ABSTRACT

The availability of clean drinking water in rural areas, disaster zones and third world countries is a major concern. A number of purification methods are available but are often energy intensive and only feasible for highly populated areas. Simple and cheap decentralized water treatment systems can however be produced for isolated locations. Quartz particles have been modified via an inductively coupled radio frequency plasma reactor fitted with a rotating barrel chamber. Plasma polymerization was undertaken using allylamine as the monomer to produce amine terminated surfaces. Amine functionalisation produces surfaces with higher isoelectric points which become positively charged in solution, thus removing negatively charged contaminants via electrostatic attraction. Polymerization time, RF power and monomer flow were varied for optimal humic acid removal. The effect of these parameters on surface chemistry was determined using XPS and electrokinetic analysis. The effectiveness of plasma polymerized allylamine coated quartz particles for water treatment was investigated via humic acid removal. Plasma polymerization has shown to be a successful method for modifying quartz particles for water treatment. Further development of the plasma polymerization process and investigation of additional contaminants will aid in its development as a decentralized water treatment system.

INTRODUCTION

Safe drinking water is a global concern with a large proportion of the world’s population unable to access clean water supplies (Peter-Varbanets et al., 2009). Pathogens are the major cause of water related diseases. Conventional centralized water treatment i.e. coagulation-sedimentation-filtration-disinfection is widely used (Majewski, 2007) but this type of water treatment is generally only feasible for densely populated areas. In developing countries, centralized water treatment is often not feasible due to remote locations and lack of finance (Peter-Varbanets et al., 2009). Decentralized water treatment enables clean drinking water to be produced on demand from existing water sources (Arnal Arnal et al., 2001). Examples of decentralized water treatment include boiling, solar disinfection, filters and membranes (Peter-Varbanets et al., 2009).

Organic matter in drinking water, such as humic acid results from the biodegradation of plants (Kamari et al., 2009) producing colour, taste and odour problems (Tao et al., 2010). Humic acid also reacts with chlorine during drinking water disinfection (Zhan et al., 2010) to produce carcinogenic disinfection by-products (Tao et al., 2010). Natural waters tend to have humic acid concentrations below 10 – 15 mg/L (Wang et al., 2008).
Adsorption of humic acid is the most promising removal method (Zhan et al., 2010) as it is simple and economical. A number of low cost adsorbents have been investigated to remove humic acid from water including bentonite (Salman et al., 2007) and vermiculite (Abate and Masini, 2003). Surface modification of adsorbents can be carried out to introduce surface functional groups to improve humic acid adsorption (Deng and Bai, 2003).

Plasma polymerization is an effective surface modification technique as it only modifies the surface layer without changing the bulk properties. Advantages of plasma polymerization are the uniformity of modification, specificity of functional groups and its ability to modify all surfaces, regardless of structure and surface chemistry (Chan et al., 1996). Radio frequency is often used to produce a glow discharge where applying power to a monomer results in ionization. Excited atoms emit photons and create the glow that is generally referred to as plasma. Within the plasma, fragmentation of the monomer occurs resulting in polymerization on the surface of a substrate in contact with the plasma. The thickness of the polymer layer, structure and surface functionalities produced via plasma polymerization are dependent on monomer flow rate, input power and time (Gaur and Vergason, 2000). Allylamine is a commonly used monomer for surface modification (Ren et al., 2008; Yang et al., 2009), producing an amine terminated surface which increases hydrophilicity and improves cell attachment. Low input power limits monomer fragmentation thus resulting in a higher amine density but the films are not stable in water due to their low crosslinking (Abbas et al., 2009). Increasing input power produces a more rigid film due to higher crosslinking, however the number of amine groups are reduced by greater allylamine fragmentation (Myung and Choi, 2006). In solution allylamine modified surface can protonate to become \( \text{NH}_3^+ \) species and are therefore able to adsorb humic acid via electrostatic attraction. Humic acid is negatively charged due to the dissociated carboxylic acid groups (COO\(^-\)) which enables adsorption via electrostatic attraction to the protonated \( \text{NH}_3^+ \) groups of the plasma polymerized allylamine quartz particles at low pH, therefore humic acid adsorption is highly pH dependent (Abate and Masini, 2003; Wan Ngah et al., 2008).

Plasma polymerized modification of particles has been investigated, with a number of different methods applied. Modification of particles via plasma polymerization is complex due the large surface area per unit mass of particles (Kim and Choi, 2002). Surface modification of particles by plasma polymerization has been undertaken using a fluidized bed reactor (Karches et al., 1999), particle injection (Murata and Aradachi, 2001), suspension plasma spraying (Kumar et al., 2001) and rotating reactors (Favia et al., 2006).

This research investigates the modification of quartz particles by allylamine plasma polymerization for the removal of humic acid from water. Polymerization time, monomer flow and power were varied to determine their impact on humic acid removal. Surface chemistry was analysed via XPS while electrokinetic analysis was undertaken to characterize zeta potential. Humic acid concentration, solution pH and adsorption time were varied to maximize humic acid removal.
EXPERIMENTAL

Plasma Polymerization
Plasma polymerization was undertaken on 50g batches of quartz particles (Unimin, average diameter 430 µm, BET surface area 0.305 m²/g). A homemade rotating plasma reactor, consisting of a pyrex tube 50 cm long and 16cm in diameter was used. The reactor was rotated at a constant speed of 14 rpm. Inside the reactor, a glass blade ensured even particle mixing during rotation. Quartz particles were loaded into the plasma chamber which was pumped down to approximately 4 x 10⁻³ mbar. The flow of previously degassed allylamine monomer (Aldrich) was adjusted using a needle valve to achieve flow rates of 4 – 10 standard cubic centimetres per minute (sscm). Radiofrequency (RF) powers of 4 – 40 W and polymerization times of 5 -60 minutes were utilized.

X-ray Photoelectron Spectroscopy
X-ray photoelectron spectroscopy (XPS) of quartz particles was carried out using a SPECS metastable impact electron spectrometer with a SPECS XR-50 X-ray source operating at 100 W and a SPECS Phiobos hemispherical analyser. A Mg Kα radiation source was used. High resolution C 1s spectra were collected using a pass energy and resolution of 20 and 0.05 eV respectively. The spectra were fitted using CASA XPS software. The binding energies of the peaks were normalized by modifying the binding energy of the C 1s peak for C-C to 285 eV. The shift between 285 eV and the C-C binding energy was applied to all peaks.

Electrokinetic Analysis
Zeta potential measurements of uncoated and allylamine coated quartz particles were undertaken using an Anton Paar Electro Kinetic Analyzer with a remote titration unit. Quartz particles were packed into a powder cell. The initial pH of the 10⁻³ M KCl electrolyte was adjusted to approximately 9 using 0.1 M KOH. The titration unit injected appropriate volumes of 0.1M HCl into the electrolyte solution to lower the pH enabling zeta potential measurements to be taken approximately every 1 pH unit. At each pH value, a zeta potential measurement was taken when the electrolyte was pumped from left to right and from right to left. These measurements were repeated 3 times and averaged to produce a final zeta potential value.

Humic Acid Removal
Humic acid solutions of 2.5, 5 and 10 mg/L were made from solid (Aldrich). The solutions were pH adjusted by HCl or NaOH. 10 mL of humic acid was added to 1 g of quartz particles. The dispersions were stirred on a magnetic stirrer for 5-30 minutes followed by filtration with a 0.45 µm filter. Humic acid concentration of the remaining solution was analysed using a Varian Cary 50 UV-Vis spectrophotometer at a wavelength of 254 nm.
RESULTS AND DISCUSSIONS

Optimization of Plasma Polymerization Parameters for Humic Acid Removal

To determine the optimal surface for humic acid removal plasma power, monomer flow and time for humic acid removal were varied. Initially monomer flow and time were kept constant while plasma power was varied. Monomer flow was set at approximately 4.5 sccm with a polymerization time of 5 minutes while plasma power was varied from 4 to 40 W. After plasma polymerization, samples were immersed in 5 mg/L humic acid at pH 7 and stirred for 5 minutes. Humic acid removal is shown in Figure 1 and it was observed that maximum humic acid removal was achieved with a plasma power of 25 W. Increasing plasma power increases fragmentation of the allylamine monomer (Myung and Choi, 2006). It can therefore be suggested than plasma powers below 25 W do not produce sufficient fragmentation for optimal humic acid removal while at higher powers, greater fragmentation reduces the number of NH₂ groups retained which reduces humic acid removal. Power is also linked to the structure of plasma polymerized films. Higher powers result in greater crosslinking of the films which are more stable in solution (Myung and Choi, 2006). Although low powers produce films with higher NH₂ concentrations, less crosslinking occurs therefore they are much less stable in solution (Abbas et al., 2009). The allylamine films produced below 25W may initially have had higher NH₂ concentrations, but these films could have degraded in solution thus reducing the mass of humic acid removed.

![Graph showing humic acid removal vs plasma power](image)

Fig. 1: Humic acid removal at pH 7 after 5 minutes from quartz particles coated with allylamine plasma at varied powers

The second set of plasma polymerization optimization experiments were carried out at 25W for 5 minutes with varied allylamine flow. Flow rates of 4.72 – 10.01 sccm were investigated with maximum humic acid removal at 4.72 sccm, as seen in Figure 2. The decrease in humic acid removal with increasing allylamine flow rates suggests that higher allylamine flow rates produce lower NH₂ concentrations, which agrees with previous research (Ren et al., 2008).
Surface Characterization

Optimal humic acid removal was achieved at a plasma power of 25 W and allylamine flow of ≈ 4.5 sccm therefore surface characterization of time variable samples with these parameters were conducted. From Figure 3a, it can be observed that with an increase polymerization time, the atomic concentrations of carbon and nitrogen increase while oxygen and silicon decrease. Carbon and nitrogen increase with polymerization time as more allylamine fragments are deposited onto the surface. Silicon and oxygen atomic concentrations decrease with polymerization time as the polymer layer gets thicker therefore the signal from the underlying quartz particles, which are made up of silicon and oxygen, are obscured. From the atomic concentrations it can be concluded that increasing the polymerization time beyond 30 minutes does not have a significant effect on surface chemistry. For a polymerization time of 60 minutes, the atomic concentration of oxygen is still approximately 10%. Oxygen is often present in the XPS spectra of plasma polymerized surfaces from oxygen in the air after treatment (Wang et al, 2010).

High resolution C 1s XPS spectra were curve fitted to investigate the effect of polymerization time on surface chemistry. Atomic concentrations of the individual species were determined from these spectra, and are shown in Figure 3b. Plasma polymerization results in an initial decrease in the C-C, C-H, C=O, C=N and COOH peaks. Such behaviour is likely to be due to the addition of allylamine species to the surface thus decreasing the C-C, C=O and COOH signals from the hydrocarbon species on the underlying quartz substrate. The increase in the atomic concentration of C-O, C-N is likely to be due to the addition of C-N species to the surface, however the C-O and C-N peaks are too closely positioned and cannot be distinguished from one another. The gradual increase in the atomic concentration of C-C, C-H with polymerization time is due to the increase in allylamine fragments on the surface thus building up a more substantial polymer layer. Interestingly, a decrease the C-O, C-N peak is observed, when it would be expected to increase due to the addition of additional nitrogen to the surface. The decrease in this peak could possibly be due to a loss in the contribution of the C-O peak from the hydrocarbon species on the underlying quartz substrate which cancels out.
the potential increase in C-N bonds in the polymer layer. Further investigation is required to accurately determine the concentration of C-N species of the polymer layer. XPS analysis of surfaces that unsuccessfully and successfully remove humic acid from solution needs to be conducted to be able to accurately determine the species responsible.

Fig. 3: XPS atomic concentrations from a) survey and b) high resolution C 1s spectra for allylamine coated quartz particles at 25W and 4.5 sccm as a function of polymerization time

Electrokinetic analysis of allylamine plasma polymerized quartz particles was conducted to investigate the effect of polymerization time on the isoelectric point (IEP). The isoelectric point is the pH at which a surface has no charge. Therefore at pH values above the isoelectric point the surface will be negatively charged while below the isoelectric point the surface will be positively charged. Plasma polymerization with allylamine was conducted to produce amine (NH$_2$) groups on the surface. In solution these species will protonate to become NH$_3^+$ species and thus adsorb humic acid via electrostatic attraction. The goal of plasma polymerization with allylamine is to produce the highest isoelectric point so the quartz surface will be positively charged over the greatest pH range. From Figure 4, it can clearly be observed that the changes in surface chemistry with polymerization time significantly impact the IEP values. Uncoated quartz particles have an IEP of 3.1 due to the surface SiO$_2$ groups. Plasma polymerization for 5 minutes increases the IEP to 4.7. Increasing the polymerization time further gradually increases the IEP which reaches a maximum of 7.4 for a polymerization time of 30 minutes. Increasing the polymerization time further to 45 and 60 minutes results in a slight decrease in the IEP, although it is not significant. Such behaviour correlates with the XPS spectra which indicated minimal change in surface chemistry for polymerization times greater than 30 minutes. Increasing polymerization times introduce more NH$_2$ species therefore surface is more positively charged. It is anticipated that a polymerization time of 30 minutes produces the maximum concentration of NH$_2$ species and therefore the highest IEP. Further increases in polymerization time still increase the atomic concentration nitrogen from 9.2% after 30 minutes to 9.9% and 10.8% after 45 and 60 minutes respectively, however there is no accompanying increase in IEP. It is therefore suggested that while longer polymerization times increase the atomic concentration of nitrogen, this nitrogen is incorporated into
the cross linked polymer layer as species other than NH$_2$, thus having minimal effect on IEP.

Fig. 4: Zeta potentials of uncoated and allylamine plasma polymerized quartz particles as a function of pH for varied polymerization times

Humic Acid Removal

Humic acid removal was undertaken at pH values of 5 to 9 to investigate the effect of pH. From Figure 5, it can be observed that an increase in pH decreases the mass of humic acid removed. Negligible humic acid removal was observed for uncoated particles. Previous research has shown that humic acid adsorption is highly pH dependent (Abate and Masini, 2003; Wan Ngah et al., 2008). Humic acid is negatively charged due to the dissociated carboxylic acid groups (COO$^-$) which enables adsorption via electrostatic attraction to the protonated NH$_3^+$ groups of the plasma polymerized allylamine quartz particles at low pH. Therefore increasing the pH of the system will reduce the positive charge of the quartz particle and fewer humic acid molecules will be adsorbed via electrostatic attraction (Wan Ngah et al., 2008). The carboxylic acid groups of humic acid has a pKa of 3 and will therefore remain negatively charged at higher pH values (Tao et al., 2010). Humic acid can however still adsorb at pH values above the IEP, where both humic acid and the surface is negatively charged (Wang and Zhu, 2007). At higher pH values, where electrostatic repulsion occurs, humic acid can adsorb via hydrogen bonding between nitrogen containing functionalities on the surface and phenol groups of humic acid which will be uncharged as it has a pKa of 9 (Tao et al., 2010).

Polymerization time has a significant effect on the pH dependency of humic acid removal. For polymerization times of 5-10 minutes, humic acid removal is highly pH dependent with negligible removal at pH 9. Polymerization times of 20-60 minutes are less pH dependent with more humic acid removed at pH 9. Previous research has shown that lower NH$_2$ concentration result in more pH dependent behaviour (Zhan et al., 2010), and it is expected that this is the case here too. It is suggested that this behaviour is attributed to different surface chemistries influencing the adsorption mechanism. At low pH electrostatic attraction is the dominant adsorption mechanism as the surface will have the greatest positive charge thus the most humic acid is removed. Such behaviour is most apparent for shorter polymerization times where more humic acid is removed at pH 5 than for longer polymerization times. It is postulated that shorter polymerization
times produce surfaces which are more charge dependent, resulting in high humic acid removal at low pH and minimal removal at higher pH. Longer polymerization times may produce surfaces which are less charge dependent, where humic acid adsorption occurs via hydrogen bonding. Less humic acid will be removed at low pH due to less charged species on the surface but a similar mass of humic acid is removed at higher pH values as hydrogen bonding is not pH dependent. More surface characterization is required to ascertain the exact nitrogen species on the surface to allow more accurate conclusions to be made.

**Fig. 5:** Humic acid removal from uncoated and allylamine plasma polymerized quartz particles as a function of pH for varied polymerization times. Initial humic acid concentration 5 mg/L, removal time 5 minutes

Time variable humic acid removal was investigated to determine the length of time required for optimal removal and if polymerization time plays a role. From Figure 6 it can be observed that polymerization time influences humic acid adsorption kinetics. Polymerization times of 5 and 10 minutes had the slowest humic acid adsorption rates which required 20 minutes to reach their maximum. Polymerization times of 20-60 minutes only required 10 minutes to achieve maximum humic acid adsorption. Such behaviour was expected as longer polymerization times produced higher IEP values, and will therefore have a higher concentration of NH$_3^+$ groups on the surface resulting in faster adsorption. After 30 minutes, similar masses of humic acid were adsorbed for polymerization times of 10-45 minutes which were within the range of 2.43 -2.89 mg/L. It has been previously shown that more humic acid is adsorbed for higher NH$_2$ concentrations (Zhan et al., 2010), therefore Figure 6 suggests than polymerization times of 10 – 45 minutes produce similar concentrations of NH$_2$ on the surface.
Fig. 6: Humic acid removal from uncoated and allylamine plasma polymerized quartz particles as a function of time for varied polymerization times. Initial humic acid concentration 5 mg/L, pH 7

The effect of initial humic acid concentration on adsorption kinetics and the total mass adsorbed has also been investigated. Humic acid adsorption for initial concentrations of 2.5, 5 and 10 mg/L for polymerization times of 5 and 20 minutes are shown in Figure 7. An increase in the mass of humic acid adsorbed was observed upon increasing the initial humic acid concentration. Such behaviour is due to a simple mass effect where a greater humic acid concentration in solution forces more humic acid molecules onto the surface (Zhan et al., 2010), which has been observed for other adsorbents (Deng and Bai, 2003) and produces Langmuir shaped adsorption isotherms. For a polymerization time of 20 minutes, the initial humic acid concentration also affects adsorption kinetics where at 5 mg/L maximum adsorption is achieved after 10 minutes while for 10 mg/L, 20 minutes is required to reach equilibrium. Higher initial humic acid concentrations increase the initial rate of humic acid adsorption, especially in the first 5 minutes but longer times are required to reach equilibrium. Such behaviour is due to more humic acid being adsorbed onto the surface which requires longer times to find available adsorption sites as the surface becomes more crowded with adsorbed humic acid (Anirudhan and Ramachandran, 2007).

![Fig. 7: Humic acid removal from allylamine plasma polymerized quartz particles for 5 and 20 minute polymerization times.](image)

**CONCLUSIONS**

Modification of quartz particles via allylamine plasma polymerization has shown to be an effective method for the removal of humic acid. Varying plasma power, monomer flow and polymerization time produced optimal humic acid removal. Humic acid removal was highly pH dependent with greater removal at low pH. Maximum humic acid removal was achieved in 10 – 20 minutes, depending on polymerization time. Further development of the plasma polymerization process and investigation of additional contaminants will aid in the development of a low cost decentralized water treatment system.
ACKNOWLEDGEMENTS

The Government of South Australia is gratefully acknowledged for their funding. Dr. Robert Acres and Dr. Gunther Andersson from the School of Chemical and Physical Sciences, Flinders University are thanked for their assistance with XPS analysis.

REFERENCES

Karyn completed her PhD in 2010 at the Ian Wark Research Institute, University of South Australia with a thesis entitled ‘Optimising the interfacial properties of porous silicon for effective control of molecular and biomolecular interactions’. Karyn then moved to the Mawson Institute at the University of South Australia. Karyn is working on the modification of low cost adsorbents via plasma polymerization for the removal of water contaminants.