Chapter 3
REMOVAL OF ACTINIDES FROM AQUEOUS SOLUTION BY ULTRAFILTRATION (UF) AND DENDRIMER ASSISTED ULTRAFILTRATION (DAUF)

3.1 Introduction

Removal of radionuclides from aqueous waste by membrane separation process is being adopted in nuclear industries. Pressure driven membrane processes including Reverse Osmosis (RO), Nano-filtration (NF), Microfiltration (MF), Ultrafiltration (UF), Polymer Assisted Ultrafiltration (PAUF) etc., offer advantages such as high decontamination factor, large volume reduction and low energy consumption [16,125]. RO membranes are very effective in retaining dissolved inorganic and organic solutes with molar mass below 1000 Da. NF membranes, on the other hand, are very effective in removing hardness (e.g., multivalent cations) and organic solutes with molar mass between 1000–3000 Da. Both RO and NF membranes require high pressure (600-1000 kPa) for operation. In case of UF and MF membranes, relatively low pressure (100–700 kPa) is required for operation. But they are not very effective in removing dissolved organic and inorganic solutes with molar mass below 3000 Da [126]. However, removal was achieved in UF by increasing size of species through sorption/precipitation/complexation.

The size enhancement by using water soluble metal binding polymers coupled with UF (PAUF) for selective concentration and recovery of metal ions from wastewater has been reported [36-51]. Diallo et al [127] have developed a dendrimer-enhanced ultrafiltration (DEUF) process for recovery of metal ions from aqueous solution. Binding of metal ions to the polymer/dendrimer macromolecular ligands allow effective removal of metal ions through ultrafiltration. Dendrimers have much lower intrinsic viscosities than linear polymers with similar molar mass because of their globular shape [121].
They also have a very low tendency to fouling (plugging the pores) in membranes [128]. Hence, DEUF could be operated at lower pressures.

In the present study, removal of U(VI) and Th(IV) from aqueous solution by UF and dendrimer assisted ultrafiltration (DAUF) is described. Experiments were carried out using regenerated cellulose acetate ultrafiltration membrane and poly(amido)amine (PAMAM) dendrimer chelating agent. Effect of U(VI) and Th(IV) speciation on adsorption/mass deposition at membrane surface and binding with PAMAM dendrimer are discussed. The speciation of U(VI) and Th(IV) ions in the presence of PAMAM dendrimer were investigated by potentiometric and fluorescence studies. Effect of pH, ionic strength, PAMAM dendrimer generation and its concentration on removal of U(VI) and Th(IV) metal ions are discussed. Studies on selective and collective removal of U(VI) and Th(IV) metal ions from SNLW by UF and DAUF are presented in this chapter.

3.2 Experiments

3.2.1 Ultrafiltration

The feed solutions of U(VI) and Th(IV) metal ions (5 mg L\(^{-1}\) concentration in 10 mL) were prepared and pH was adjusted from 3 to 9 by adding either 0.1M HNO\(_3\) or 0.1M NaOH. Before ultrafiltration, the solutions were analyzed for corresponding metal ions to find out any precipitation or adsorption on polypropylene centrifuge tube during pH equilibration. Solutions were transferred into Millipore Amicon Ultra-15 centrifugal filter device and centrifuged for 50 minutes at 6000 rpm. After ultrafiltration through regenerated cellulose acetate membrane, the concentrations of metal ion in retentate and permeate were determined by spectrophotometry using Arsenazo(III) complexing agent [115].
The percentage removal (\(\% R\)) was calculated using equation 3.1.

\[
\% R = \left( \frac{C_f - C_p}{C_f} \right) \times 100
\]

(3.1)

where \(C_f\) is the concentration of metal ion in feed and \(C_p\) is the concentration of metal ion in permeate.

The percentage of metal ions in the retentate (\(R_r\)), permeate (\(R_p\)) and percentage total recovery (\(R_t\)) were calculated using equations 3.2 to 3.4.

\[
\% R_r = \left( \frac{W_r \times C_p}{W_o \times C_o} \right) \times 100
\]

(3.2)

\[
\% R_p = \left( \frac{W_f \times C_f}{W_o \times C_o} \right) \times 100
\]

(3.3)

\[
\% R_t = \% R_r + \% R_p
\]

(3.4)

where, \(W_r\) = total weight of retentate before assay, \(W_o\) = weight of feed solution, \(W_f\) = weight of permeate, \(C_r\) = concentration of metal ion in the retentate, \(C_o\) = concentration of metal ion in the feed solution, \(C_f\) = concentration of metal ion in the permeate.

Membrane was equilibrated with 0.01M nitric acid and the percentage mass of metal ion adsorbed/deposited on the membrane was calculated by analyzing equilibrated acidic solution. Membrane was regenerated by equilibrating with 0.01M NaOH followed by rinsing with Millipore water at the end of each experiment.

### 3.2.2 PAMAM assisted ultrafiltration

A feed solution containing 5 mg L\(^{-1}\) of U/Th metal ion and 2 mg L\(^{-1}\) of PAMAMG\(_4\) was prepared in 10 mL. The pH of resultant solution was adjusted by adding either 0.1 M HNO\(_3\) or 0.1 M NaOH and then equilibrated for one hour using an orbital shaker at 200 rpm. The equilibrated solution was transferred into Millipore Amicon
Ultra-15 centrifugal filter device and centrifuged for 50 minutes at 6000 rpm for separation of metal-laden PAMAM from aqueous solution. The concentration of U(VI) and Th(IV) in the retentate and permeate was determined. The percentage removal, retentate and permeate were calculated using equation 3.1-3.3 respectively. The percentage mass deposition on the membrane was calculated by measuring concentration of metal ions in acidic solution equilibrated with membrane surface.

DAUF experiments were carried out with increasing concentration of PAMAMG₄ dendrimer in the range of 0.5 mg L⁻¹ to 5 mg L⁻¹ at pH 6 to optimize the concentration of PAMAMG₄ required for preventing the mass deposition on the membrane surface. Similarly, effect of PAMAM dendrimer generation on retention of U(VI) and Th(IV) in the retentate was studied.

The effect of ionic strength on removal of U(VI) and Th(IV) in both UF and DAUF were investigated with electrolytes such as Ca(NO₃)₂ and NaCl in the concentration range of 0.5 - 2.5 mM.

3.3 Results and Discussion

3.3.1 Removal of U(VI) and Th(IV) by Ultrafiltration

Ultrafiltration of U(VI) and Th(IV) solutions over the pH range 3-9 reveal that these metal ions are retained by membrane at pH > 4 due to adsorption/mass deposition on the membrane surface. The formation of characteristic species due to hydrolysis of UO₂²⁺ and Th⁴⁺ ions over the pH range 3-9 leads to adsorption/mass deposition on membrane surface.

Uranium exists as uranyl ion (UO₂²⁺) under acidic conditions (pH < 3), whilst a range of U(VI) complexes are formed with increasing basicity. Carbonate and hydroxide are two important ligands of uranyl ion complex formation in aqueous solution. Uranium species such as UO₂(OH)⁺, (UO₂)₂(OH)₂²⁺, (UO₂)₃(OH)₅⁺, UO₂(OH)₂, UO₂(CO₃)(OH)₅⁻,
UO$_2$(CO$_3$)$_2^{2-}$ and UO$_2$(CO$_3$)$_3^{4-}$ (Fig. 3.1(a)) are formed in the aqueous solution at pH > 3 [129,130]. Th(IV) mostly exist as Th$^{4+}$ at pH ≤ 2, the species such as Th(OH)$_3^+$, Th(OH)$_2^{2+}$, Th(OH)$_4$ are formed in aqueous solution at pH > 2 (Fig.3.1(b)) [131,132]. The relative abundance of above species is a strong function of pH and concentration of U(VI) and Th(IV) in the solution.

Fig.3.1 Speciation diagram of (a) U(VI) and (b) Th(IV) ions as a function of pH in aqueous solution at atmospheric condition [130,131]

The maximum removal of uranium at pH 5-7 is due to adsorption/mass deposition of uranium species such as (UO$_2$)$_2$(OH)$_2^{2+}$, (UO$_2$)$_3$(OH)$_3^+$ and UO$_2$(OH)$_2$ on the membrane surface. Giblin et al. [133] confirmed that adsorption of hydrolyzed species occurs more easily than UO$_2^{2+}$ ion. This is due to weak attraction of hydrolyzed uranium species with surrounding water molecules, allowing them to interact with the membrane surface. It was observed that 70–90 % of uranium adsorbed on the membrane (Fig.3.2 (a)) and the percentage removal of uranium was found to be 80-97 % (Fig.3.2 (b)) at pH 5-7. The pH is an important parameter that influences both the speciation of metal ions and charge on the membrane surface. At pH > 7, the percentage of uranium deposited on the membrane surface decreased due to the repulsion between the anionic uranium species.
(UO₂(CO₃)²⁻, UO₂(CO₃)(OH)³⁻ and UO₂(CO₃)⁴⁻) and negatively charged membrane surface [23]. Hence, uranium gets concentrated in the retentate and the removal of uranium was observed to be more than 80%. At pH < 5, the percentage uranium removal decreased due to weak interaction of hydrated UO₂²⁺ species with membrane.

![Graph](image-url)

**Fig.3.2** Effect of pH on (a) U(VI) deposition and (b) uranium removal

The effect of pH on removal of thorium by ultra filtration is shown in Fig.3.3 (b). At pH 3, the percentage removal of thorium was observed to be < 20% due to the existence of stable hydrated Th⁴⁺ ions which passes through the membrane. When pH is increased above 3, the percentage removal of thorium increases and attains maximum at about pH 6 (~97 %). Further increase in pH, does not have any significant effect on removal of thorium (Fig 3.3 (b)). The increase in thorium removal at pH > 3 is due to adsorption/deposition of [Thₙ(OH)ₙ]⁶⁺⁻ species on the surface of regenerated cellulose acetate membrane.
3.3.2 PAMAM dendrimer assisted UF removal of U(VI) and Th(IV)

The role of PAMAM dendrimer chelating agent on removal of U(VI) and Th(IV) in ultrafiltration technique was studied. It was observed that both the metal ions get concentrated in the retentate by binding with PAMAM dendrimer and mass deposition on the membrane surface was significantly reduced. The PAMAM dendrimer present in aqueous solution effectively forms complexes with U(VI) and Th(IV) and hence concentrates these metal ions in the retentate.

3.3.3 Effect of pH on binding of U(VI) and Th(IV) with PAMAM dendrimer

PAMAM dendrimer assisted ultrafiltration removal of U(VI) and Th(IV) over the pH range 3-9 are shown in Fig.3.2 (b) and 3.3 (b) respectively. At pH < 4, the removal of U(VI) and Th(IV) was observed to be less than 20 % and 30 % respectively. The pH of aqueous solution plays an important role in both metal ion speciation and charges on chelating agent. The charge on chelating agent depends on pKa of the functional group. The pKa of tertiary and primary amine group of PAMAM dendrimer are in the range of 6.3-6.9 and 9.3-9.8 respectively. Hence, at pH < 4, all amine groups of PAMAM dendrimer are completely protonated and only amide groups are available for coordination. The hydrated UO$_2^{2+}$ and Th$^{4+}$ ions are the predominant species in aqueous
solution at lower pH (pH < 4). Though the large number of amide functional groups is available, strong electrostatic force of attraction is needed to overcome hydration sphere for coordination with metal ions. Hence, the availability of limited number of complexing sites as well as weak electrostatic force of attraction leads to poor binding of UO$_2^{2+}$ and Th$^{4+}$ cations with PAMAM dendrimer at pH < 4. When pH is increased above 4, deprotonation of tertiary and primary amine functional groups lead to increase in electron density. Moreover, the actinides undergo hydrolysis at pH > 3 and the hydrolyzed species are less hydrated than UO$_2^{2+}$ and Th$^{4+}$ ions. At pH > 4, the hydrolyzed species are effectively binding with PAMAM dendrimer leading to increase in percentage removal of U(VI) and Th(IV) metal ions. In aqueous solution, actinides form strong complexes with hard donor ligands such as CO$_3^{2-}$, F$^-$, SO$_4^{2-}$, PO$_4^{3-}$, -COO$^-$ etc. In case of soft donor ligands, hydrolysis of actinides occurs predominantly in aqueous solution [134]. Hydrolysis of UO$_2^{2+}$ and Th$^{4+}$ cations in the presence of PAMAM dendrimer was confirmed from fluorescence and potentiometric studies.

3.3.3.1 Fluorescence study

It is reported that speciation strongly affects lifetime as well as emission spectrum of excited uranium [135]. The fluorescence emission spectrum of uranium solution over the pH range of 2-8 is shown in Fig.3.4. The emission spectrum of U(VI) was measured between 475 and 545 nm with an excitation wavelength of 304 nm. The spectrum displays well-resolved peaks at 493, 514 and 539 nm at pH 2. When pH is raised from 2 to 3.8, there is peak broadening with poor band resolution due to the formation of dimer (UO$_2$)$_2$(OH)$_2$$^{2+}$ species [136]. This reveals that hydrolysis of uranyl ions starts at pH > 3. At pH 4.4, the emission is mostly due to trimer (UO$_2$)$_3$(OH)$_5^+$ species and the emission intensity increases with further increase in pH upto pH 6 without much change in shape of the emission spectrum. The increase in emission intensity is due to the formation of
more and more \((\text{UO}_2)_3(\text{OH})^{5+}\) species in the solution. In the range of pH 6-8, the fluorescence emission intensity further increases due to the formation of \(\text{UO}_2(\text{CO}_3)\) species. Thus, fluorescence emission spectra reveal the formation of various uranium species as a function of solution pH.

**Fig. 3.4** Fluorescence emission spectra of U(VI) solution as a function of pH

**Fig. 3.5** Fluorescence emission spectra of U(VI) as a function of PAMAMG2

The variation in fluorescence emission intensity of uranium as a function of PAMAM dendrimer concentration (1 to 5 \(\mu\)M) is shown in Fig.3.5. It is observed that the emission intensity increases initially up to 3 \(\mu\)M PAMAM dendrimer concentration and then decreases with further increase in PAMAM concentration. The gradual addition of PAMAM increases pH of the uranium solution due to the protonation of amine groups in PAMAM. As discussed earlier, with increase in pH the emission intensity increases due to formation of various hydrolyzed uranium species. Hence, the emission intensity increases with increase in PAMAM concentration up to 3 \(\mu\)M. Further increase in concentration of PAMAM decreases the emission intensity due to binding of hydrolyzed uranium species with PAMAM. The emission spectrum of U(VI) with 3 \(\mu\)M PAMAM (Fig.3.5) closely resemble the emission spectrum of uranium solution at pH 4.4 (Fig.3.4). At pH 4.4, the emission is predominantly from \((\text{UO}_2)_3(\text{OH})^{5+}\), with small contribution
from $\text{(UO}_2\text{)}_2\text{(OH)}_2^{2+}$. The binding of these hydrolyzed uranium species with PAMAM dendrimer at pH > 4.4 causes quenching of fluorescence and hence, the emission intensity decreases with further increase in PAMAM dendrimer (i.e above 3 µM).

3.3.3.2 Potentiometric titration

Potentiometric titration of PAMAMG$_3$ with UO$_2^{2+}$ and Th$^{4+}$ ions are shown in Fig.3.6. The equal molar concentration of PAMAMG$_3$ and metal ion in 20 mL was titrated against potassium hydroxide under argon atmosphere. The potentiometric curve of PAMAMG$_3$ with UO$_2^{2+}$ shows similar behavior of PAMAMG$_3$ upto pH 4. When pH is raised further (> 4), the curve deviates and continued upto the end of titration. This reveals that at pH < 4, uranium mostly exists as uranyl ion (UO$_2^{2+}$). The hydrolysis of UO$_2^{2+}$ ions lead to the formation of UO$_2$$_3$$(\text{OH})_5^+$, (UO$_2$)$_2$(OH)$_2^{2+}$ and UO$_2$(OH)$_2$ species showing deviation in potentiometric curve at pH > 4. In case of thorium, hydrolysis starts at pH 3 and the formation of hydrolyzed species such as Th(\text{OH})$_3^{3+}$, Th(\text{OH})$_2^{2+}$, Th(\text{OH})$_3^{3+}$ and Th(\text{OH})$_4$ lead to deviation in potentiometric curve at pH > 3. Thus, potentiometric titration confirms the hydrolysis of UO$_2^{2+}$ and Th$^{4+}$ cations even in the presence of PAMAM dendrimer.

![Fig.3.6 Potentiometric titration of PAMAMG$_3$ with UO$_2^{2+}$ and Th$^{4+}$ ions](image-url)
3.3.4 Effect of dendrimer concentration and generation

DAUF experiments carried out with various concentration of PAMAM dendrimer showed that binding of both uranium and thorium increases with increasing concentration of PAMAMG₄ dendrimer and reaches more than 95% at about 2.5-3 mg L⁻¹ of PAMAMG₄ dendrimer for an initial concentration of 5 mg L⁻¹ of U(VI) and Th(IV) (Fig. 3.7). Hence, the quantity of PAMAMG₄ dendrimer required for retaining 1g of U(VI)/Th(IV) in the retentate at pH 6 is calculated to be about 0.6 g. The mole ratio of U(VI)/Th(IV) to PAMAMG₄ dendrimer is determined to be about 59 and hence, all subsequent experiments were carried out with a constant mole ratio of 59.

![Fig.3.7](image)

**Fig. 3.7** Effect of PAMAMG₄ concentration on retention and mass deposition of (a) U(VI) and (b) Th(IV)

The number of functional groups and size of PAMAM dendrimer increases as a function of dendrimer generation (Table 2.1). As expected, the concentration of PAMAM dendrimer required for effective binding of U(VI) and Th(IV) metal ions decreases with increase in PAMAM dendrimer generation. It is estimated that about 1.1, 0.6 and 0.45 g of PAMAMG₃, PAMAMG₄ and PAMAMG₅ dendrimers are required for the retention of 1g of U(VI) and Th(IV) in the retentate at pH 6.
3.3.5 Effect of ionic strength on metal ion removal

The effect of Ca(NO$_3$)$_2$ on removal of U(VI) and Th(IV) is shown in Fig.3.8. In both UF and DAUF, the gradual decrease in percentage removal of U(VI) and Th(IV) were observed with increase in concentration of Ca(NO$_3$)$_2$. The decrease in percentage removal of U and Th is due to increase in calcium ion which could compete for the co-ordination with PAMAM dendrimer and adsorption on membrane surface.

![Fig.3.8 Effect of Ca(NO$_3$)$_2$ concentration on removal of (a) U(VI) and (b) Th(IV)](image)

The effect of chloride ion on percentage removal of uranium and thorium is shown in Fig.3.9. In UF, the initial increase in percentage removal of uranium (upto 1 mM NaCl) is due to the formation of species such as UO$_2$Cl$^+$ and UO$_2$(OH)Cl [137,138] followed by their adsorption on the membrane surface. With further increase in concentration of NaCl, the percentage removal of U(VI) is decreased due to increase in ionic strength which reduces the interaction of uranium species with the membrane. In DAUF, the percentage removal of uranium gradually decreases with increase in chloride ion concentration. It is due to the formation of uranium chloride complex as well as increase in ionic strength which suppresses the binding of uranium with PAMAM.
Similarly in the case of thorium, the percentage removal gradually decreased with increase in concentration of NaCl in both UF and DAUF.

![Graph](image)

**Fig.3.9** Effect of NaCl concentration on removal of (a) U(VI) and (b) Th(IV)

### 3.3.6 Removal of Eu(III) and Co(II) metal ions by UF and DAUF

Radioactive waste generated in nuclear industry along with actinides will also contain lanthanides, fission product and activated transition metal ions. Hence, UF and DAUF studies were extended for removal of Eu(III) (representative of lanthanides and surrogate of americium) and Co(II) ions (representative of divalent transition metal ions) from aqueous solution. The removal of Eu(III) and Co(II) metal ions over the pH range 3-11 by UF and DAUF technique are shown in Fig.3.10 (a & b). In the absence of PAMAM dendrimer, the removal of these metal ions by UF is maximum at pH > 7. At pH > 7, Eu(III) and Co(II) cations undergo hydrolysis resulting in formation of hydrolyzed species such as Eu(OH)$^{2+}$, Eu(OH)$_2^+$, Eu(OH)$_3$ and Eu(OH)$_4^-$ [139] and Co(OH)$^+$, Co(OH)$_2$ and CoOOH species [140]. The adsorption/mass deposition of those hydrolyzed species on the membrane surface lead to increase in their removal. The addition of PAMAM dendrimer in aqueous solution effectively binds with hydrolyzed species of Eu(III) and Co(II) metal ions at pH >7 and gets concentrated in the retentate.
The deviation in potentiometric curve for Eu(III) and Co(II) (Fig.3.11) confirms the hydrolysis of Eu(III) and Co(II) metal ions in the presence of PAMAM dendrimer.

![Graph](image1.png)

**Fig.3.10** Effect of pH on removal of (a) Eu(III) and (b) Co(II) by UF and DAUF

![Graph](image2.png)

**Fig.3.11** Potentiometric titration curve of PAMAMG₃ with Eu³⁺ and Co²⁺ metal ions

3.3.7 **Selective and collective removal of U(VI) and Th(IV) metal ions**

For successful remediation of wastewater, the chelating agent should possess the ability to bind selectively with metal ions. Separation of target ions allows for proper waste disposal or recycling. Studies on UF and DAUF of U(VI), Th(IV), Eu(III) and Co(II) as a function of pH depict that metal ions speciation plays an important role on
removal of these metal ions. The presence of PAMAM dendrimer in aqueous solution does not prevent hydrolysis of metal ions. Instead, it effectively binds with hydrolyzed species of metal ions. The above removal studies also reveal that both U(VI) and Th(IV) metal ions are effectively removed at pH 5-7. In case of Eu(III) and Co(II) metal ions, the removal is maximum at pH > 7. Hence, the selective removal of U(VI) and Th(IV) from SNLW at pH 5.5 were investigated. In both UF and DAUF, the removal of U(VI) and Th(IV) are greater than 90 % whereas for other metal ions it is less than 40 % (Table 3.1).

**Table 3.1** Percentage removal of metal ions from SNLW in UF and DAUF at pH 5.5 and 12.5

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<tr>
<th>Metal ions</th>
<th>% Removal in UF pH 5.5</th>
<th>% Removal in UF pH 12.5</th>
<th>% Removal in DAUF pH 5.5</th>
<th>% Removal in DAUF pH 12.5</th>
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Hence, selective removal of U(VI) and Th(IV) from SNLW could be achieved by carrying out UF and DAUF at pH 5.5. Experiments repeated with SNLW at pH 12.5, shows that except alkali and alkaline earth metal ions (Ba, Sr and Cs) the percentage
removal of all other metal ions was found to be > 80 % (Table 3.1). Hence, DAUF technique can be used for decontamination of radioactive waste.

### 3.4 Conclusion

- Removal of U(VI) and Th(IV) ions from aqueous solution by ultrafiltration (UF) and dendrimer assisted ultrafiltration (DAUF) were investigated.

- In UF process, removal of U(VI) and Th(IV) metal ions are observed to be based on adsorption/mass deposition on membrane. Though both U(VI) and Th(IV) ions could be removed in UF by adsorption/mass deposition on the membrane surface, membrane fouling (plugging of membrane pores) occurs on repeated use.

- The pH of the solution plays an important role in removal of both U(VI) and Th(IV) ions. The maximum adsorption of uranium on membrane occurs at pH 5-7 and thorium at pH > 5.

- PAMAM dendrimer effectively binds with U(VI) and Th(IV) in aqueous solution thereby preventing the mass deposition of U(VI) and Th(IV) species on membrane surface. Binding is very effective for both metal ions at pH > 4 and get concentrated in the retentate. The concentration of PAMAM dendrimer required for preventing the mass deposition of metal ions decreases with increase in dendrimer generation.

- PAMAM dendrimer effectively forms complex with hydrolyzed U(VI) and Th(IV) species in aqueous solution. The hydrolysis of U(VI) and Th(IV) ions in presence of PAMAM dendrimer was confirmed from fluorimetric and potentiometric studies.

- Studies on effect of ionic strength revealed that removal of Th(IV) and U(VI) metal ions decreases with increasing concentration of electrolytes (NaCl and Ca(NO\(_3\)_2) in both UF and DAUF. However, removal of Th(IV) and U(VI) in DAUF is more effective than UF in the presence of electrolytes.
Selective and collective separation of Th(IV) and U(VI) was achieved by carrying out UF and DAUF at pH 5.5 and 12.5. The binding of metal ion with PAMAM is very less at acidic pH (pH < 3). Hence, the loaded metal ions can be recovered and regeneration of the PAMAM chelating agent can also be achieved by reducing the pH of aqueous solution.