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A Short Review of CO_2 Responsive Polymeric Adsorbents and Membranes for Water Quality Control

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Abstract. Separation processes using adsorbents and membranes can be regulated by incorporating stimuli-responsive materials. A wide range of polymers demonstrates changes in characteristics and performance reacted to an external stimulus including pH, temperature, gases, or pressure. Among the stimuli, CO_2 is a nontoxic and abundant stimulus that can also be easily added or removed from the separation processes. In this paper, the progress of CO_2 responsive adsorbents and membranes was studied. The tertiary amine or amidine groups of the CO_2-responsive polymers could be easily protonated by CO_2 bubbling, causing characteristic changes to regulate the separation. The synthesis, characteristics, and separation performance were examined. Poly(diethyl-amino-ethyl methacrylate) (PDEAEMA) modified microparticles were used to adsorb protein, but protein recovery remained unclear. The grafting of PDEAAMA and poly(2-(di-methylamino)ethyl methacrylate) (PDMAEMA) on microparticles allowed the adsorption of heavy metals, but higher recovery was attained by PDMAEMA modified microparticles under CO_2 bubbling. The CO_2-responsive polymeric microparticles were successfully applied in forward osmosis, producing water from salt solution without high temperature or pressure. PDEAEMA modified membranes were extensively studied in the separation of oil and water mixture due to their switchable surface hydrophilicity. PDEAEMA and PDMAEMA modified membranes were also tested in nanofiltration since they exhibited changes in pore size and zeta potential to control pollutant rejection. Nevertheless, CO_2-responsive membranes could be cleaned under CO_2/N_2 bubbling.

INTRODUCTION TO CO_2 RESPONSIVE MATERIALS

Responsive materials can attain reversible or irreversible changes based on specific stimulation. The changes include molecular structure, wettability, miscibility, and ionic strength and more. They can be stimulated by more than one stimulus such as light, voltage, frequency, mechanical stress, pH, temperature, and chemical depending on the functional groups. Compared to other stimuli of responsive materials and systems, CO_2 is of great interest as it is safe and sustainable. Moreover, the functional groups such as amines and carboxylate react to CO_2 are generally cheaper than voltage- or light-responsive functional groups. Apart from being less toxic, it is more compatible with health and the environment than many acids and bases used in redox-responsive materials [1].

Yang et al. [2] studied the past research works on CO_2-responsive materials for separation purposes. The CO_2-responsive materials cover solvent, surfactant, ionic liquid, water additive and polymers. The CO_2-responsive solvents with amines, secondary amines or amidines groups can adjust their miscibility in water, applicable for extraction and demulsification purposes. The anionic surfactants with long phenolates and carboxylates turn to be inactive in the presence of CO_2. In contrast, the cationic surfactants with long nitrogen groups (amidines, guanidines, tertiary amines, or imidazoles) turn to be active in the presence of CO_2 for leaching and demulsification. The CO_2-

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responsive ionic liquids with amidine/alcohol, guanidine/alcohol, amidine/amine, alkanolguanidine, secondary amine, and primary amine components change to be highly polar in the presence of CO_2 for extraction and carbon capture. Polyamines are responsive water additives useful in demulsification since their ionic strength increases with CO_2 bubbling. Monomers such as diethyl-amino-ethyl methacrylate (DEAEMA) and 2-(di-methylamino)ethyl methacrylate (DMAEMA) are useful to develop CO_2-responsive polymers, but their applications have not been extensively discussed.

Hu et al. [3] described the synthesis of different types of responsive polymers in a review paper. The responsive polymers are commonly produced through the polymerization of unsaturated vinyl or acryl-modified responsive moieties. The controlled free-radical polymerization, including atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization, and nitroxide mediated radical polymerization (NMP), and open-loop translocation polymerization (ROMP) are the common approaches to construct linear and nonlinear polymers. The preparation of CO_2 responsive polymers is briefly discussed besides the thermoresponsive, pH-responsive, photoresponsive, enzyme responsive, electro responsive polymers. Monomers with tertiary amine groups are used to produce poly(dimethylaminoethyl methacrylate) (PDMAEMA) and poly(N,N-diethylaminoethyl methacrylate) (PDEAEMA) with CO_2 responsiveness.

Bratek-Skicki [4] explained different stimuli-responsive mechanisms of responsive polymers in a recent review article. The solubility of temperature-responsive polymers changes between the lower and upper dissolution temperatures because of the formation and rupture of hydrogen bonding. The electrostatic repulsion and attraction of pH-responsive polymers brushes can be altered by altering the ionic strength of the solution. The tertiary amine or amidine groups of the CO_2-responsive polymers could be easily protonated by CO_2 bubbling, causing characteristic changes to regulate the separation as shown in Fig 1. They further discussed different geometries of responsive polymers, including mixed polymer brushes, layer-by-layer coating, and core-shell particles that are useful in developing self-healing materials, sensors, actuators, and drug delivery systems. CO_2 sensors were developed from PDMAEMA and PDEAEMA [5]. In addition, polymers with CO_2-responsive groups such as imidazole, guanidine, and amidine have been investigated for sensing purposes [6–9].

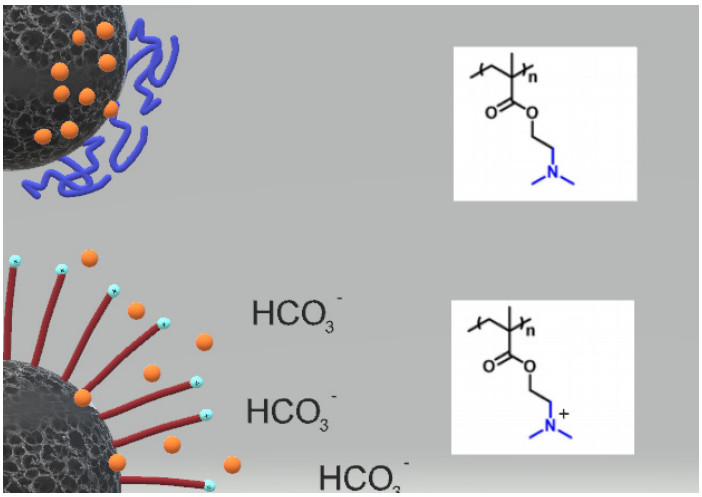

FIGURE 1. Protonation of PDEAEMA for ion adsorption and desorption.

Shu et al. [10] reviewed the responsive polymers used in biosensing. The responsive polymers can seize the analytes, deactivate the functional compounds such as fluorophores, transform the analyte signal into a readable signal. Etalon, fluorescent and electrochemical sensors developed from responsive polymers for biological purposes were studied. In response to different stimulation, the responsive polymers between 2 Au layers in etalon sensors react to cause optical changes for the detection of glucose, protein, DNA, antigen, and hydrogen peroxide. The responsive polymers swell or collapse, causing the alteration of Au layer spacing and reflectance of different wavelengths of light. Responsive polymers were also coated on the electrodes of electrochemical sensors, which can generate current, potential or impedance changes due to the variation of analyte concentration. The responsive polymers were chemically altered to enhance the detection of cytokine, dopamine, and glucose. Fluorophores were immobilized in responsive polymers to form fluorescence sensors with improved quenching and biocompatibility in

the detection of dopamine, glucose, and ions. Similarly, the responsive polymers were incorporated with a wide range of nanoparticles for magnetic resonance imaging, fluorescent imaging, and photoacoustic imaging.

Jiang et al. [11] detailed the synthesis of CO_2-responsive polymers with variation in chain functionality, composition, and topology or incorporation of inorganic nanoparticles. Guanide, amidine, amine, carboxyl groups were used to functionalize the polymers through polymerization or post modification. Co-polymerization allowed the design of the sequential structure in random, alternating, block, gradient, and statistical copolymers, resulting in multiple functionalities and characteristics. Besides linear structure, the CO_2-responsive polymers can be constructed with grafting, hyperbranching, networking, and more. The variation of chain topology can result in different physical and chemical characteristics. Inorganic nanoparticles with optical, electrical, magnetic, catalytic properties can be further used to produce CO_2-responsive polymer-based nanohybrids for different applications. In addition to catalysis and emulsification, the application of CO_2-responsive polymers in separation was briefly discussed. Polyethylenimine (PEI) was mainly used in CO_2 absorption and extraction. The CO_2-responsive polymers were also used to produce adsorbents to remove heavy metal, dye, and oil. The CO_2-responsive membranes were developed for oil emulsion filtration or CO_2 separation. However, the synthesis and characteristics of these CO_2-responsive absorbents, adsorbents, and membranes were not compared in detail.

In this short review, the CO2-responsive adsorbents and membranes developed to regulate pollutant removal from water were examined. The regulation can be subjected to a structural, morphological, or molecular conformation shift in response to external stimuli. This review further focuses on fabrication materials and methods, characteristics, performance, and principles. More importantly, they were compared to identify the gap for engineering applications.

POLYMERIC PARTICLES WITH CO_2 RESPONSIVE PROPERTIES FOR WATER POLLUTANT ADSORPTION

CO_2 responsive polymers were extensively used to construct adsorbents that could adsorb and then release different pollutants. The pollutant release enables the reuse of adsorbents and the recovery of valuable pollutants. As summarized in Table 1, CO_2-responsive polymeric adsorbents had been tested in the adsorption of protein and heavy metals besides showing positive results in forward osmosis. Guo et al. [12] synthesized Fe_3O_4 nanoparticles through the decomposition of $Fe(acec)_3$ at high temperature and then mixed the nanoparticles with silica sol-gel containing fluorescein isothiocyanate dye to form the silica core for poly(N,N-diethylaminoethylmethacrylate) (PDEAEMA) modification. The modified silica adsorbent with magnetic properties adsorbed bovine serum albumin (BSA) up to 40 mg/g at pH 7 as the PDEAEMA collapsed. The CO_2 bubbles induced the formation of charged ammonium bicarbonate on the tertiary amine groups in PDEAEMA, converting polymer brush on silica adsorbent from hydrophobic to hydrophilic for protein desorption. Bai et al. [13] grafted poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) on polyhedral oligomeric silsesquioxane (POSS) with a nanocage for the adsorption of Cu^{2+} ions. An adsorption capacity of 145 mg/g was attained in 2 min at pH 5.5. At pH 5.5, amino pendant groups were protonated for metal ion adsorption. CO_2 bubbles triggered the desorption of Cu^{2+} ions as PDMAEMA brushes were protonated to dissociate from the polymer-metal complex.

The CO_2-responsive polymers were not only grafted on inorganic or hybrid cores; they were also grafted on other biopolymers to form CO_2-responsive adsorbents. Madill et al. [16] grafted PDEAEMA on chitosan after functionalization with glycidyl metacrylate (GMA) to create a CO_2-responsive adsorbent to remove Ni^{2+} ions. The polymer reduced the adsorption capacity of chitosan compared to the unmodified chitosan but allowed the desorption of Ni^{2+} ions after CO_2 protonation. The CO_2 regeneration of modified adsorbent for 1 h could raise the Ni(II) adsorption capacity near 100 mg/g, up to 241% enhancement compared to chitosan. Abousalman-Rezvani et al. [17] prepared copolymers and cellulose nanocrystals (CNC)-grafted copolymers from DMAEMA and coumarin monomers through reversible addition-fragmentation chain transfer (RAFT) polymerization. Nitrate ions within the concentration range of 300 – 600 ppm were adsorbed faster into free copolymers than CNC grafted copolymers. Because of the low PDMAEMA amount, the CNC-grafted copolymers attained lower adsorption than the free copolymers. The copolymers showed CO_2 responsive adsorption and desorption because of the protonation and deprotonation of the tertiary amine groups. The positively charged chains of the adsorbent absorbed the negative nitrate ions effectively. The crosslinking of coumarin in copolymer adsorbent under UV enhanced the nitrate adsorption near 350 ppm due to the increment of surface area, but less than 50% of nitrate ions were desorbed after N_2 purging. Eskandari et al. [14] grafted copolymers of *N*-isopropylacrylamide (NIPAAm) and (2-dimethylaminoethyl) methacrylate (DMAEMA) on cellulose nanocrystal (CNC) to form temperature and CO_2-

responsive adsorbent for nitrate ions. This adsorbent showed changes in turbidity, hydrodynamic diameter, and zeta potential due to the variation in temperature and the presence of CO_2. The adsorption capacity of CNC grafted copolymers (340 mg/g) was slightly lower than the free copolymers (420 mg/g) but more responsive to temperature changes. CO_2 induced the protonation of PDMAEMA and improved the adsorption capacity more significantly than temperature. More importantly, the adsorbent released more than 80% of adsorbed ions under N_2 purging.

TABLE 1. CO_2-responsive adsorbents for water quality control

Adsorbent	Absorbate	Adsorption capacity and responsive changes	Reference
PDEAEMA grafted on Fe_3O_4 nanoparticles with silica and dye	BSA	40 mg/g dropped after CO_2 bubbling	[12]
PDMAEMA grafted on POSS	Cu^{2+},Cd^{2+},Zn^{2+},Pb^{2+},Cr^{3+}, Ni^{2+}	110.4, 145, 75.7, 555, 86.8, 56.9 mg/g; >97.1% desorption after CO_2 bubbling	[13]
PDEAEMA grafted on chitosan	Ni^{2+} ions	~ 100 mg/g; 61% desorption after CO_2 bubbling	[14]
PDMAEMA and coumarin grafted CNC	NO_3 ions	~ 350 ppm adsorbed under CO_2 bubbling and UV irradiation, ~ 200 ppm desorbed under N_2 bubbling and UV irradiation using 0.01 g adsorbent	[15]
*PDMAEMA and P*NIPAAm grafted on CNC	NO_3 ions	400 mg/g (60 °C) and 420 mg/g (37 °C) under CO_2 bubbling, < 25 mg/g under N_2 bubbling	[16]
DEAEMA-PEGDA microgels	H_2O	~ 60 LMH of water flux under CO_2 bubbling, 55% recovery under under N_2 bubbling	[17]
PDMAEMA grafted on polystyrene	BSA	5190 mg/g	[18]
PHEA-HIS microparticles	Cu^{2+} and Ni^{2+} ions	42.35 mg Cu(II) /g and 78 mg Ni(II)/g; dropped to < 20 mg Cu (II)/g and < 40 mg Ni(II)/g with pH changed from pH 5 to pH 3; CO_2 responsive study focus on swelling ratio changes only	[20]
g-PDMAAm microparticles	H_2O	~ 44 LMH of water flux under CO_2 bubbling at 60 °C, 94% recovery under under N_2 bubbling	[21]

Moreover, CO_2-responsive monomers could be polymerized by themselves to form useful adsorbents. Rabiee et al. [18] produced PDEAEMA microgels through surfactant-free emulsion polymerization and PDMAEMA microgels using dispersion polymerization. Both microparticles were used to recover water by microgel deswelling. Three crosslinkers incorporated into DEAEMA microparticles are N, N′-methylene-bisacrylamide (BIS), poly(ethylene glycol diacrylate) (PEGDA), and ethylene glycol dimethacrylate (EGDMA). DMAEMA microparticles with 1 wt% PEGDA were also synthesized to analyze the effects of cationic monomers on total forward osmosis throughput. To ensure the full protonation of microgels, CO_2 was purged for approximately 1 h. DEAEMA microparticles with 1 wt% PEGDA achieved the maximum water flux. However, the presence of crosslinkers in microgels only created a slight impact on water recovery. Since pK_a of PDEAEMA is 7.4 and pK_a of PDMAEMA is 7, the microparticles became hydrophilic for water adsorption after protonation with CO_2. The water

flux of DEAEMA microparticles (56 L/m^2·h) was higher than the DMAEMA microgels (41 litre/m^2/h) due to the difference in dissociation. Rui et al. [19] coated PDMAEMA on polystyrene through photoemulsion polymerization for the adsorption of BSA up to 5190 mg/g. The adsorption could be controlled using CO_2 and N_2 besides pH, ionic strength and temperature. The expansion and relaxation of PDMAEMA caused the responsive adsorption and desorption of BSA without causing changes in BSA properties. The hydrodynamic diameter of PDMAEMA coated polystyrene microparticles could change significantly from 112.8 nm to 236.7 nm by reducing solution pH from 9.7 to 6.0.

Besides PDEAEMA and PDMAEMA, more CO_2-responsive polymers were introduced in the synthesis of adsorbents through co-polymerization or crosslinking. Mu et al. [20] fabricated CO_2-responsive interpenetrating network microspheres from polyacrylamide (PAM)/polydimethyl aminopropyl methacrylamide) (PDMAPMA) trough inverse seed suspension polymerization. The particle size increased from 312 to 432 μm after CO_2 purging and pH adjustment from 8.8 to 4.9 simultaneously, causing the protonation degree to increase from 7.3% to 99.8%. Following N_2 gas bubbling for 1 h, the particle size returned to 315 μm, and the solution pH adjusted back to 8.7. The swelling and shrinkage of the IPN-particles also affected the changes in hydrophilicity caused by the protonation and deprotonation of the PDMAPMAe. The final volume expansion of the IPN particles is facilitated by the water inclination to enter the protonated PDMAPMA·H^+ network during distilled water swelling and the CO_2-induced expansion process. Tran et al. [21] produced polyaspartamide hydrogel with histamine and hydroxyethyl pendent groups (PHEA-HIS) through crosslinking with hexamethylene diisocyanate. The solubility of PHEA-HIS polymer in a mixture of IPA and water was reduced when CO_2 was bubbled into the solvent. HIS groups were protonated to reduce polymer solubility in the presence of CO_2 but deprotonated to increase polymer solubility when N_2 gas was introduced. The swelling ratio of PHEA-HIS hydrogel could be similarly switched as low as 15% in CO_2 but as high as 50% in the presence of N_2. The swelling ratio was reduced by more than 40% when solution pH was adjusted from 11 to 3. The adsorption of Cu^{2+} and Ni^{2+} ions was adjustable by changing solution pH. The adsorption capacity dropped at low pH due to competition between metal ions and H^+ for adsorption sites. Adsorption capacity raised from 6 mg Cu(II)/g to 42.35 mg Cu(II) /g for Cu(II) and from 27 mg Ni(II)/g to 78 mg Ni(II)/g when pH was adjusted from pH 3 to pH 5. Ellis et al. [15] synthesized poly(*N,N*-dimethylallylamine) (g-PDMAAm) hydrogel via one-pot methylation and crosslinking of poly(allyamine) (PAAm). The methylation was achieved with an Eschweiler-Clarke reaction with formaldehyde and formic acid. After crosslinking, the g-PDMAAm hydrogel exhibited both temperature and CO_2 responsiveness. The g-PDMAAm hydrogel exhibited a swelling ratio of 74 $\pm$ 7 in the water at 20 °C because of the low protonation degree of the amine groups. At 60 °C, the g-PDMAAm hydrogel only swelled in the water with a swelling degree of 0.04 $\pm$ 0.01 because the g-PDMAAm hydrogel reduced interaction with water above its volume phase transition temperature. The swelling degree of g-PDMAAm hydrogel increased to 198.5 $\pm$ 0.5 in carbonated water at 20 °C because of amine protonation that resulted in hydrophilic gel with high osmotic pressure. The swelling degree of g-PDMAAm hydrogel reduced to 65 $\pm$ 8 when it was deswollen on a glass frit under air at 20 °C. Hence, the g-PDMAAm hydrogel could be used to absorb water as much as 2000% of its weight in the carbonated water and release water at 20 °C for achieving forward osmosis

POLYMERIC MEMBRANE WITH CO_2 RESPONSIVE PROPERTIES FOR WATER FILTRATION

In addition to CO_2-responsive adsorbents, pollutants in water such as oil could be removed using CO_2-responsive membranes with switchable surface properties through size exclusion, as summarized in Table 2. Che at al. [22] produced CO_2 responsive membrane through electrospinning of PMMA-co-PDEAEMA copolymer prepared from radical co-polymerization. At a polymer concentration of 25 wt%, nanofibers with an average diameter around 700 nm formed near superhydrophobic membrane with a thickness of about 100 μm and water contactct angle (WCA) near to 140 ° in 10 hr of spinning duration. By introducing CO_2 bubbles, the WCA dropped to 36 ° in 300 s. The under-water oil contact angle increased from 38 ° to 150 °. CO_2 and N_2 stimulation could switch the permeation of oil and water through the membrane. Water in emulsion could permeate through CO_2 stimulated membrane while oil in emulsion could permeate through N_2 stimulated membrane. Dehkordi et al. [23] also synthesized a porous membrane by electrospinning PMMA-*co*-PDEAEMA matrix, but doped the membrane with hydroxyl functionalized spiropyran. The bubbling of CO_2 switched the hydrophobic membrane to hydrophilic due to the protonation of tertiary amines. Meanwhile, the electric potential switched back membrane properties via deprotonation into PDEAEMA$H^+HCO_3^-$. These changes could be observed by colour changes from white to pink as spiropyran was

isomerized into merocyanine. The polarity changes permitted the permeation of water but not oil. Hence, the electrospun membranes could be applied in oil/water separation. For the same filtration purpose, Huang et al. [24] grafted PDEAEMA brushes on anodic aluminium oxide (AAO) membrane through surface-initiated reversible addition-fragmentation chain-transfer polymerization. Upon CO_2 purging, the water contact angle of the modified AAO decreased drastically from 140.38 ± 0.88 ° to 12.80 ±3.77 °, indicating polymer brush hydration. The initial water contact angle was recovered after exposure to N_2 gas for 10 min, indicating that PDEAEMA deprotonation caused water loss at the collapsed state. Furthermore, the permeate water flux decreased sharply from a higher range of 462-510 L m^{-2} h^{-1} to a lower range of 187-69 L m^{-2} h^{-1} due to CO_2 stimulation. N_2 purging caused the PDEAEMA brushes to collapse and the permeability to increase. The modified AAO membrane showed reversible WCA and permeability when CO_2 and N_2 bubbling were alternated. Moreover, the modified AAO membrane could be used to filter toluene-in-water and water-in-toluene emulsions.

TABLE 2. CO_2-responsive membranes for filtration

Membranes	Switchable properties	Regulated permeation	Reference
PMMA-co-PDEAEMA	140 ° before CO_2 bubbling; 36 ° after CO_2 bubbling	Oil permeation ~ 16000 LMH; Water permeation ~ 8000 LMH	[22]
PMMA-*co*-PDEAEMA with spiropyran functionalization	138 ° before CO_2 bubbling; <5 ° after CO_2 bubbling	Water permeate flux ~ 0 LMH; ~ 1.59 LMH with *n*-hexane rejection of 87%	[23]
PDEAEMA grafted anodic aluminum oxide	140.38 ± 0.88 ° before CO_2 bubbling; 12.80 ±3.77 ° after CO_2 bubbling	Water permeate flux of 187-69 LMH, Water-in-toluene permeate flux 300 LMH; Water permeate flux of 462-510 LMH, Toluene-in-water permeate flux of 100 LMH	[24]
PDEAEMA and PDA modified PVDF)	Mean pore size ~ 84 nm, Porosity ~ 80% before CO_2 bubbling; ~ 79 nm, 88% after CO_2 bubbling	Water permeate flux ~ 1500 LMH; ~ 500 LMH with 90% rejection of Au nanoparticles	[25]
Py-PDEAEMA grafted GO	-	Water permeate flux ~ 15 LMH before CO_2 bubbling; ~ 50 LMH with >95% rejection of Rhodamine B and methyl orange after CO_2 bubbling	[26]
GO/Py-PDMAEMA	Zeta potential -18.5 mV before CO_2 bubbling; +17 mV after CO_2 bubbling,	Water permeability maintained at 62.61 $L{\cdot}m^{-2}{\cdot}h^{-1}{\cdot}MPa^{-1}$ with $MgCl_2$ rejection ~ 75%, Na_2SO_4 rejection ~ 15%; $MgCl_2$ rejection ~ 40%, Na_2SO4 rejection ~ 45%	[27]
PAN/PAN-*co*-PDEAEMA)	-	Water permeate flux ~ 260 LMH before CO_2 bubbling; ~ 240 LMH with 90% flux recovery under CO_2/N_2 cleaning	[28]

Unlike surface hydrophilicity, the changes in pore size and zeta potential are beneficial to control the permeation of nanoparticles and salts. Dong et al. [25] coated polydopamine on polyvinylidene fluoride porous membrane for the Michael addition reaction between PDEAEMA and polydopamine thiol groups. Water permeability was increased by the CO_2 stimulation but reduced by Ar stimulation. The membrane pore size dropped with increasing CO_2 bubbling duration, but membrane porosity showed the opposite trend. The tertiary amine groups of PDEAEMA were protonated by CO_2, resulting in polymer conformation for pore size shrinkage. Hence, the rejection of Au

nanoparticles was increased beyond 90%. Dong et al. [26] integrated graphene oxide (GO) with poly(N, N-diethylaminoethyl methacrylate) bearing a pyrene end group (Py-PDEAEMA) to produce a smart nanofiltration membrane by the simple vacuum filtration process. The mean thickness of Py-PDEAEMA/GO nanofiltration membrane is 60 nm. The membrane fabricated with a mass ratio of Py-PDEAEMA to GO at 6 attained the highest water permeability (53.6 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$). However, the water permeability reduced by 66.0% after 30 min of CO_2 gas bubbling due to pore size reduction. The pore size reduction enabled the membrane to reject salts such as $MgCl_2$. Ar bubbling caused the recovery of the water permeability because the membrane pores were enlarged. Yin et al. [27] prepared GO/Py-PDMAEMA membrane with the mass ratio of 3:1 by vacuum filtration. The membrane showed switchable zeta potential, changing between 17 mV and -18.5 mV under the stimulation of CO_2 and N_2, respectively. The water permeance of the membrane with an average thickness of about 155 nm remained constant at 62.61 $L \cdot m^{-2} \cdot h^{-1} \cdot MPa^{-1}$ even under the alternate simulation of CO_2 and Ar. This is because that the hydrophilicity of PDMAEMA chains remained in the presence of CO_2. Besides that, the rejection of negatively charged Congo Red and the positively charged Methylene blue was maintained above 95% even by introducing CO_2 or Ar. The membrane only showed responsive rejection of salts such as $MgCl_2$ and Na_2SO_4.

More importantly, membrane cleaning could be achieved without using harsh chemicals. Zhang et al. [28] synthesized the CO_2 responsive polyacrylonitrile (PAN) membrane by blending polyacrylonitrile-*co*-poly(2-diethylaminoethyl-methacrylate) (PAN-*co*-PDEAEMA) copolymer resulted from free-radical suspension polymerization into the dope polymer solution before phase inversion. PAN/PAN-*co*-PDEAEMA membrane could be protonated with CO_2 bubbling, stretching the copolymer to close the pores. Hence, the permeate water flux reduced under the CO_2 stimulation but increased under the N_2 treatment. Besides alkaline-acid cleaning, the PAN/PAN-*co*-PDEAEMA membrane fouled by BSA could be cleaned under CO_2/N_2 bubbling as illustrated in Fig. 2. Although protein deposition caused a sudden drop in the permeate flux, the permeate flux could be restored by alternative gas bubbling. A cleaning efficiency up to 90% was attained without using harmful chemicals.

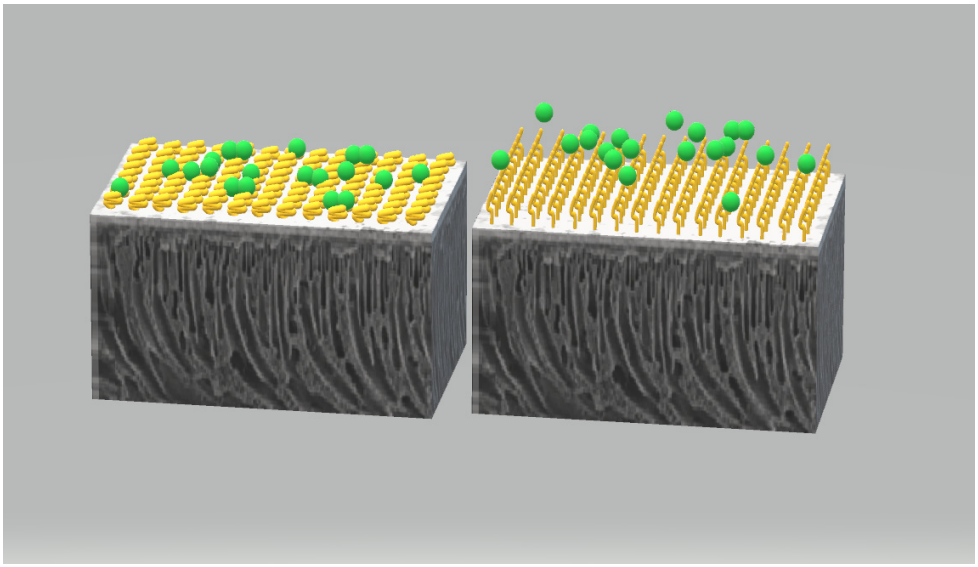

FIGURE 2. Protonation of CO_2-responsive polymeric membrane for foulant removal in CO_2/N_2 cleaning.

CONCLUSION

The pH responsive polymers such as PDEAEMA and PDMAEMA have been widely used to develop CO_2-responsive adsorbents and membranes. These polymers could be protonated by carbonic acid to achieves changes in zeta potential, hydrodynamic size, surface hydrophilicity, and pore size that are vital factors in the regulation of adsorption and permeation. Nevertheless, their practical use in water pollution control should be mainly considered before extending the studies summarized in this work.

Although both PDEAEMA and PDMAEMA grafting on microparticles allow the adsorption of BSA, the desorption of protein for recovery had not been reported. PDMAEMA and PDEAEMA grafting attained the similar

adsorption of Ni^{2+} ions, but PDMAEMA allowed near full recovery of Ni^{2+} ions under CO_2 stimulation. The CO_2-responsive polymeric adsorbents showed encouraging results in forward osmosis as the pure water was successfully recovered from salt solution without the requirement of high temperature or pressure. More engineering studies, including techno-economic evaluation, should be conducted to understand the full potential of CO_2-responsive polymeric microparticles in forward osmosis.

PDEAEMA modified membranes were extensively studied in the separation of oil and water mixture due to their switchable surface hydrophilicity. In addition, PDEAEMA and PDMAEMA modified membranes were further tested in nanofiltration to separate nanoparticles, dye, and salts. These membranes exhibited not only changes in pore size but also zeta potential that resulted in switchable pollutant rejection. However, CO_2-responsive membranes were more practically developed for cleaning purposes. Under CO_2/N_2 cleaning, protein fouled on PDEAEMA modified membranes could be removed. More membrane cleaning using CO_2 should be conducted to confirm the efficiency of eliminating other foulants.

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