

Influence of Film Stability and Aging of Plasma Polymerized Allylamine Coated Quartz Particles on Humic Acid Removal

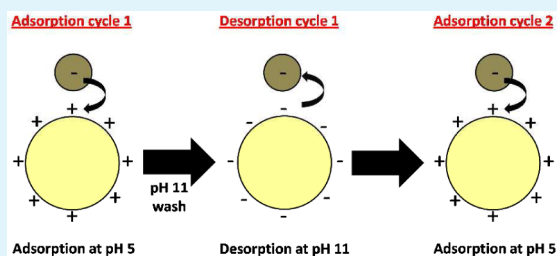
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ABSTRACT: Plasma polymerized allylamine (ppAA) films have been successfully deposited on to the surface of quartz particles via a rotating barrel plasma reactor for humic acid removal. The films were deposited at a power of 25 W, allylamine flow rate of 4.4 sccm and polymerization times of 5 to 60 min. X-ray photoelectron spectroscopy was used to investigate the influence of short-term stirring in water and film age on surface chemistry. Stirring results in a reduction in the nitrogen concentration, which was greatest for shorter polymerization times. Film aging of up to 52 weeks appeared to result in a reduction in the concentration of C–N species. The influence of batch, recycling, and film age on humic acid removal was investigated. Humic acid removal appeared to be reproducible across three separate batches for polymerization times of 20 min or more, which was attributed to film thickness. Recycling of the ppAA films was most successful at pH 11 for up to 4 humic acid removal/regeneration cycles. Successful regeneration at pH 11 was attributed to electrostatic repulsion of the adsorbed humic acid molecules. Decreasing the pH of the regeneration solution reduced the number of successful regeneration cycles due to greater retention of adsorbed humic acid via electrostatic attraction. Film age appears to have minimal effect on humic acid removal where freshly deposited and 52-week-old films removed similar masses of humic acid. Successful production and development of ppAA coated quartz particles has resulted in a functional material that can be incorporated into a water treatment system to improve water quality.

KEYWORDS: plasma polymerization, humic acid, adsorption, water treatment, allylamine



1. INTRODUCTION

A significant proportion of the world's population do not have access to an adequate supply of clean water.¹ Conventional centralized water treatment consisting of coagulation, sedimentation, filtration, and disinfection stages is widely used² but is only really practical for densely populated areas. Centralized water treatment is less practical in developing countries due to high costs and remote locations. Clean water can be produced from natural water sources such as a river, rain, and groundwater via decentralized water treatment. Some already existing decentralized water treatment methods include boiling, filtration, and solar disinfection.¹ Decentralized water treatment can be of great benefit in disaster zones, where following a disaster people are highly susceptible to diseases that originate from sanitation and problems with water supply.³

Humic acid is naturally present in water sources due to plant biodegradation.⁴ Although humic acid itself is not toxic, undesirable taste, color, and odor do result from its existence in drinking water.⁵ Carcinogenic disinfection byproducts⁶ can be produced during conventional drinking water disinfection when chlorine reacts with humic acid.⁷ A number of methods have been used for the removal of humic acid from drinking water such as coagulation, membrane separation, and adsorption. Coagulation with alum is frequently used in centralized water treatment, but it is expensive and results in high sludge volumes. Humic acid removal via membrane

separation has limited removal capacity and has a tendency to result in membrane fouling.⁴ The removal of humic acid via adsorption appears to be the most promising method due to its simplicity and cost effectiveness.⁷ Several adsorbents have been investigated for humic acid removal from water such as fly ash,⁸ biomass,⁹ vermiculite,¹⁰ and polystyrene.¹¹ The carboxylic acid and phenol groups of the humic acid molecule result in its negative charge in solution. The surfaces of naturally negatively charged adsorbents such as silica are often modified to add positively charged groups to increase humic acid removal via electrostatic attraction. Humic acid adsorption has shown to be pH dependent where adsorption decreases for increasing pH values. At lower pH values, humic acid adsorption occurs via electrostatic attraction between the protonated positively charged groups on the adsorbent surface and dissociated negatively charged carboxylic acid groups of humic acid. When the pH is increased, the surface begins to deprotonate and thus becomes less positively charged, which reduces humic acid adsorption.¹²

Plasma polymerization is a frequently used surface modification technique, where the surface is modified while leaving the bulk material unaffected.¹³ There are a number of

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advantages of plasma polymerization such as uniform modification, deposition of specific functional groups and its ability to modify all surfaces irrespective of surface chemistry and shape.¹⁴ Plasma polymerization is undertaken when radio frequency is used to produce a glow discharge through an organic gas or vapor at low pressure.¹⁵ Fragmentation of the vapor molecules occurs within the plasma, which results in the deposition of polymer fragments on the surface of a substrate. Plasma polymers do not have the regular repeating structure of conventional polymers.¹⁶ During plasma polymerization, the monomer flow rate, input power, and time can be varied and used to control the thickness of the deposited layer, the degree of cross-linking, and the surface functionalities produced.¹⁵ The modification of particles using plasma polymerization has been investigated by a number of different techniques. Modification of particles via plasma polymerization can be difficult due to the large surface area of particles where good contact is required between the plasma and the surface of the particles.¹⁷ Particle modification via plasma polymerization has previously been investigated using suspension plasma spraying,¹⁸ particle injection,¹⁹ a fluidized bed reactor,¹⁷ and rotating reactor.²⁰ Our previous research has demonstrated effective modification of the surface of quartz particles using a rotating plasma reactor for allylamine²¹ and ethylenediamine²² films.

Allylamine is a frequently used to produce amine terminated plasma polymerized films,²³ which have shown to be positively charged surfaces at acidic pH.²⁴ The input power and polymerization time has been shown to control the chemistry and structure of allylamine plasma polymerized films. Monomer fragmentation is lower at low input power, which produces a higher amine density due to the deposition of relatively intact allylamine molecules; however, these films are less cross-linked and thus less stable in water.²⁵ More rigid and higher cross-linked films results from deposition at a higher input power due to greater allylamine fragmentation, but less amine groups are then present on the surface. Thicker plasma polymerized allylamine films are produced by increasing the polymerization time.²⁶

Several studies have shown that plasma polymer films undergo aging upon storage.^{13,16,24,27} These films likely contain trapped radical species, which can then react with oxygen upon exposure to air. Oxygen incorporation into the film can continue for months after fabrication.¹⁶ Surface adaptation also occurs during aging, where polymer chains from the film surface can move into the bulk.²⁸ Understanding the aging process enables the development of films with predictable properties at the intended time of use.²⁷ For amine monomers, it has been shown that the N/C ratio tends to decrease over time.¹³ The decrease in nitrogen has been suggested to be due to the movement of amine groups away from the surface into the bulk of the film.¹⁶ Shifts in the nitrogen XPS peak to higher binding energies over time suggest a fall in amine and imine groups and an increase in amide groups due to oxygen incorporation.^{13,27} Decreasing amine reactivity²⁴ and density²⁹ with increasing time has also been observed.

This research investigates the reproducibility, recyclability, and aging of allylamine plasma polymerized films on quartz particles for humic acid removal. Three batches of plasma polymerized allylamine coated quartz particles were produced to investigate reproducible humic acid removal. The recyclability was tested via regeneration and further humic acid removal. Coated particles were stored for up to 52 weeks with humic acid removal undertaken at regular intervals to

investigate the effect of film aging on humic acid removal. Plasma polymerized allylamine films could be produced reproducibly, with recyclability and film aging minimally influencing humic acid removal.

2. MATERIALS AND METHODS

2.1. Materials. Humic acid and allylamine were purchased from Sigma-Aldrich and used as received. Quartz particles were obtained from Unimin Australia Limited.

2.2. Plasma Polymerization. Plasma polymerization was carried in a custom built rotating barrel plasma reactor using a 13.56 MHz RF generator and matching network (Coxial Power Systems Ltd.), which has been previously detailed.²¹ Briefly, the particles were placed into the reactor and pumped down to approximately 7×10^{-3} mbar. The allylamine monomer was degassed by at least 3 freeze-thaw cycles using liquid nitrogen. Allylamine flow was controlled using a needle valve to set a flow rate of 4.4 standard cubic centimeters per minute (sccm). The RF power was set at of 25 W, while the polymerization time was varied from 5 to 60 min. Three identical batches were made for each polymerization time for comparison.

2.3. X-ray Photoelectron Spectroscopy. The surface chemistry of plasma polymerized allylamine coated quartz particles was investigated using a SPECS SAGE HR 100 X-ray photoelectron spectrometer and the same parameters described previously.²¹

2.4. Allylamine Film Aging. Samples were stored in a clear plastic container under ambient laboratory conditions for up to 52 weeks. Initial humic acid removal and XPS measurements were taken within 24 h of film deposition.

2.5. Allylamine Film Stability. Particles (1 g) were immersed in 10 mL of Milli-Q water. The dispersions were stirred using a magnetic stirrer for time periods of 5 to 60 min. The water was removed and the particles dried at 60 °C for 2 h followed by XPS analysis.

2.6. Humic Acid Removal. Humic acid powder was used to make a solution at a concentration of 10 mg/L. The solution was adjusted to pH 7 by HCl and NaOH. Quartz particles (1 g) were weighed, and 10 mL of humic acid solution was added. The samples were agitated using a magnetic stirrer for 30 min. The humic acid solution was then filtered using a 0.45 μm hydrophilic cellulose acetate filter. The humic acid concentration was then analyzed using a Varian Cary 50 UV-visible spectrophotometer at a wavelength of 254 nm. The mass of humic acid removed by the particles was determined by subtracting the final humic acid concentration from the initial concentration. Humic acid removal was carried to investigate reproducibility and ppAA film aging. Three measurements were taken for each sample and averaged.

2.7. Film Regeneration. To test the regeneration of plasma polymerized allylamine coated quartz particles, successive humic acid adsorption/desorption steps were carried out. Humic acid was adsorbed onto ppAA coatings as outlined in section 2.3, except at pH 5 to maximize the mass of humic acid adsorbed.²¹ The humic acid solution was removed and filtered using a 0.45 μm hydrophilic cellulose acetate filter. The mass of humic acid adsorbed was determined as outlined in section 2.3. The particles were rinsed three times with pH 5 Milli-Q solution to remove loosely bound humic acid molecules. Humic acid desorption was carried out by adding 10 mL of pH 3, 7, or 11 Milli-Q solution added to the particles, and the dispersions were stirred on a magnetic stirrer for 30 min. The desorption solution was removed, and the particles were rinsed again three times with pH 5 Milli-Q solution. These adsorption/desorption steps were repeated for up to a total of four cycles.

3. RESULTS AND DISCUSSION

3.1. Allylamine Film Stability in Solution. To determine the stability of plasma polymerized allylamine (ppAA) films on quartz particles in solution, particles were immersed in Milli-Q water and stirred using a magnetic stirrer for time periods of 5 to 60 min. XPS measurements determined the effect of immersion and stirring on the nitrogen concentration, as shown

in Figure 1. A general trend of decreasing nitrogen with increasing stirring time was observed for all polymerization

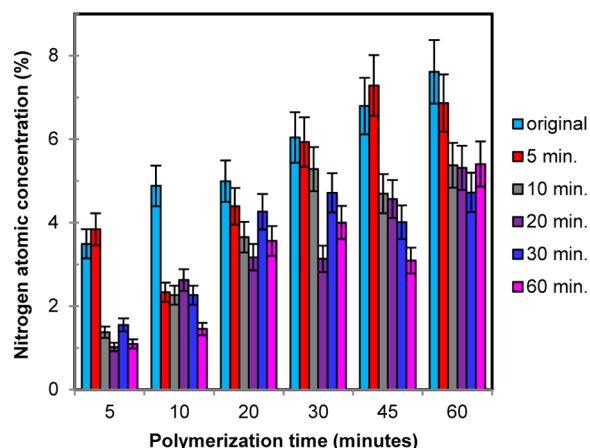


Figure 1. XPS nitrogen concentrations of allylamine coated quartz particles as a function of polymerization time for stirring times of 5 to 60 min.

times. As the nitrogen concentration of the quartz particles is solely due to the ppAA coating, decreases in the nitrogen concentration indicates a reduction in film thickness. For a Mg $K\alpha$ XPS X-ray source, silicon only had a sampling depth of 8.4 nm.³⁰ If silicon is observed in the spectrum, then the film thickness is less than 8.4 nm. Due to the nature of XPS analysis being depth dependent, as the film thickness increases up to approximately 8.4 nm, the atomic concentration of nitrogen will increase as the contribution nitrogen makes to the overall signal increases. Although the film chemistry is expected to be the same throughout, this phenomenon is observed until the film thickness is greater than that of the XPS sampling depth then the atomic nitrogen concentration will remain constant even with for longer polymerization times. The reduction in nitrogen upon stirring is likely to be due to the abrasive nature of the quartz particles where longer stirring time resulted in more of the ppAA being abraded away. Dissolution of the ppAA films in solution may have also occurred, but since a significant nitrogen concentration is retained for the majority of polymerization times for 60 min of stirring, it is unlikely to play a significant role in the reduction of the ppAA film over such a time period. For the majority of samples, stirring for 5 min does not appear to significantly influence the nitrogen concentration while more significant decreases in nitrogen concentration were observed for stirring times of 10 min or more. It appears that a stirring time of 10 min provides sufficient abrasion to result in a reduction in film thickness, which thus reduces the nitrogen concentration. Greater overall reductions in nitrogen concentrations were observed for shorter polymerization times. For a polymerization time of 5 min, the nitrogen concentration decreased from 3.5% initially to 1.1% after 60 min of stirring, which is a reduction of almost 70%. A similar reduction in the nitrogen concentration was also observed for a polymerization time of 10 min while polymerization times of 20 min or more only had decreases in the nitrogen concentration of 29–55%. Longer polymerization times may result in a higher retention of nitrogen due to the thickness of the ppAA films. Previously, it has been shown that longer polymerization results in thicker films, as estimated from the XPS silicon concentration.²¹ Thicker films result from longer polymerization times as there

is more time to deposit allylamine fragments on the surface and thus build up a thicker film. XPS analysis provides the best indication of film thickness as traditional techniques used to measure film thickness, such as AFM and ellipsometry, cannot be used on particles. For thicker films produced by longer polymerization times, a lower proportion of nitrogen will be lost from the surface even if a similar thickness of the ppAA film is abraded due to the greater nitrogen concentration initially. Changes in ppAA film thickness upon stirring are indicated by observing the silicon atomic concentrations of the film. Reductions in the silicon atomic concentrations indicate an increase in film thickness as the contribution from the underlying quartz particles is obscured. For polymerization times of 5 and 60 min, the atomic silicon concentrations increased from 5.79% to 10.53% and from 0% to 4.6%, respectively, thus demonstrating the reduction in film thickness due to abrasion during the stirring process. Polymerization time does not appear to significantly influence ppAA film stability in solution, but a greater loss of nitrogen is observed for shorter polymerization time due to lower nitrogen concentrations initially.

3.2. Allylamine Film Aging. The aging of ppAA films on quartz particles was investigated using XPS analysis. XPS measurements were taken of the freshly coated ppAA coated quartz particles and then weekly for the first 4 weeks. Final XPS measurements were taken 52 weeks after coating. Changes were observed in the atomic concentrations of carbon, nitrogen, oxygen, and silicon for aging times up to 52 weeks, as shown in Figure 2. Only polymerization times of 10, 30, and 60 min are shown; however, similar trends were observed for all polymerization times. In the first 4 weeks of aging, little change in the surface chemistry was observed. Small fluctuations in the atomic concentrations over the first 4 weeks were attributed to slight inhomogeneities across the particle in a batch. For film ages of 52 weeks, more obvious changes are observed in the atomic concentrations of ppAA films. Similar trends were observed for the majority of polymerization times, where in comparison to the freshly deposited ppAA films, aging for 52 weeks resulted in increases in the atomic concentrations of carbon and decreases in the atomic concentrations of nitrogen and oxygen. Silicon could be detected for polymerization times of 45 and 60 min after 52 weeks of aging but was not detected over the first 4 weeks. Such behavior suggests that thicker ppAA films formed by longer polymerization times may contract over time, which results in a greater contribution of silicon from the underlying quartz particle. The decreasing nitrogen and increasing carbon concentrations with film age could be attributed to the movement of amine groups from the interface into the bulk of the plasma polymer film, which has been previously observed. Such migration decreases the probability of detecting emitted photoelectrons, which produces an apparent reduction in the amount of nitrogen detected.²⁷ Interestingly, for all polymerization times, a decrease in the oxygen atomic concentration by 1.9 – 4.4% was observed, which is in contrast to previous studies that have shown an increase in oxygen concentration with aging due to oxygen incorporation.^{13,27} Such a result was unexpected and possibly suggests a difference in the aging behavior of ppAA films of particles versus planar surfaces. The geometry of particulate versus planar surfaces may be favorable to reduce oxidation of the ppAA surface. Having the particles packed closely could inhibit the contact of oxygen with the surface, thus reducing film oxidation.

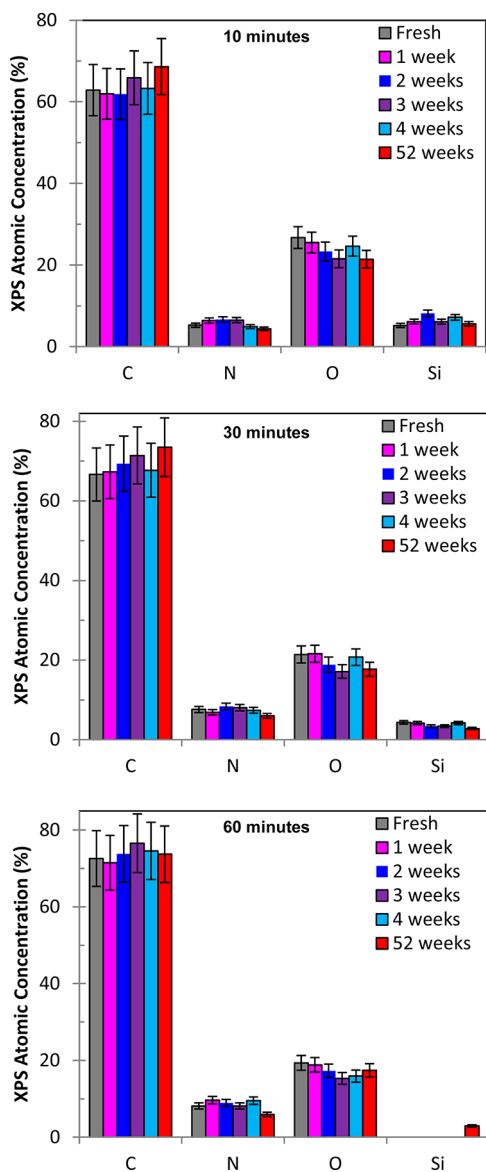


Figure 2. XPS atomic survey concentrations of allylamine coated quartz particles with polymerization times of 10, 30, and 60 min for aging times up to 52 weeks.

Curve fitted high resolution C 1s XPS were produced to further investigate the effect of aging on ppAA surface chemistry, as shown in Figure 3. Four peaks were fitted to the high resolution C1s XPS spectra of uncoated quartz particles; C–C, C–H at ≈ 285 eV, C–O, C–N at ≈ 286.5 eV, C=O, N–C=O at ≈ 288 eV, and COOH at ≈ 289 eV. The same peaks were fitted to the spectra of ppAA coated quartz particles, except for the COOH peak at 289 eV, which was attributed to oxidized adventitious carbon species on the uncoated particle surface, which is obscured following the deposition of a ppAA film. After the deposition of the ppAA film, a significant increase in the C–O, C–N peak was observed. Unfortunately, the C–O and C–N peaks are situated too closely together to be curve fitted individually, but the increase in the intensity of this peak can sensibly be attributed to an increase in the C–N species on the surface from allylamine plasma polymerization. Only the spectra for ppAA films deposited for 60 min were curve fitted to investigate the effect of aging on the thickest film; however, other polymer-

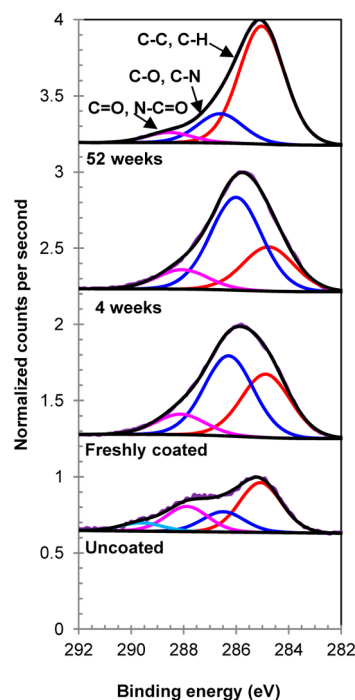


Figure 3. High resolution C 1s XPS spectra uncoated and of 60 min allylamine coated quartz particles for aging times up to 52 weeks.

ization times showed similar aging behavior. Aging the film for 4 weeks does not appear to significantly change the surface chemistry of the ppAA film. A significantly larger C–O, C–N than C–C, C–H peak was observed in both the freshly deposited and 4 week ppAA films due to nitrogen species within the ppAA film. Aging for 52 weeks alters the ppAA film surface chemistry where a significant reduction in the intensity of the C–O, C–N peak was observed. Such a reduction was attributed to the migration of nitrogen from the surface of the ppAA film into the bulk which has been previously observed for amine monomers.²⁷ XPS characterization of ppAA coated quartz particles for aging times of up to 52 weeks have shown some changes in the surface chemistry. The ppAA films appear to contract slightly over time and show a reduction in nitrogen species.

3.3. Reproducibility of ppAA Films for Humic Acid Removal. Adsorption is a highly efficient method for humic acid removal.^{7,8} Humic acid has a negatively charge due to its dissociated carboxylic acid groups. The amine groups on the ppAA surface are protonated and therefore positively charged at pH values below their isoelectric point. These opposing charges therefore enable humic acid adsorption via electrostatic attraction. To determine the reproducibility of humic acid removal using ppAA films, three separate batches were produced for each polymerization time followed by humic acid removal. In Figure 4, it can be observed that for the majority of polymerization times, the mass of humic acid removed was similar for all three sample sets. For the shortest polymerization times of 5 and 10 min, humic acid removal was less reproducible. A polymerization time of 5 min was the most variable, where only one of the three samples sets resulted in humic acid removal. The lack of reproducibility for a polymerization time of 5 min may be related to film thickness and stability in solution. Previous characterization of these films via time-of-flight secondary ion mass spectrometry (ToF-SIMS) has shown that a polymerization time of 5 min is

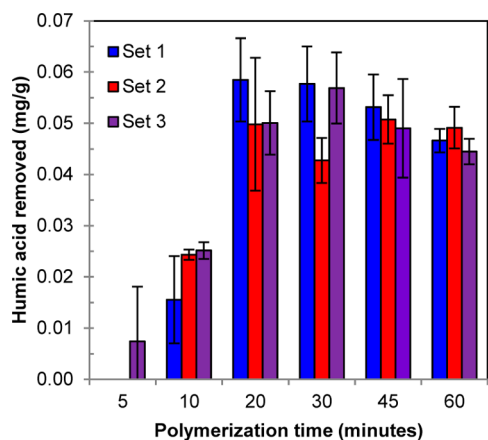


Figure 4. Humic acid removal by allylamine plasma polymerized quartz particles as a function of polymerization time for three separate sample sets.

sufficient to produce a uniform film on the particles.²¹ ToF-SIMS is a highly surface sensitive characterization technique with an analysis depth of only 1–2 nm.³¹ A small amount of silicon could be observed on the surface for a polymerization of 5 min,²¹ thus indicating the film is likely to be less than 2 nm thick. Five minutes of polymerization is likely to be insufficient to produce a thick enough coating to withstand the abrasion within solution. In Figure 1, it was observed that 30 min of stirring only resulted in a reduction in the atomic nitrogen concentration from 3.5% to 1.5%. Such a nitrogen concentration on the surface appears to be insufficient to result in significant humic acid removal. Increasing the polymerization time to 10 min increases the reproducibility of humic acid removal where only one sample set was significantly different from the other two. For polymerization times greater than 10 min, thicker coatings result in more reproducible humic acid removal. Although the atomic nitrogen concentration is reduced by the stirring during humic acid removal, the thicker coatings will still likely result in a similar nitrogen concentration at the very surface therefore minimally affecting humic acid removal. Even though the majority of polymerization times produced relatively reproducible humic acid removal, large error bars were observed. Such deviations in humic acid removal are proposed to be due to the heterogeneous nature of humic acid. Humic acid contains both hydrophobic and hydrophilic segments with carboxylic, phenolic, carbonyl, and hydroxyl functionalities.³² The humic acid used also had a large molecular weight range of 2000–500 000 Da. The heterogeneous nature of humic acid may have resulted in different components being present in each sample, which thus resulted in slightly variable humic acid removal.

The masses of humic acid removed by ppAA coated particles are significantly lower than the values of 10–110 mg/g previous reported in the literature.^{6–8,10,33,34} The higher mass of humic acid removed in these previous studies, however, can be attributed to their significantly higher surface areas than that of ppAA coated particles (0.305 m²/g). Higher surface areas have shown to result in significant increases in the humic acid removal. Fly ash with surface area of 4.0 m²/g has shown to remove less than 1 mg/g of humic acid;⁵ however, increasing the surface area of fly ash to 224 m²/g resulted in humic acid removal of 50 mg/g.⁸ Mesoporous silica with a surface area of 407 m²/g was able to remove 120 mg/g of humic acid.³⁵ The high masses of humic acid removed can also be attributed the

high initial masses of humic acid used, up to 100 mg/L.^{9,36} A greater initial humic acid concentration increases humic acid adsorption due to the greater number of humic acid molecules in solution, which forces more humic acid to adsorb onto the adsorbent surface,⁷ which has been previously observed for a number of adsorbents.^{7,10,12,37} For this study, a humic acid concentration of 10 mg/L was used, as natural waters normally have humic acid concentrations less than 10–15 mg/L.¹¹ Similar masses of humic acid have been removed by ppAA coated quartz particles as was previously observed for chitosan coated PET granules,³² which are also amine terminated.

3.4. Regeneration/Recycling of ppAA Films for Humic Acid Removal. ppAA coated quartz particles have shown to be successful for humic acid removal;²¹ however, the ability to regenerate these particles for future use would render them an even more useful material. After humic acid adsorption at pH 5, regeneration at pH 3, 7, or 11 influenced the mass of humic acid removed in subsequent adsorption cycles, as shown in Figure 5. Regeneration at pH 3 shows similar masses of humic acid removed for the first two cycles, with significantly less removal for the third and fourth cycles. Increasing the pH of the regeneration solution to pH 7 resulted in greater humic acid removal for the third and fourth cycles in comparison to regeneration at pH 3. Further increasing the pH of the regeneration solution to pH 11 resulted in even greater humic acid removal again for the third and fourth cycles but only for polymerization times of 30 min or more. The general trend of greater humic acid removal after regeneration for higher pH values can be attributed to electrostatic repulsion as humic acid adsorption occurs via electrostatic attraction.

Humic acid has a negative charge due to the dissociation of the carboxylic acid group, which has a pK_a of 3, and therefore, humic acid will retain its negative charge at higher pH values.⁶ The amine groups of the ppAA surface have shown to have isoelectric points ranging from 6 to 7.5,²¹ depending on polymerization time. At pH values lower than the isoelectric point, the surface is positively charged, thus resulting in humic acid removal via electrostatic attraction. At pH values higher than the isoelectric point, the ppAA surface will be negatively charged. At higher pH values, the humic acid remains negatively charged, which results in desorption of the humic acid due to electrostatic repulsion as the ppAA surface and humic acid are both negatively charged, which allows for further humic acid removal after regeneration. At pH 3, the ppAA surface remains positively charged and therefore desorption via electrostatic repulsion is less likely. Similar masses of humic acid, however, were removed after one regeneration cycle in comparison to the masses initially removed. Such desorption suggestions that simply washing the surface, independent of pH, may be sufficient for regeneration of the surface. Washing, however, does not appear to be effective for subsequent regeneration cycles as significantly less humic acid was removed after additional regeneration cycles. Regeneration of surfaces for humic acid removal at lower pH values have previously shown to be minimally effective where less than 30% desorption was reported.¹⁰ Increasing the pH of the regeneration solution to 7 and then 11 results in the surface becoming more and more negatively charged, and thus, a greater proportion of the humic acid desorbs due to electrostatic attraction, thus allowing for further humic acid removal. Adsorbent regeneration via pH reversal is commonly used for electrostatically attracted small molecules such as dyes.^{38–40} Although a number of surfaces have been

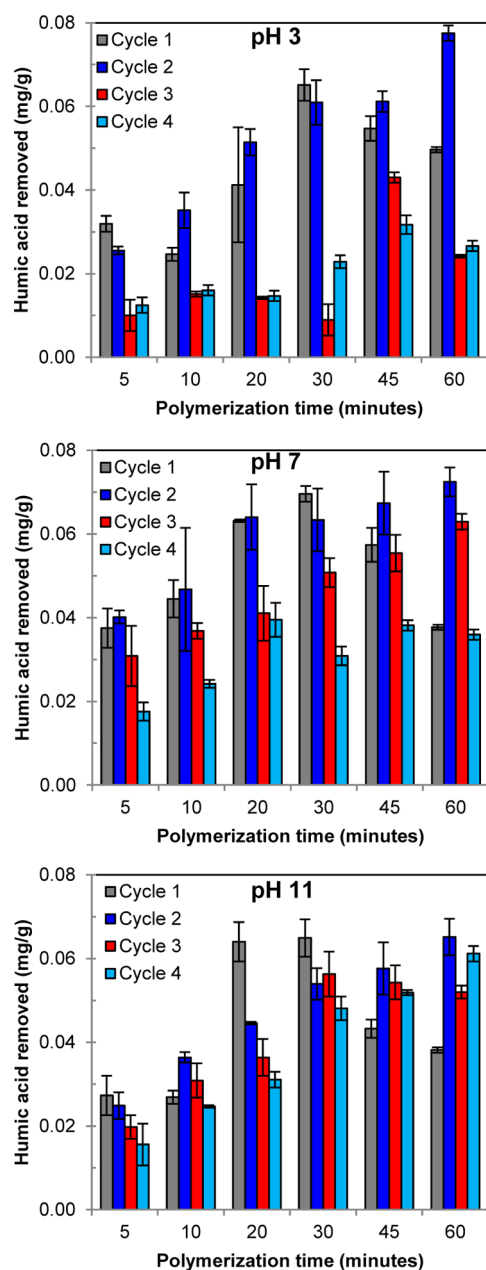


Figure 5. Regeneration of allylamine plasma polymerized quartz particles at pH 3, 7, and 11 for humic acid removal.

investigated for humic acid removal, only a small number extend the research to include regeneration. It has been previously observed that significant humic acid desorption could be achieved using basic solutions⁹ where increasing the pH increases humic acid desorption. Previous research has also shown that amine terminated surfaces can be regenerated for up to 5 cycles with only slight decreases in the mass of humic acid removed after each regeneration cycle.^{34,36}

It was observed that for some samples across all pH values, regeneration actually increased humic acid removed. Such behavior could be due to removal of the surface oxide layer via dissolution or abrasion during the regeneration. It has been previously shown that allylamine films can have amide groups at the surface due to oxygen incorporation.^{13,27} Removal of this oxide layer during regeneration could then expose a higher

concentration of amine groups, which would thus result in greater humic acid removal.

3.5. Influence of ppAA Film Aging on Humic Acid Removal. The influence of ppAA film age on humic acid removal was investigated by carrying out humic acid removal experiments for up to 52 weeks after film deposition. In comparison to the masses of humic acid initially removed, film age does not appear to significantly influence humic acid removal, as shown in Figure 6. For shorter polymerization

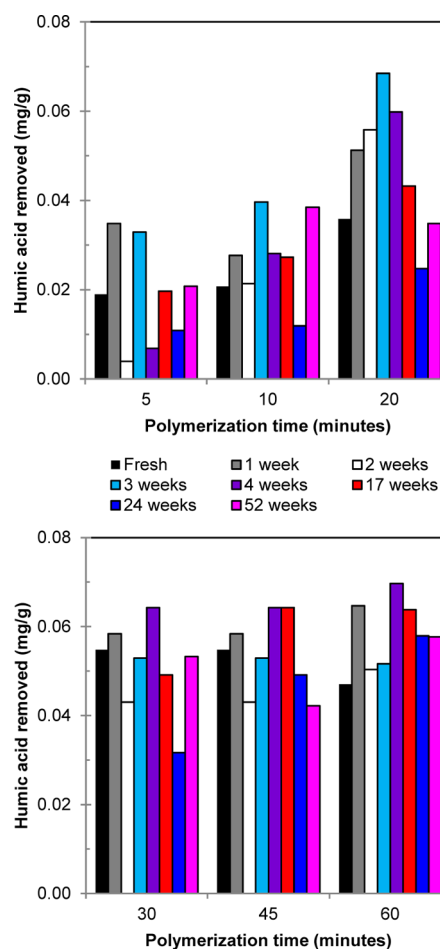


Figure 6. Humic acid removal by allylamine plasma polymerized quartz particles as a function of polymerization time for film ages up to 52 weeks.

times (5–20 min), the masses of humic acid removed appeared to be more variable than for longer polymerization times (30–60 min). The variable nature of humic acid removal for shorter polymerization times, despite similar masses removed initially and after 52 weeks, may be attributed once again to the thickness of the films. Shorter polymerization times produce thinner films that may not produce completely uniform coating across the entire mass of particles, thus some deviation in humic acid removal would occur between samples. The deviations in humic acid removal for polymerization times greater than 20 min may be due to the heterogeneous nature of humic acid which may have resulted in different components being present in each sample.

ppAA films have been shown to undergo aging where decreases in the N/C ratio¹³ and primary amine concentration²⁴ have been observed. Although the aging process of

allylamine films is well understood, the influence of such aging on interactions at the solid/liquid interface, such as humic acid adsorption, have not been investigated. Decreasing amine groups and increasing amide groups during aging would be expected to decrease humic acid removal over time due to the loss of positively charged amine groups. Decreasing humic acid removal over time was, however, not observed and may be due to a few different factors. The geometry of particulate versus planar surfaces may be favorable to reduce oxidation of the ppAA surface. Having the particles packed closely could inhibit the contact of oxygen with the surface, thus reducing film oxidation and preventing the decrease in humic acid removal. Surface characterization techniques, however, would be required to confirm this hypothesis. The immersion of the ppAA coated quartz particles in solution may also be contributing to the retention of humic acid removal due to the removal of any oxide layer on the surface via dissolution/agitation. It has previously been proposed that aging causes the movement of amine groups away from the surface into the bulk of the film.¹⁶ Removal of the outer layers of the ppAA film via dissolution/agitation in solution could therefore expose a similar concentration of amine groups as was originally found on the surface.

4. CONCLUSIONS

The removal of humic acid using plasma polymerized allylamine coated quartz particles has shown to only be minimally influenced by batch, recycling and film age. The use of a rotating barrel plasma reactor produced reproducible humic acid removal across three separate samples for polymerization times of 10 min or more. Less reproducible humic acid for shorter polymerization times was attributed to thinner films. Regeneration of the ppAA films could be achieved via simple washing, but was influenced by the pH of the solution. The number of cycles that the ppAA films could be regenerated for increased with increasing pH, where similar masses of humic acid could be removed for four regeneration cycles at pH 11 for the majority of polymerization times. A greater number of successful regeneration cycles could be achieved using pH 11 solution due to maximized humic desorption via electrostatic repulsion. Film aging of 52 weeks appeared to reduce the concentration of C–N species but did not significantly influence humic acid removal where similar masses of humic acid were removed as were observed for freshly deposited films. The minimal influence of film age on humic acid removal was attributed to immersion/agitation in solution during humic acid removal may also have removed the outer oxide layer on the particles thus exposing a similar concentration of amine groups as was originally found on the surface. The functionality of ppAA coated quartz particles have been extended by the demonstration of reproducible humic acid removal, successful regeneration, which enables reuse, and the minimal influence of film age, which enables storage. The deposition of ppAA films on quartz particles has shown to produce a functional material, which could be incorporated into a low cost decentralized water treatment system.

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Notes

The authors declare no competing financial interest.

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