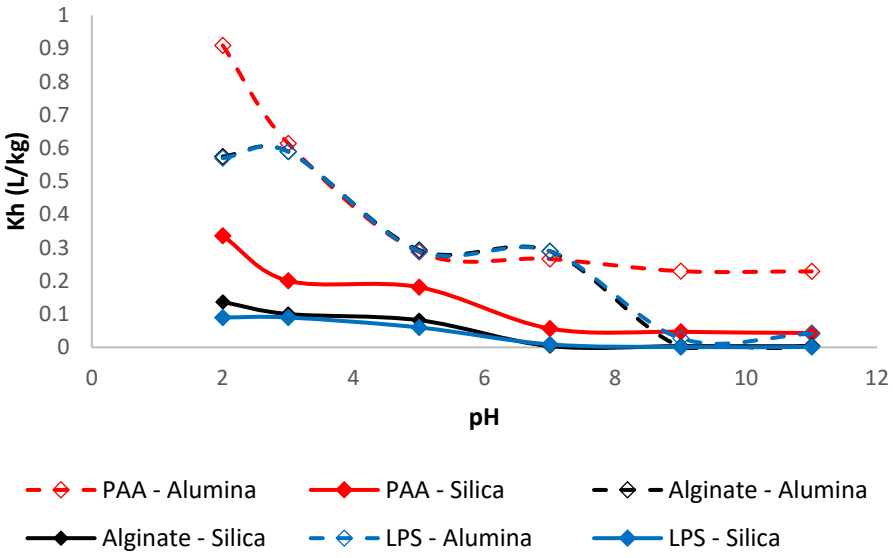


Figure ESI 9.1 Absorption Isotherm Data

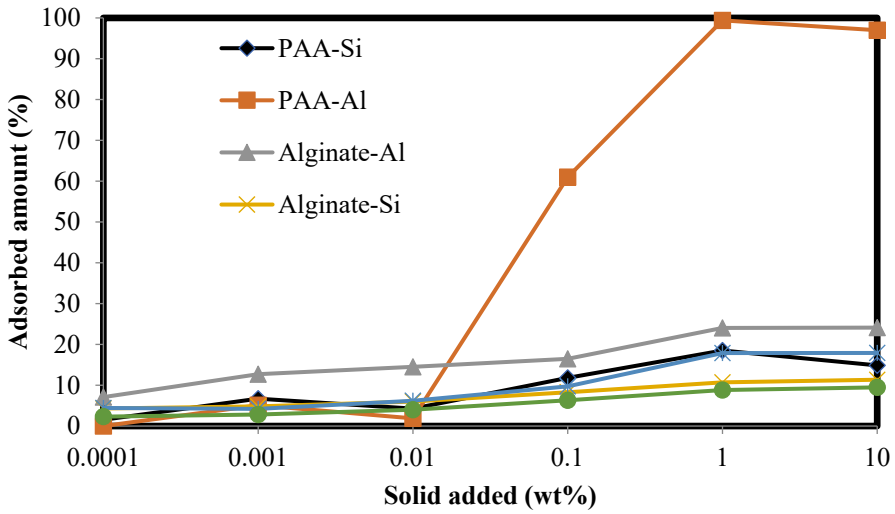


Figure ESI 9.2 The percentage of macromolecules-minerals interference at pH 3.

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