



Application of polyelectrolytes for contaminant removal and recovery during water and wastewater treatment: A critical review

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ABSTRACT

The combination of polymeric characteristics and electrolyte behaviour endow aqueous polyelectrolytes with a strong potential for use in water and wastewater treatment. A correct and effective application of polyelectrolytes or polyelectrolyte complexes can remove different types of contaminants from aqueous solutions efficiently. Polyelectrolytes can be utilized directly as a water treatment material or indirectly as additives or modifiers to improve the effectiveness of existing water treatment processes. Previous reviews on this general research topic focused mainly on the function of polyelectrolytes in coagulation and flocculation processes, but they neglected other potential functions during water treatment processes. The current review introduces the typical polyelectrolytes utilized in water processing, including their properties and their interaction with contaminant species in water, and then summarizes and reviews the various unique applications of polyelectrolytes in water processing, including the polyelectrolyte enhanced ultrafiltration (PEUF) process, the application of polyelectrolytes to efficiently functionalize membranes and adsorbents, and the formation of polyelectrolyte-surfactant aggregates (PSAs) to recover metallic species from water. Finally, the challenges and opportunities for future investigation of the application of polyelectrolytes in water processing and treatment are discussed.

1. Introduction

Polyelectrolytes are a type of water-soluble polymer with a multitude of ionizable groups. The combination of their polymeric characteristics and ionizable behaviour give polyelectrolytes various useful properties, and thus they offer a broad spectrum of applications in a wide variety of fields, including but not limited to pharmaceuticals, biomedicine, medicine, petroleum engineering, cosmetics, the food and paper industries, water treatment, and so on. [1–5] The utilization of polyelectrolytes in water process engineering has a long history [6,7]. Polyelectrolytes were introduced into water and wastewater treatment due to their potential as functional materials to remove contaminants [8] or to recover useful resources [9] from aqueous feed streams, and to enhance the technical efficiency of treatment [10]. However, until now, most review articles have focused almost exclusively on polyelectrolyte application to coagulation and flocculation processes for potable water

purification [11–14], as well as the dewatering of wastewater sludge [11,15]. Yet a direct application of polyelectrolytes or polyelectrolyte complexes can remove contaminants from different types of water or wastewater efficiently, while overcoming the shortfalls of inorganic coagulants, such as requiring a large dosage of coagulants and generating a large volume of sludge. Nevertheless, reviews highlighting other functions or applications of polyelectrolytes during water and wastewater treatment are scarce. This review intends to redress this imbalance. First, it introduces the polyelectrolytes generally used for water and wastewater treatment, summarizing their typical useful properties in water engineering processes for those polyelectrolytes which are commonly utilized. Next, the different applications of polyelectrolytes in various forms during water and wastewater treatment are reviewed, namely the polyelectrolyte enhanced ultrafiltration (PEUF) process, the application of polyelectrolytes to efficiently and functionally modify membrane surfaces to improve the separation process, the modification

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of adsorbents by polyelectrolytes to enhance contaminant elimination from water, and the formation of polyelectrolyte-surfactant complexes to recover metals from water. Finally, the challenges and opportunities for future investigation of the application of polyelectrolytes in water processing and treatment are discussed.

2. Polyelectrolytes utilized in water processing

2.1. Properties of typical polyelectrolytes

Polyelectrolytes can be defined as any water-soluble polymeric materials or macromolecules with repeating units or groups for which the latter carry either positively or negatively charged ionizable groups. The charge on the repeating units is neutralized by oppositely charged counter-ions in solution (e.g., Cl^- , Na^+ , or H^+) to maintain electro-neutrality of the overall molecule, i.e., an uncharged state. When dissolved in water or other polar solvents, polyelectrolytes dissociate as highly charged polymeric molecular chains of those repeated units; the smaller counterions are released as free ions into the solution either partially or completely, depending on the degree of dissociation. The dissociation can in turn be influenced by solution conditions, such as the pH.

Polyelectrolytes show a range of physical, chemical and mechanical properties due to differences in chemical structure, molecular weight (MW), functional groups, charge density (CD), solubility, and so on. [14] For both direct and indirect application in water and wastewater treatment, familiarity with the properties of the polyelectrolytes is critical, as the treatment efficiency associated with their use can be affected by the type, properties and dosage. Depending on the arrangement of repeated polyelectrolyte units (i.e., the monomers), possible configurations include linear, branched and cross-linked structures [16].

The molecular weight of polyelectrolytes ranges from a few thousand to tens of millions of Daltons (Da), with low, medium and high MWs in the range $< 10^5$, 10^5 – 10^6 , and $> 10^6$ Da, respectively. MW is a key factor when intramolecular processes occur via the polymeric bridging effect, especially during the coagulation process. Basically, linear polyelectrolytes of high MW, when presenting in water, generally show a random coil configuration, with a diameter on the order of a few hundred nanometers [11]. The radial extent of the random coil depends on the interaction between the polyelectrolyte charged segments.

Polyelectrolytes can be classified into univalent or multivalent polymers. Univalent polyelectrolytes bear functional groups which are homogeneous in terms of the sign of charge [17]. Typically, cationic polyelectrolytes possess quaternary amine groups or amino groups [18], while anionic polyelectrolytes have sulfonate or carboxylate groups [19,20]. Charge density (CD), defined as molar percentage of charged groups, is generally considered as a more important property of polyelectrolytes than MW. Characteristics of polyelectrolytes, such as solubility, ionization constant, and others, can be altered should the pH, ionic strength, counterions concentration and temperature change. For example, a polyelectrolyte tends to expand in solutions with lower ionic strength due to the thicker Debye layer and hence the stronger repulsive interactions between the molecules or monomers; conversely, the repulsion between monomers is reduced as ionic strength increases, so that the expansion weakens [11]. Ions in solution of higher multivalent charge might also induce precipitation of polyelectrolytes, probably due to the induced bridging between polyelectrolytes [21].

2.2. Typical polyelectrolytes utilized for water purification processes

Polyelectrolytes are available in synthetic and natural (e.g., chitosan) forms. Depending on the ionic charge on the polymeric chains of dissociated polyelectrolytes, they can be classified as cationic, anionic, and ampholytic. Based on the charge density, they can be further classified as strongly charged and weakly charged polymers, i.e., pH

independent or dependent. Generally speaking, cationic and anionic polyelectrolytes are chiefly used in water process engineering because of the electrostatic interaction or other association between the polyelectrolyte and contaminant. On the other hand, the application of polyampholytes is comparatively rare during water process engineering [22]. The commonly studied or used polyelectrolytes in water and wastewater treatment are listed in Table 1.

Typically, strongly charged cationic polyelectrolytes possess quaternary ammonium groups (or pyrrolidinium) bearing positive charge, irrespective of pH level. For example, poly (diallyldimethylammonium chloride) (PDADMAC or polyDADMAC) is the most commonly utilized industrial cationic polyelectrolyte, with a high charge density, containing five-membered pyrrolidinium units and chloride ions as counterions. PDADMAC is typically produced by polymerization of diallyldimethylammonium chloride, of low-to-medium MW. PDADMAC can be used as a primary organic coagulant in water treatment or sludge treatment, the function of the coagulant being to neutralize negatively charged colloids and reduce sludge volume [23,24]. It can also be applied during membrane processes to eliminate anionic contaminants from water [25].

Polyethyleneimine (PEI), an organic polyamine with linear or branched molecular structures, is one of the most ubiquitous examples of cationic polymers and can be used as a metal ion binding (chelating) agent. Geckeler et al. [26] first introduced PEI as a chelating polymer to assist in removing heavy metals from aqueous solutions in the 1980s, and PEI has subsequently been studied extensively during polyelectrolyte enhanced ultrafiltration (PEUF). Furthermore, the PEI chains can be modified to interact selectively with specific metal ions (e.g., palladium, mercury, gold, and platinum) by grafting or copolymerizing certain complexing groups [27]. Polyvinylamine (PVAm) is also a cationic water-soluble polymeric material, with up to 95 % of its side chain occupied by highly reactive primary amino groups. Because of these amino groups, PVAm can be used as an ideal chelating material to capture heavy metals and remove them from wastewater [28]. The synthesis and production of PVAm have both been improved since the 1990s, and it has received more attention recently as one of the simplest water-soluble and amine-containing polymers. Polyacrylamide (PAM) is a long-chain linear polymer, containing highly active phthalamine groups which can easily form hydrogen bonds and undergo chemical reactions, so that PAM has good water solubility and high chemical activity. PAM and its derivatives are among the most important and extensively used flocculants [29].

Common anionic polyelectrolytes can be divided into four main categories, namely carboxylic acid polymers, sulfonic acid polymers, phosphonic acid polymers and natural anionic polymers. The use of anionic polyelectrolytes in water treatment includes Poly(sodium 4-styrenesulfonate) (PSS), Polyacrylic acid (PAA), Sodium Carboxymethyl Cellulose (CMC-Na), and so on. PSS is a typical, commercially available anionic polyelectrolyte with repeating sulfonate functional groups [30]. It can be used not only for wastewater treatment and water softening [31–33], but also for produced water treatment and pretreatment for seawater desalination [34,35]. In addition, PSS is a critical material for the synthesis of thin film nanocomposite membranes to improve the membrane efficiency [35]. PAA is a weak anionic polyelectrolyte, which can be considered to be polyethylene with carboxylic acid (CO_2H) substituents on alternating carbons; the degree of ionization is dependent on the solution pH [21]. PAA may associate with various non-ionic polymers and form hydrogen-bonded interpolymer complexes in its non-ionized form at low pH values [36]. In aqueous solutions, PAA can also form complexes with oppositely charged molecules such as chitosan, surfactants, and streptomycin [37]. CMC-Na is a cellulose derivative with carboxymethyl groups ($-\text{CH}_2-\text{COOH}$) bound to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbone. CMC-Na has a promising potential for various applications in water treatment. CMC-Na can be used to modify polyacrylamide gel to become an adsorbent. CMC-Na can also be blended

Table 1
Typical polyelectrolytes used in water and wastewater treatment.

Type	Name	Abbr.	Molecular formula	MW of a unit	Structure	Ref.
Synthetic cationic	Poly(diallyldimethyl ammonium chloride)	PDADMAC (or PDAA)	$(C_8H_{16}N)_n$	126.2		[42]
	Polyethyleneimine	PEI	$(C_4H_9NO)_n$	87		[43]
	Polyvinylamine	PVAm	$(C_2H_5N)_n$	43.07		[44]
	Poly(allylamine)	PAH	$[CH_2CH(CH_2NH_2)]_n$	57		[45]
	Polyacrylamide	PAM	$(C_3H_5NO)_n$	71		[46]
Synthetic anionic	Poly(sodium 4-styrenesulfonate)	PSS	$(C_8H_7NaO_3S)_n$	206		[47]
	Polyacrylic acid	PAA	$(C_3H_4O_2)_n$	72		[48]
	Carboxymethyl Cellulose	CMC-Na	$(C_8H_{16}NaO_8)_n$	242.16		[49]
Natural	Chitosan	-	$(C_6H_{11}NO_4)_n$	161.2		[50]

with poly (vinyl alcohol) to prepare nanofiltration membranes via interfacial polymerization at ambient temperature [38].

Chitosan, a natural low-cost polymeric material, is formed by deacetylation of chitin. It is a translucent, pearly white, amorphous and flaky solid. According to different raw materials and preparation methods, its relative MW ranges from hundreds of thousands to millions [39]. The amino and hydroxyl groups on the molecular chain of chitosan have a good coordination effect, and can form stable chelates with heavy metal ions such as Hg^{2+} , Cu^{2+} , Ag^+ , etc. [40] It is considered as potentially one of the most environmentally-friendly adsorbent materials in water and wastewater treatment [41]. Other natural polyelectrolytes used during water or wastewater treatment include guar gum, starch, gelatin galactomannans, cellulose derivatives and tannin.

2.3. Interaction between polyelectrolytes and contaminants

Regardless of the nature of the application, a polyelectrolyte generally works via bonding or capturing contaminants during the water treatment process, separating them from the aqueous phase. This is particularly true for ionic contaminants. The two dominant interactions between polyelectrolytes and ionic contaminants are a) coordination complexation, and b) electrostatic association between the charged polyelectrolyte groups and the contaminant ions (effectively ion exchange), as shown in Fig. 1. The functional groups on the polyelectrolyte chain with free electron pairs act as electron donors, forming coordination covalent bonds with metal ions which have unfilled electron orbitals (electron acceptors). For instance, PEI can form a strong complex with Cu^{2+} in a natural pH condition, with the most stable complex at a PEI/Cu chelation ratio of 4 [9]. Strongly charged polyelectrolytes

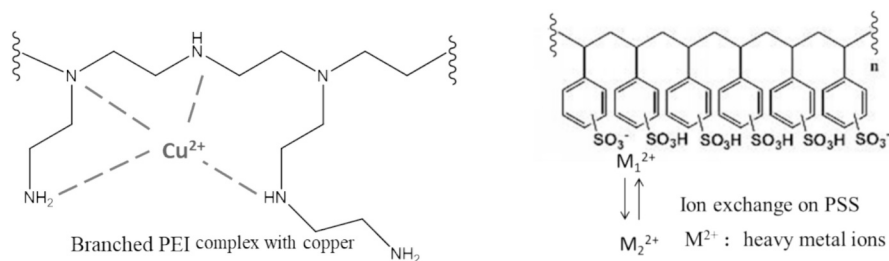


Fig. 1. The two principal interactions between a polyelectrolyte and an ionic contaminant. Left: PEI complex with a copper ion; Right: ion exchange on PSS.

(e.g., with sulfonate groups) can also associate with counter-ions via electrostatic forces, and various ions compete on the polyelectrolyte until equilibrium is reached. The affinities of various cations, including heavy metal cations and naturally occurring cations, for PSS were investigated using an ion exchange model, and showed a decreasing order of selectivity as follows: $Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Mg^{2+} > H^+ > K^+ > Na^+ > Li^+$, and their affinity for PSS was proportionally related to their ionic radii for cations with the same valence [30]. Our recent research reveals the affinities of anions including arsenate towards PDADMAC decrease in the order of $SO_4^{2-} > HPO_4^{2-} > HAsO_4^- > Br^- > NO_3^- > Cl^- > H_2AsO_4^- > H_2PO_4^- \approx HCO_3^-$. It should be noted that ionic organics, such as dyes, phenols and organic acids, generally show stronger bonding than inorganic ions to polyelectrolytes, due to their organic nature [51]. Sometimes, both of the above interactions coexist with ionic contaminants e.g., although carboxyl groups alone on PAA can form coordination compounds with metals, the attraction of metals by anionic charges on PAA is also essential [21,51]. Interactions can arise with other contaminants, such as organic matter. Common organic pollutants in industrial effluents include dyes, phenols and their derivatives, and some aromatics, and the dominant interactions include hydrogen bonding and van der Waals forces [27]. In any event, all these types of interaction can lead to the capture of contaminants from water.

3. Applications of polyelectrolytes in water and wastewater treatment

3.1. Polyelectrolyte enhanced ultrafiltration (PEUF)

Pressure-driven or concentration gradient-driven membrane separation technologies have established themselves as important processes for water purification and wastewater treatment [52,53]. To enhance

the rejection of low molecular weight species (e.g., heavy metal ions, toxic anions, or dyes), colloidal entities, nano-materials or macromolecules can be introduced into the solution of interest, the latter associating with the target aqueous pollutants and forming larger “particles” before or during the membrane filtration process [6,54,55], as shown in Fig. 2.

Polyelectrolytes can function like a linear or mesh capture agent in water, interacting with soluble contaminants via electrostatic forces, coordination/complexation, hydrogen forces or Van der Waals forces, to form complexes which are larger than the membrane pore size [56]. Furthermore, given the similarities between charged surfactant micelles and polyelectrolytes, and based on the existing basic principles of micellar enhanced ultrafiltration (MEUF) [57–59], the extension to polyelectrolyte enhanced ultrafiltration (PEUF) has been recognized as a promising hybrid separation technology for water treatment [27,60,61]. On the basis of previous studies on similar hybrid processes [7,62], Scamehorn’s research group first reported copper ion removal using the PSS assisted UF process in the 1980s [63]. To achieve some special separation applications, PEUF is preferable from an energy and efficiency perspective in comparison with the RO or NF process. PEUF has the capacity to remove contaminants such as heavy metal ions, dissolved organic matter and inorganic anions with low molecular weights, such removals being relatively difficult to perform using the conventional UF process because the structure of the UF membrane is loose [64]. A schematic of the PEUF process is shown in Fig. 3. The advantage of PEUF over MEUF is that a low concentration of polyelectrolyte can be used to remove pollutants in trace concentrations. On the other hand, because micelles cannot form when the concentration of surfactants is less than the critical micelle concentration, the surfactant monomers would simply pass through the UF membrane [58]. To better understand and review the current status of PEUF technology and its potential for further development, it is useful to summarize its various applications.

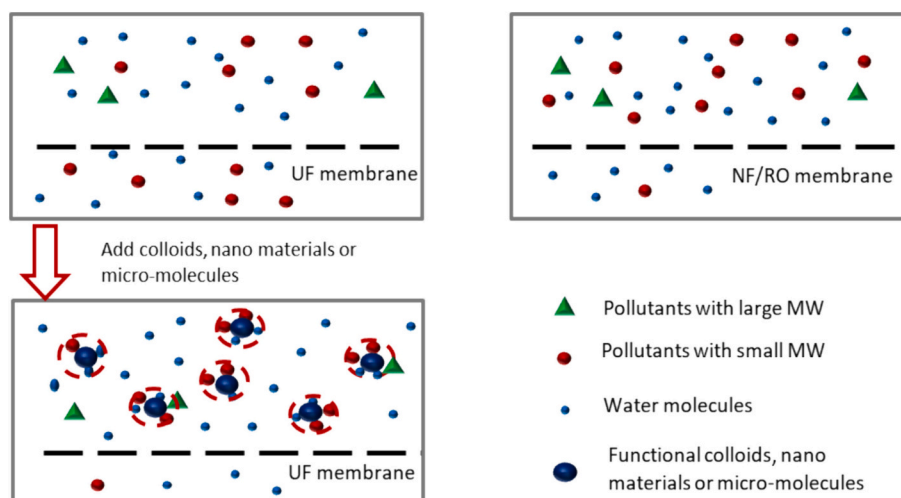


Fig. 2. Schematic of an enhanced UF process, compared to NF or RO.

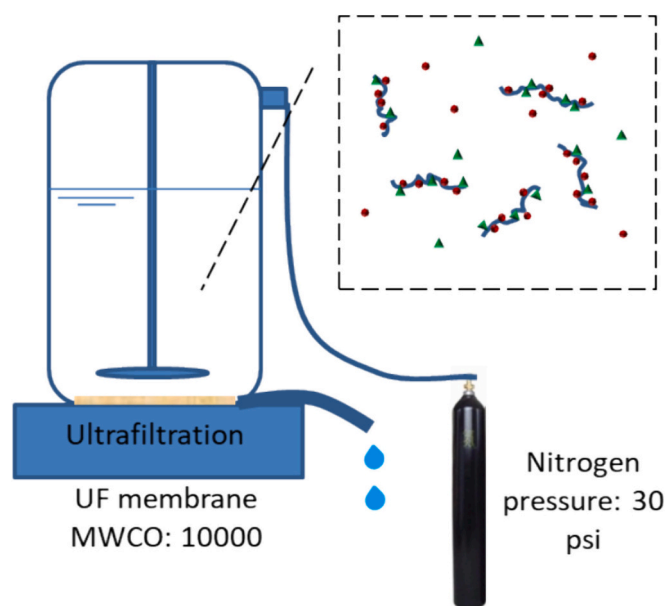


Fig. 3. The schematic of a dead-end PEUF process.

3.1.1. Influence of factors on the performance of PEUF

As a semipermeable membrane, an ultrafiltration (UF) membrane can be utilized to separate solutes and colloidal particles of high molecular weights (e.g., proteins, viruses) from those of low molecular weights (including water molecules) by applying a pressure or concentration gradient. Those factors influencing the UF process, e.g., temperature, pressure, membrane pore size and structure, and material, would also affect the performance of PEUF. In addition, type, properties and dosage of polyelectrolyte used during UF can also affect the performance and efficiency of separation.

The molecular weight cut-off (MWCO) is a critical factor in the selection of both the UF membrane and the polyelectrolyte. The necessary MWCO or pore size of the membrane can be determined, based on the polyelectrolyte MW. Using a membrane with a larger MWCO will cause massive loss of polyelectrolyte molecules transporting across the membrane pores, while using one with too low a MWCO may require the input of more energy (i.e., higher operating pressure) or result in a reduced flow. UF membranes with a MWCO of 5–10 kDa appear to be used for a typical PEUF application. Commercially available polyelectrolytes will usually have a significant MW distribution, even if they have quite a high average MW. Therefore, the polyelectrolyte molecules with small MW may not be completely rejected by the UF membrane, but complete retention would be achieved after membrane screening (i.e. where the small molecular weight components are removed prior to PEUF application by, for example, dialysis) [30]. The polyelectrolytes used during PEUF may accumulate easily on the membrane surface and inside the pores, thus increasing the hydraulic resistance and transmembrane pressure, leading to membrane fouling and a decline of flux. Although both dead-end and cross-flow modes of operation can be applied for UF, dead-end filtration is more likely to be blocked by gel cake due to the accumulation of polyelectrolyte-contaminant complexes.

3.1.2. Application of PEUF for contaminants removal

3.1.2.1. Heavy metals. In the past decades, the PEUF process has been shown to be promising for the removal of macro and trace metallic ion species from aqueous streams when assisted with a water-soluble polyelectrolyte. Among all heavy metal contaminants present in domestic and industrial wastewater, the cationic metal ions including manganese, cobalt, nickel, copper, zinc, cadmium, mercury, and lead are

particularly important. Using PEUF technology, the removal efficiency for heavy metals is high and the concentration of residual heavy metal in the permeate can drop to the ppb level (this depends on the type of heavy metal to be removed), which in general meets the maximum allowable emission pollutant level proposed for most heavy metals [63,65].

Table 2 shows the removal of cationic metals using PEUF. From the table, it can be seen that PEI, PSS and CMC-Na are commonly used for metals removal from water. Scamehorn's group [63,66] developed the PSS-assisted UF process for Cu^{2+} removal in the late 1980s, based on their extensive research of MEUF. PSS enhanced UF has also been applied to recover the rare earth elements neodymium (Nd) [67] and lanthanum (La) [68] from aqueous solutions (up to 99%). However, the interaction between PSS and metals is basically ion exchange. The affinity of divalent cations including metals is similar, so PSS struggles to separate target metals from mixed-cation solutions [30]. Nevertheless, the simultaneous removal of several metals can be achieved via an increase in the concentration of PSS because of a greater number of ion exchange sites. PEI can also form chelating complexes with metals, and in this way capture them easily from water, while the influence of other salts is negligible [9]. Consequently, the association of metals towards the amine groups of PEI is stronger than that of PSS. Therefore, researchers have widely studied the removal of PEI-metal complexes by ultrafiltration using PEUF, including Hg, Cd, Co, Sr, Cu, and so on. [60,69–71]. PVAm, another polyelectrolyte with amine groups, has been used during PEUF to remove multiple metals, including Co (II), Cu (II), Ni (II), Pb (II), Fe (III), Cd (II), Zn (II) and Mn (II). A rejection of over 99% of Pb (II), Fe (III), and Cu (II) was observed, indicating a higher affinity of these metal cations to PVAm than others (around 20–60% under the same conditions) [72]. The carboxylic acid groups, which are dependent on pH, of CMC and PAA play an important role in metal removal. It is believed that the combined processes of chelation and electrostatic interaction operate during PEUF using PAA and CMC [21]. Barakat and Schmidt [73] investigated the removal of toxic heavy metals (including Cu^{2+} , Ni^{2+} , Cr^{3+}) from synthetic wastewater using PEUF with CMC. The results showed rejection of these metals increased as the pH increased from 3 to 7, indicating that the protonation of CMC adversely affects the removal of heavy metals. Chou et al. [74] compared various polyelectrolyte types (PSS, PAA and PEI) for copper recovery during PEUF under various pH conditions. The pH had a negligible influence on PSS, as Cu removal remained at up to 75% at a pH value of 3. PAA was slightly affected at pH 3 with a lower removal of 60%, but increased substantially at pH 4. The branched PEI showed the highest Cu removal of 94% at pH 3. In addition, from the table, the MWs of polyelectrolytes are generally 5 to 10 times larger than the MWCO of the membranes. Compared to nanofiltration and reverse osmosis, the water permeability obtained here would be much higher, and generally in the range of 0.1–3 $\text{L}/(\text{m}^2 \cdot \text{h} \cdot \text{kPa})$, but the fouling caused by the aggregation of polyelectrolytes on the membrane surface remains a concern.

3.1.2.2. Inorganic anions. It is also often useful to remove inorganic anions from different aqueous solutions. Target anions usually include metal oxygen-containing anions (e.g., chromate), metalloid anions (e.g., arsenate, borate), nutrients (e.g., NO_3^-) and perchlorate. The removal of these inorganic anions during PEUF is based in general on the electrostatic interaction between cationic polyelectrolytes (e.g., PDADMAC) and anions, and ion exchange with the initial anion (e.g., Cl^-) [77]. Table 3 lists some typical studies focusing on inorganic anions removal using PEUF. Lots of research studies [78–80] have been conducted on chromate removal with PEUF using PDADMAC for the main part and based on the ion exchange between CrO_4^{2-} and Cl^- ; in this case, divalent anions have a higher affinity than monovalent anions, and therefore, the elimination of CrO_4^{2-} from water is usually achieved to a satisfactory level. Similar to chromate, arsenate can also be removed

Table 2
Removal of metallic cations from aqueous solutions by PEUF.

Target species	Polymer (MW, kDa)	Membrane (MWCO, kDa)	UF module	Pressure (kPa)	Rejection (%)	Performance	Ref.
Cu ²⁺	PSS (85)	5	Dead end	414	80–99.95	Retention ratios as large as 1000 have been measured. Reasonably good separations are achieved even in the presence of 40–80 mM NaCl.	[63]
Cu ²⁺	PSS (85)	Cellulose acetate (1, 5, 10)	Dead end	414	Up to 99.1	As the retentate becomes more concentrated in polyelectrolyte, the rejection decreases and the flux decreases. Still, the rejections remain higher than 96 %.	[66]
Hg ²⁺	PEI (50)	Flat sheet (5)	Dead end	100	45.1–99.7	Effects of mercury-to-polymer ratio, pressure drop and feed solution circulation rate on retention of mercury and permeate flux were studied.	[69]
Hg ²⁺ and Cd ²⁺	PEI (50)	Lab: flat sheet (5) Pilot: spiral Wound (10)	Lab: dead end Pilot: cross flow	60	Hg ²⁺ up to 98 Cd ²⁺ up to 97	Rejection of mercury was dependent on the mercury-to-PEI ratio rather than their concentrations.	[70]
Cd ²⁺	PEI (70)	10	Dead end	207	Exceed 90 at pH 5–6	Experiments were conducted for binary solutions at different pH and loading ratios for selective separation of mercury and cadmium. The increased pH and decreased metal/polymer ratio, and loading (L), resulted in higher retention of both metals.	[71]
Cu ²⁺ , Ni ²⁺ and Cr ³⁺	Carboxymethyl cellulose (viscosity 25–75 mPa s)	Polyethersulfone (10)	–	100	Cu ²⁺ up to 97.6 Ni ²⁺ up to 99.1 Cr ³⁺ up to 99.5	The removal and recovery of Cd species was greatly dependent on the chemistry of organic ligands according to solution pH, particularly being related to the distribution of Cd-ligand complexes at different pH levels.	[73]
Sr ²⁺ and Co ²⁺	PAA(15, 100, 250) and PEI(250)	Regenerated cellulose (1, 10, 100)	–	50, 75, 300	Co ²⁺ up to 80 % using PEI and Sr ²⁺ exceeding 90 % using PAA	Different parameters affecting the percentage rejection of the metals, such as pH, metal ion concentration, CMC/metal ratio, and permeate flux (F) have been investigated.	[60]
Nd ³⁺	PSS (70) and PEG (35)	Polyethersulfone (10)	Cross flow	100–300	Nd ³⁺ up to 99 using PSS and up to 86 using PEG	The retention increased with the increase of pH. The ionic strength effect has shown a retention decrease with increasing salt concentration. Finally, the permeate flux declined following the increment in volume concentration factor, while the retention remained constant around 98 %.	[67]
Cu ²⁺	PSS (70), PAA (250) and PEI (60)	Polyethersulfone (10)	Cross flow	170	Achieved the complete copper recovery using PSS, Cu ²⁺ exceed 95 using PAA and up to 96 using PEI	The PEUF with PAA achieved metal removal as high as LPRO, with relatively high-water permeability.	[74]
Zn ²⁺	PAA (250)	Polyethersulfone (PES, 30)	–	0.01 to 250 depending on radius	Zn ²⁺ up to 95.3	The retention increased with the increase of pH. The ionic strength effect has shown a retention decrease with increasing salt concentration. Finally, the permeate flux declined following the increment in volume concentration factor, while the retention remained constant around 98 %.	[75]
Cu ²⁺ and Pb ²⁺	PSS (200, 70, 1000)	1, 10	Dead end	344.7	Cu ²⁺ and Pb ²⁺ all exceed 80 by 200 kDa PSS with 10 kDa UF	A branched PEI with an amine group achieved the highest Cu removal of 94 % at pH 3. The copper removal efficiency decreased slightly with increasing pH due to the high permeation of PEI through the membrane.	[30]

(continued on next page)

Table 2 (continued)

Target species	Polymer (MW, kDa)	Membrane (MWCO, kDa)	UF module	Pressure (kPa)	Rejection (%)	Performance	Ref.
La ³⁺	PSS	Regenerated cellulose (10)	Cross flow	250	–	The La(III) retention increased with the increase of transmembrane pressure and PSS concentration. Rejection of La(III) ions using ultrafiltration was widely influenced by solution pH. A better retention was observed at 10 ⁻⁴ mol L ⁻¹ PSS concentration and 2.5 bar transmembrane pressure.	[68]
Cd ²⁺	Chitosan (620), PVA (86), PAA (4000)	Hollow fiber UF membrane (6)	Dead end	100	Cd ²⁺ up to 100 using PAAS	The higher the P/M was, the lower the pH, and the higher the HA concentration, then the more serious the UF membrane fouling was. The dissociation rate of PAAS–Cd reached 99.8 % at a pH of 2.5.	[76]

using PDADMAC, and our recent research (as yet unpublished) has achieved an As (V) removal as high as 96 % from water in the absence of competing anions. The arsenic removal can be predicted based on mass action (i.e. ion exchange selectivity) and the material balance equations [59].

Nutrients are also a type of anionic matter which need to be controlled in water. Nitrogen in water is the main cause of eutrophication. Nitrate removal from contaminated water using PEUF was shown to be feasible. Three different polyelectrolytes with quaternary amine groups or pyrrolidinium groups (i.e., PDADMAC) were applied in PEUF to remove nitrate from contaminated groundwater [81].

For the removal of boron, a previous study using PEUF showed that the max rejection of boron from boric acid solutions was only 33 % in

dead end filtration mode using PVA as the polymer [82].

3.1.2.3. Hardness. Water frequently contains numerous solutes, many of which are undesirable for either industrial or residential purposes. As one category of solutes, the divalent cations of calcium and magnesium are responsible for water hardness, and Tabatabai et al. [31,32] determined the effectiveness of PEUF as an alternative method for the removal of hardness ions from water. Chen and Peltier [5,21,30] also reported scale-forming cations, including Ca²⁺ and Mg²⁺, and their removal from produced water using polyelectrolytes with membranes. It can be concluded that when a water-soluble anionic polyelectrolyte, such as PSS or PAA, is added to hard water, then calcium and

Table 3

Typical inorganic anion removal using PEUF.

Species	Polyelectrolyte	MW	Membrane material	Membrane MWCO	Pressure (kPa)	UF	Performance	Ref.
Chromate (CrO ₄ ²⁻)	PDADMAC	240 kDa	Cellulose acetate	10 kDa	414	Dead end	Without added electrolytes, rejection up to 99.8 %; NaCl reduces CrO ₄ ²⁻ rejection.	[79]
CrO ₄ ²⁻ , sulfate, nitrate	PDADMAC	240 kDa	Cellulose acetate	10 kDa	414	Dead end	Rejections of chromate and sulfate are similar and >98 %, and nitrate can be as high as 97 %.	[83]
Arsenate	PDADMAC	240 kDa	Cellulose acetate	10 kDa	414	Dead end	Arsenic rejections as high as 99.95 % are obtained and increase with increasing polymer concentration and decrease with increasing ionic strength.	[84]
Nitrate	PDADMAC	200–350 kDa	Regenerated cellulose	3, 10, 30, 100 kDa	100	Dead end	Substantial nitrate removal up to >90 % at high molar ratios of quaternary amine groups to nitrate was achieved, depending on the types of chelating polymers and UF membranes used. The branched polymers removed nitrate better than the linear polymers.	[81]
Borate	PVA and synthesized polymers	220 and 40 kDa	–	–	–	–	pH 7–10, 28–37 % removal.	[82]
Perchlorate	PDADMAC	–	Regenerated cellulose; polyether sulfone	3, 10 kDa and 10 kDa	200	Dead end	In the absence of other anions, PDADMAC (0.5–1 mM) can remove >90 % of perchlorate from the aqueous phase. However, in the presence of 5 mM nitrate, perchlorate removal decreases as the available binding sites of PDADMAC for perchlorate are reduced.	[85]
Perchlorate	PDADMAC	400–500 kDa	Regenerated cellulose	10 kDa	414	Dead end	Polyelectrolyte concentration, pH, and ionic strength were investigated. Removal of perchlorate from synthetic groundwater initially containing 10.3 ppm perchlorate and containing chloride, sulfate, and carbonate was examined. Perchlorate separations of >95 % were achieved, even in the presence of 10-fold excesses of competing ions.	[25]
CrO ₄ ²⁻	Synthesized polymer (PDAM)	42 kDa	Polyether sulfone	5 kDa	100	Dead end	Effect of operating parameters such as pH, loading, polymer, and competing ion concentrations were examined. Highest Cr(VI) retention was obtained at a loading of 0.01 at pH 4.	[86]

magnesium bind to the polyelectrolyte. The latter polyelectrolyte is chosen to have a high enough molecular weight to be rejected by an ultrafiltration membrane. In addition, acids or salts can be added to regenerate PSS or PAA [21,31]. Juang and Chiou [87] also focused on the feasibility of PEUF for brackish water softening. However, Ca and Mg removal competed adversely with other cations; all metals usually have high affinities to polyelectrolytes, and monovalent cations (e.g., Na and K) at high concentrations hindered the complexation with the hardness-causing divalent cations.

3.1.2.4. Dyes. Recently, increasing attention has been paid to the efficient removal of synthetic dyes using PEUF [88–90], and reviews have also focused on its application [91,92]. The most commonly used classification to differentiate the various types of synthetic dyes is based on the nature of their charge after dissolving in water, that is to say as anionic dyes (including acid dyes, reactive dyes, azo), cationic dyes (including basic dyes), and non-ionic dyes (including dispersing dyes that do not ionize in aqueous media). It is generally believed that the interaction between organics and polyelectrolytes is caused by hydrophobic and energetic interactions such as chemical interactions, hydrogen bonding and electrostatic interactions [93,94]. Ionic dyes are the main objects of studies which investigate removal by PEUF, and the dye-polyelectrolyte complexation is not significantly affected by the presence of interfering ions [95].

The effective removal of the triphenylmethane dyes from aqueous solutions, including malachite green (MG), brilliant green (BG) and new fuchsin (NF), was achieved using a polysulfone hollow fiber ultrafiltration membrane with the aid of the anionic polyelectrolyte PSS, and the study also demonstrated that the cationic and nonionic polymers such as PDADMAC and PVA were not suitable for the removal and decolorization of these dyes in aqueous solutions [96]. Removal of the cationic dye crystal violet (CV) from aqueous solutions by continuous PEUF assisted with PAA or PEI has been investigated, and the permeate flux and decolorization of CV were studied as a function of dye and polyelectrolyte concentrations, applied pressure, ionic strength and pH values. The PAA application showed a higher rejection (99 %) of CV than PEI (around 60 %), due to the electrostatic interaction between anionic PAA and the cationic dye molecules. PAA was influenced by ionic strength and pH markedly; on the contrary, the same parameters showed a negligible effect in the case of PEI [97]. In a previous study, retention as high as 98 % of methylene blue (MB), a phenothiazine cationic dye, was obtained using PAA during PEUF with a 10 kDa MWCO cellulose membrane [98]. The complete removal of the anionic dye methyl orange (MO, up to 50 mg/L) was achieved using PEUF with a synthesized cationic polyelectrolyte, for which the removal was higher than achieved with MEUF. The PEUF removal was also associated with a much lower carbon leaching into the purified stream than MEUF. [99]

3.2. Enhancing membrane performance by polyelectrolytes

Membrane technology has gained rapid acceptance as a cost-effective and efficient approach for water purification since the 1960s [100]. Polymeric membranes are well-developed, and have demonstrated great potential for almost all membrane processes in water industry due to their low price, ease of preparation, flexible configuration, small footprint and high-quality effluent [101,102]. In recent years, there has been a surge of interest in developing state-of-the-art polymeric membranes with novel properties, including improved separation performance and selectivity for different pollutant types [103]. Polyelectrolytes are among the most promising materials for the modification of membranes to satisfy these needs, due to their unique charge properties. Further, such advances have brought additional benefits including separation under extreme pH conditions [104], enabling long term operation [104], mitigating membrane fouling [105], etc.

The current section focuses on the preparation and application of

polyelectrolytes-coated polymeric membranes for aqueous pollutant removal.

3.2.1. Membrane modification

3.2.1.1. Layer-by-layer (LBL) assembly. Polyelectrolytes, as water-soluble polymers, are charged, due to the dissociation of charged repeating units in the molecular chains which exist in an aqueous phase. Based on non-covalent forces, such as electrostatic attraction, van der Waals forces, hydrogen bonding, and hydrophobic interactions [104], many polyelectrolytes of varying charge can form stable, insoluble polyelectrolyte complexes (PECs). This can take place either by bulk mixing in water, or by interfacial complexation on a substrate (e.g., membrane) [106]. As first reported by Decher and Hong in the 1990s [107], layer-by-layer (LBL) assembly has been investigated extensively for making polyelectrolyte-coated membranes [108–112]. This is commonly done through alternate dip or spin coating of polymeric membranes in polyelectrolyte solutions, in order to form polyelectrolyte multilayer (PEM) membranes via static or dynamic adsorption and in combination with a rinsing step between each coating step to remove weakly bounded polymers.

LBL assembly has many advantages such as being economically viable and environmentally benign, scalable, the possibility of controlled layer thickness, rapid coating, and high versatility [102,113]. Different parameters such as polyelectrolyte structure, molecular weight, charge density, pH and ionic strength of the coating solution, number of bilayers, terminating PE layer of the membrane, and weak or strong activity, can play pivotal roles for the LBL process, and thus the resultant membrane surface chemistry, stability and layer growth [104,114–116]. Many polyelectrolyte pairs have been reported so far for building PEM membranes, such as poly(allylamine hydrochloride) (PAH)/PSS [109], PAH/PAA [10,113], and PDADMAC/PSS [103,117,118].

3.2.1.2. Interfacial crosslinking. Interfacial polymerization (IP) has been used widely for the fabrication of thin film composite (TFC) membranes, especially nanofiltration (NF) and reverse osmosis (RO) membranes. Conventional TFC membranes have been very industrialized for water treatment, and comprise of a polyamide (PA) selective layer and a polymeric membrane support [119]. The PA skin layer is typically produced by crosslinking reactions between reactive diamines (e.g., piperazine (PIP)) and acid chloride monomers (e.g., trimesoyl chloride (TMC)) [119]. However, commercial TFC membranes have low permeability, are fouling-prone, and exhibit poor solvent and chlorine resistance [105].

Over the past years, polyelectrolytes have also been adopted to prepare novel TFC membranes with improved mechanical stability and surface chemistry, through a similar interfacial crosslinking approach. For instance, PEI has been used widely for covalent modification of membrane surfaces, because its amine group can react with many functional groups (e.g., carbonyl group, acryl chloride, etc.). Liu et al. [120] crosslinked PEI with TMC on a nylon MF membrane substrate to produce a TFC membrane. Sun et al. [121] and Zhao et al. [122] directly crosslinked branched PEI with the surface of membrane supports, i.e., a polyamide-imide (PAI) hollow fiber membrane and a P84 flat sheet UF membrane, respectively.

Moreover, some studies have focused on covalent LBL assembled membranes with the help of other chemical agents to improve the polyelectrolyte multilayer stability. Shan et al. [123] reported the preparation of a glutaraldehyde (GA) crosslinked PEI/PSS LBL assembled PAN membrane. Qiu et al. [124] and Liu et al. [109] obtained GA crosslinked PAH/PSS LBL modified PAN and PES membranes, respectively, in which the GA aldehyde group could react with the PAH amine group. In addition, inspired by mussel catechol chemistry, dopamine (DA) can self-polymerize into adhesive polydopamine (PDA), which can

in turn crosslink with polycations (e.g., PEI and PAH) through Michael addition or Schiff base reactions [102]. Meng et al. [102] coated a covalently bonded PEI/PDA layer on PES and PAN UF membranes, followed by the alternating deposition of multilayer PSS and PEI/PDA to obtain PE-coated membranes.

3.2.2. Polyelectrolyte membranes for nanofiltration (NF)

Porous membranes (UF, NF and RO) are pressure-driven, and can be distinguished by their different pore sizes, i.e., UF (2–100 nm) > NF (0.5–2 nm) > RO (<1 nm) [125,126], and their operating pressures, i.e., UF (3–5 bars) < NF (6–10 bars) < RO (14–70 bars) [127,128]. UF separates solutes based purely on size exclusion, and only removes macroscopic contaminants. NF can remove some micropollutants as well as divalent ions, while RO assures high rejection of common ions and small organic solutes, by means of both size exclusion and membrane – solute charge interactions. Among them, the NF process has been increasingly adapted, and gives much higher rejections against many small-sized solutes while consuming less energy than RO. Recent advances in the polyelectrolyte modification of membranes permit fascinating separation characteristics for the NF process. Indeed, this provides an alternative paradigm for pollutant separation in water. Polyelectrolyte modified NF membranes for the removal of ions and organic pollutants are summarized in Table 4.

3.2.2.1. Ion removal. The polyelectrolyte modification of NF membranes has been used to enhance the selectivity and separation performance for ion removal in water. It was found that membrane separation behaviour is related to the polyelectrolyte terminating layer, and is enhanced with an increased number of bilayers and with an increased target ion valency and hydrated radius [103,112]. Cheng et al. [103] and Wang et al. [112] constructed PDADMAC/PSS LBL assembled NF membranes for divalent ion removal. Cheng et al. [103] observed improved rejection and selectivity for divalent cations (94 % for Ca^{2+} and 98 % for Mg^{2+} ; 23 % for Na^+) at low pressure (3.45 bar) for polycation PDADMAC-terminated PEM, due to enhanced Donnan exclusion. In comparison, pristine TFC NF membranes remove these ions only poorly (<20 %).

Wang et al. [112] used PSS-terminated PEMs to remove inorganic salts, and found that the negative surface charge facilitated the transport of cation Ca^{2+} while impeding the transport of anion SO_4^{2-} due to different electrostatic interactions. This led to much lower rejection of CaCl_2 than Na_2SO_4 (e.g., 14 % vs 82 %, for 4 bilayers). However, with an increase of PE bilayers from 2 to 6, rejection of both of these asymmetric salts increased due to the reduction of membrane pore radius and a correspondingly stronger size exclusion. It can be noted that commercial NF membranes usually reject <60 % of monovalent ions [117].

Malaisamy et al. [117] reported a much higher removal of Cl^- using an 8-layer PDADMAC/PSS surface deposited NF270 membrane than using a pristine membrane (91 % vs 30 %) under cross-flow in the single salt system, when Cl^- concentration was 100 mg/L. Despite the low hydration radius of Cl^- , the strong electrostatic repulsion between the membrane surface and the anion still enhanced the removal.

Ion retention is also affected by different fabrication and assembly conditions of the polyelectrolyte membranes [129]. For instance, Abtahi et al. [113] found post salt annealing of PSS/PAH LBL fabricated PEM membranes improved the salt rejection without lowering permeability. Brinke et al. [129] prepared PES hollow fiber membranes coated by different PSS/PDADMAC or PSS/PAH pair numbers and under different ionic strengths, and observed different MgSO_4 retentions (>75 %). Being controlled mainly by size, dielectric exclusion and Donnan exclusion, the difference of retention was attributed to the build up of structure, film thickness and surface charge density.

3.2.2.2. Organic pollutant removal. Polyelectrolyte-modified membranes are also extensively adopted for the removal of organic solutes

(e.g., micropollutants) in water. The separation performance is controlled by polyelectrolyte membrane physicochemical properties, the organic solute characteristics (pK_a , K_{ow} , molecular size, etc.) and solution conditions (pH, ionic strength, etc.), which collectively impacts membrane – solute interactions.

Abtahi et al. [113] studied the dead-end filtration of organic micropollutants by PSS/PAH LBL fabricated PEM membranes over long-term operation at 2 bar. The hydrophobic, uncharged micropollutant 4-nonylphenol showed 95.9 % removal at an early filtration stage, due to hydrophobic adsorption onto the membrane. However, the removal dropped over time due to membrane saturation, at which point size exclusion became the only mechanism. In contrast, electrostatic interaction was also found to be important when treating charged micropollutants, where the removal (52–82 %) of negatively charged diclofenac, naproxen and ibuprofen was controlled by both electrostatic repulsion and a sieving effect.

As reported by de Grooth et al. [108], polycation (PDADMAC), polyzwitterion (PSBMA), and polyanion (PSS) SPES PEM hollow fiber membranes showed the lowest removal to uncharged sulfamethoxazole, atrazine and bisphenol A micropollutants (cross-flow, 1.75 bar) regardless of the terminating layer, suggesting that a size exclusion mechanism alone led to low retention. Results suggested that the dual charge of these PEM membranes interacted with the charged micropollutants in several ways. The negatively-charged PSS-terminated membranes obtained the highest removal for negatively charged micropollutants, through Donnan exclusion. Most interestingly, incorporation of a zwitterionic PSBMA layer increased the removal of all charged micropollutants (naproxen, bezafibrate and atenolol) using PSBMA- or PDADMAC- terminated membranes, due to dielectric exclusion.

Ouyang et al. [111] found that the dually charged PEM NF membrane which had been LBL modified by PDA and quaternate chitosan (CS) showed good removal (>76 %) towards various pharmaceutical and personal care products (PPCPs) (ibuprofen, carbamazepine and atenolol) at a low operating pressure of 5 bar and at neutral pH. Changing feed solution pH impacts the charge of the membrane and micropollutants, and thus impacts their interaction. Rejection of, for example, atenolol ($\text{pK}_a = 9.43$) was observed to increase from 76.22 % at pH = 7 to 81.67 % at pH = 3, because atenolol became more protonated and the membrane surface charge also turned positive, leading to strong electrostatic repulsion.

3.3. Adsorbent modification using polyelectrolytes

Compared to other methods of water and wastewater treatment (e.g., membrane filtration, photocatalysis, and advanced oxidation), adsorption shows many advantages: materials are cheap and readily available, the cost is low, and the design and operation of the treatment unit is relatively simple [130,131]. The adsorbents used for water purification usually include carbonaceous adsorbents (e.g., activated carbon and carbon nanotubes), mineral adsorbents (e.g., clays and zeolites), polymer adsorbents (e.g., synthetic resins, ion exchange fibers, chitosan and its derivatives) and waste adsorbents (e.g., industrial waste and agricultural waste) [132,133]. However, common adsorbents each have their own limitations when applied to contaminants removal. Therefore, modification of these adsorbents is necessary to improve selectivity, adsorption capacity, adsorption efficiency, operation stability and economic feasibility. Polyelectrolytes are often used to modify materials, due to their ability to change the surface charge of solids or improve the selectivity and thus improve the removal performance of various inorganic and organic pollutants [134]. Many studies have been reported on the modification of common adsorbents with various polyelectrolytes, and the results show that these modified adsorbents have a greatly improved performance for pollutants removal. The polyelectrolytes commonly used in modified adsorbents include PEI, PDADMAC, PSS, chitosan (itself a good adsorbent), PAA, and PAM, etc.

Table 4
Polyelectrolyte surface modified membranes for removal of ions and organic pollutants.

Supports	Polyelectrolyte modifier(s)	Modification method	Membrane type	Target pollutants	Performance	Ref.
PA	PSS/PDADMAC	LBL assembly	Flat sheet	Ions	High rejection (up to 98 %) and selectivity to divalent cations (Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}) at low pressure (3.45 bar).	[103]
PA	PSS/PDADMAC	LBL assembly	Flat sheet	Ions	High rejection (91 %) of Cl^- in single salt filtration system. Good selectivity of F^- over Cl^- in the ternary monovalent ion mixture (F^- , Cl^- and SO_4^{2-}).	[117]
PES	CS/PDA	LBL assembly, crosslinking	Flat sheet	Organic pollutants	Removal (>76 %) of atenolol, carbamazepine and ibuprofen through Donnan exclusion and size exclusion.	[111]
SPES	PAA/PAH	LBL assembly	Hollow fiber	Organic pollutants	High retention (60–80 %) for charged micropollutants at low TMP (1.8 bar).	[10]
PES	PSS/PDADMAC or PSS/PAH	LBL assembly	Hollow fiber	Ions, organic pollutants	$MgSO_4$ retention (>75 %) is dependent on PE type and number of layers.	[129]
PAN	PAA/PAH	LBL assembly	Flat sheet	Ions, organic pollutants	Higher rejection for divalent salts for post-salt annealing treated PEM membranes. Removal of micropollutants reaches up to 82 %, and is affected by solute size, charge and hydrophilicity.	[113]
SPES	PSS/PSBMA/PDADMAC	LBL assembly	Hollow fiber	Ions, organic pollutants	Retention of micropollutants and ions are affected by their charge, size, and membrane terminating PE layer.	[108]
PSF	PSS/PDADMAC	LBL assembly	Flat sheet	Ions, organic pollutants	High rejection of divalent ions ($SO_4^{2-} > Ca^{2+}$). High retention of emerging organic pollutants (>85 %) comparable to commercial NF270 membrane.	[112]

The commonly used methods for modifying an adsorbent with polyelectrolyte include crosslinking, grafting, surface modification, impregnation, complexation, etc. This section focuses on modification methods and applications of the modified adsorbents.

3.3.1. PEI for adsorbent modification

PEI is a typical water-soluble polyamine, with two molecular structural forms: linear PEI and branched PEI. Branched PEI is fully amorphous, unlike the linear form which is crystalline at room temperature. Branched PEI has a high concentration of polar groups containing nitrogen atoms, with a respective molar ratio of primary to secondary to tertiary amines of 1:2:1. These amine groups on the chain of the PEI polymer can interact with ionic pollutant species, such as platinum group metals, dyes, and heavy metals [135–137]. However, due to the water-soluble nature of PEI, it must be immobilized on a matrix to ensure the maneuverability when used as an adsorbent. The resulting adsorbents can be divided into six broad categories of material, depending on the substrate used for PEI immobilization: magnetic, carbon-based, silica-based, clay minerals and geomaterials, biologically-derived materials, and other hybrid composites [138]. The modification method is generally cross-linking or grafting, among which grafting copolymerization provides an attractive and versatile method for imparting a variety of functional groups to the adsorbents [139]. Modified adsorbents are commonly used to remove heavy metals such as Cu(II), Ni(II), Cr(VI), and organic dyes such as methyl orange. The adsorption capacity after PEI modification has a significant increase compared with that of the original adsorbent. The reason is generally that the addition of PEI leads to an increase in the number of amine groups on the surface of the adsorbent, providing more effective adsorption sites, and thus enhancing the adsorption capacity. The adsorption effect is generally affected by pH, the type of crosslinking agent and molar ratio. Many PEI-based composite materials have been studied and used as adsorbents for contaminants removal [140]. Reddy et al. [141] reported on PEI-based epoxy coated gauzes as an efficient, reusable and economical adsorbent, with a high density of active sites. Because of the porous structure and large surface area of the adsorbent, together with the large amount of amine groups of PEI, the optimized adsorption capacity for Ni^{2+} could be as high as 650 mg/g. Zeng et al. [142] applied PEI to modify $Ti_3C_2T_x$ surfaces and synthesized $Ti_3C_2T_x$ /PEI nanocomposites to remove Cr^{6+} , with a maximum removal capacity of 186.5 mg/g. Zhang et al. [143] reported novel clay composite materials functionalized with PEI and CTAB for Cr(VI) removal, showing a high adsorption capacity at 59.3 mg/L, 4 times higher than of the initial adsorbent. Polyethyleneimine-modified magnetic peanut husk was developed by Aryee et al. [144], which showed efficient simultaneous removal of Cr(VI), Congo red and PO_4^{3-} . PEI-modified chitosan beads

can adsorb clofibrac acid, with a maximum adsorption capacity of 349 mg/g [145].

3.3.2. PDADMAC for adsorbent modification

PDADMAC is a strongly charged cationic polymer, and it can be used to modify solid surfaces, graft with adsorbents, or form composite materials for removing some organic pollutants [146–148]. The adsorption capacity of nanosilica, synthesized from rice husk and modified by PDADMAC, for beta-lactam cefixime (CEF) was investigated, with a removal rate of 93.51 % [149]. The removal efficiency of amoxicillin antibiotic (AMX) increased from 19.1 % to 92.3 % when using the same adsorbent modification [150]. PDADMAC was impregnated on mesoporous silicas and the surface charges of the mesoporous silicas were easily converted from negative to positive, which could then adsorb anionic dyes like methyl orange because of the electrostatic attractions [151]. Carbon adsorbent-catalysts modified by PDADMAC and quaternary ammonium (QA) were synthesized to degrade methyl bromide [152]. Ordered mesoporous carbon modified by PDADMAC (CMK-1/PDDA) was created and used for the removal of major aromatic compounds present in purified terephthalic acid wastewater [153]. An alternate coating of PDADMAC and polydiallylaspartate was utilized to modify mesoporous SBA-15, leading to a highly efficient porous adsorbent to remove Cd^{2+} [154]. Coating PDADMAC onto mesoporous acid-treated fly ash (AFA) and its capacity to adsorb phenol from aqueous solution were also investigated, showing an ultrathin coating of fly ash with cationic polyelectrolyte had potential as an alternative adsorbent from waste [155].

3.3.3. Chitosan for adsorbent modification

Compared with other adsorbents, chitosan has the advantages of having a large adsorption capacity and providing high purification efficiency, as well as being non-toxic and harmless, and being renewable so not creating secondary pollution [156]. However, due to the strong intermolecular hydrogen bond between the amino group and the hydroxyl group in the molecular structure, chitosan can only be dissolved in acidic aqueous solution, and it is easy to precipitate in a weak acidic medium, which hinders the scope and field of its application. [157]. Yet, as a polyelectrolyte, chitosan can be made into carboxymethyl chitosan and other derivatives to modify adsorbents. Modified chitosan or a composite adsorbent with the incorporation of chitosan has a good adsorption effectiveness in the treatment of various pollutants such as dyes, pharmaceuticals, fluorine ions, organic pollutants, and heavy metals, thus showing a huge potential for water treatment applications. Ma et al. [158] used carboxymethyl-chitosan modified Nanomontmorillonite to remove chlortetracycline. Magnetic $NiFe_2O_4$ -COF-chitosan-terephthalaldehyde film was applied for the removal of

cefotaxime [159]. Tetracycline was removed by biochar modified by Chitosan-Fe/S [160]. Phasuphan et al. [161] created a new material, chitosan-modified waste tire crumb rubber which has good performance in the removal of diclofenac, ibuprofen and naproxen. The chitosan molecule contains many kinds of active functional groups, such as amino and hydroxyl groups, which confers on it a strong ability to coordinate with metal ions, so it can be used as an adsorbent to treat heavy metal ions in wastewater [162]. Upadhyay et al. [163] reviewed the recent achievements of chitosan-based adsorbents and their adsorption performance in the removal of heavy metals, discussed the commonly used modification methods, and studied the adsorption equilibrium and kinetics. After various synthetic processes, the modified chitosan adsorbent could effectively remove most heavy metal ions, such as Cd^{2+} [164], Cu^{2+} [165], Ni^{2+} [166], Pb^{2+} [167], Zn^{2+} [168], Cr^{6+} [169], Mn^{2+} [170], Co^{2+} [171], Fe^{3+} [172], Hg^{2+} [173], and Ag^+ [174] under different conditions. It was found that the pseudo-second order kinetic model and the Langmuir adsorption isotherm were applicable for most of these adsorption experiments.

3.3.4. Other polyelectrolytes for adsorbent modification

Other polyelectrolytes such as PAA, PSS, PAH and PAM have also been reported as modification reagents for adsorbents to remove contaminants in water treatment. PAA brush is selected as a modification molecule, due to the fact that its carboxyl group can not only react, but also has strong coordination ability for metal ions [175]. It has been used successfully to decorate kaolinite and synthesize new materials such as PAA-g-KLN for the removal of Cu^{2+} from wastewater [176]. Another application of kaolinite with PAA brush is to capture the valuable rare-earth element Ce^{3+} from wastewater [177]. The laterite soil after surface modification by PSS is used to remove cationic dyes from aqueous solution, and the removal efficiencies of crystal violet and methylene blue exceeded 92 % and 83 %, respectively [134]. The removal efficiency of the antibiotic ciprofloxacin (CFX) using PSS-modified alumina can reach 98 % [178]. New material composed of examethylene-1,6-bis(dodecyl dimethylammonium bromide) and 10 % hydrolyzed polyacrylamide showed great efficiency in the extraction of methyl orange from water, owing to the cooperation of electrostatic, hydrophobic, and π -cation interaction [179]. PAH covalently cross-linked amino-modified graphene oxide has shown highly efficient (with an adsorption capacity of 373 mg/g) and ultrafast (in 10s) removal of Cr(VI) in aqueous solution to ppb level, and the reusability of the adsorbent was confirmed for at least 10 cycles [180].

3.4. Polyelectrolyte-surfactant aggregates (PSAs) for metal removal and recovery

3.4.1. Polyelectrolyte-surfactant aggregates (PSAs) process

Based on studies of surfactant and polyelectrolyte systems in solution, an emerging process for the removal of metallic ions, such as heavy metals or precious metals, from aqueous effluents has been developed in work carried out by the Hankins research group at Oxford University [9,181–185]. The process uses oppositely charged polyelectrolyte and surfactant structures, called polyelectrolyte-surfactant aggregates (or polymer-surfactant aggregates, PSAs), which are suitable for effectively and rapidly removing the metallic ions at dilute concentrations in the form of flocs. In their published studies, which are reviewed below, a typical process used PEI as a back-bone structure, and sodium dodecyl sulfate (SDS) was used to form the aggregates. The resulting PSAs structures were rapidly able to remove metallic ions (such as heavy metals or precious metals) from the solution and, as a result, to quickly form large flocculated aggregates during low shear through a process of intermolecular association. These flocculated aggregates or flocs could then be easily separated from the effluent stream through a gravity settling or coarse filtration step. After this step, the retentate/sediment was treated via pH adjustment (i.e. acidification) to recover the bound metallic ions into a small volume of highly concentrated salt solution for

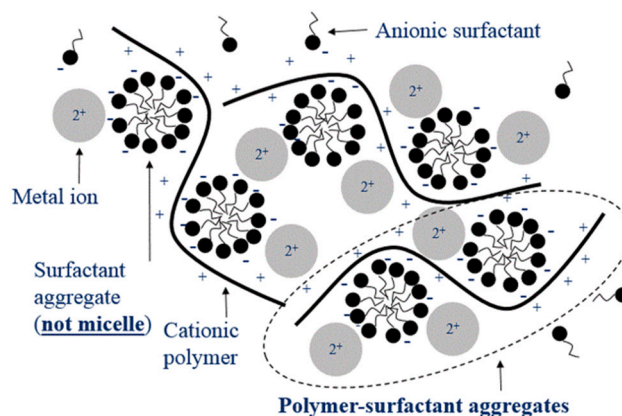


Fig. 4. A schematic of the polymer surfactant aggregate (complexation and flocculation) process [181].

either recycling back into an upstream manufacturing process or for selling directly as a product. After recovering the metallic ions from the flocs, the polyelectrolyte and surfactant flocs were dissolved into a moderately high pH solution and directly recycled, without a noticeable deterioration of removal ability in the next cycle. A schematic of the polyelectrolyte surfactant aggregates (complexation and flocculation) process to treat metal cations is shown in Fig. 4.

The PSA process operates in a homogenous aqueous phase, so that mass transfer kinetics is much faster than for the heterogeneous removal process to a solid-phase ion-exchange resin (minutes rather than hours). At the same time, the metal loading capacity per unit mass of PSA is much higher than that for the grafted resin. This is because the required mass of PSA is much lower than that of the grafted (and thus mostly unutilized) resin beads of ion-exchange media.

3.4.2. Removal of metals

Up to 99 % removal of 11.2 ppm Cd(II) was reported by Shen et al. [181] under an optimum PEI-SDS dosage using 40 ppm PEI and 0.5 mM SDS. In this study, metal ions were bound to the PSAs and these flocs were separated from the solution with a 20 μm coarse filter. The process demonstrated much higher removal efficiencies than was possible with MEUF or PEUF (which were 87 % and 86 %, respectively) and at dosages of polyelectrolyte and surfactant which were two orders of magnitude lower. It was also demonstrated that the process recovery efficiency was relatively insensitive to the presence of significant amounts of dissolved organic contaminants or salinity. In another detailed study to improve the operating efficiency of the recyclable PSA process for metal removal and recovery, branched PEI, SDS and Cu^{2+} were selected to investigate their interaction in aqueous solution [9]. PEI was able to form a strong complex with Cu^{2+} , with the most stable complex being formed at a PEI ligand/ Cu^{2+} chelation ratio of 4:1. The PEI-metal complex with positive charges reacted with negatively charged SDS to form hydrophobic aggregates. Acidification decreased the chelation capacity of PEI to Cu^{2+} , as a direct result of the competition from protons for amino groups, thus providing a strategy for metal release from PSAs. The removal of Cu^{2+} increased by increasing the total PEI concentration, or by increasing pH from 1 to above 4. The same PSA process was also tested at ppb levels for removal of the target metal ion [185], instead of at ppm levels, as attempted previously. This very dilute scenario might be the case for extremely valuable (e.g., precious metals) or highly toxic metals. It was possible to remove cadmium ions from 560 ppb down to 17 ppb (a removal of 97 %), using 2 ppm PEI and 0.02 mM SDS. Finally, it is noteworthy that in some tests the loading of the removal agent on to the PSAs increased to as high as 39 %. This high loading confers a significant advantage for precious metal recovery, because the precious metal could then be recovered directly and efficiently by pyrometallurgical methods.

In another ‘mirror image’ process developed by Shen et al. [184],

anionic polyelectrolytes such as poly(sodium 4-styrenesulfonate) (PSS) or poly(acrylic acid) (PAA) were used as a backbone structure onto which cationic surfactants such as myristyl trimethyl ammonium bromide (MTAB) were used as the flocculants to remove Cr and Fe ions in anionic form from aqueous solutions. The interaction among metallic anions, polyelectrolytes, and surfactants is different from that with the PEI-SDS process, as there is no coordination between polyelectrolytes and metals and electrostatic interactions instead appear to dominate the removal process prior to flocculation. This work has clearly proven that metallic anions can also be separated from aqueous solutions using the PSA process. 99 % of 0.1 mM $\text{Fe}(\text{CN})_6^{3-}$ and 80 % of 0.2 mM CrO_4^{2-} were removed from aqueous solutions. However, a disadvantage of this process is that, unlike with metallic cations, the removal efficiency can be

moderately affected by the presence of organic contaminants and salinity, because the electrostatic interaction between metallic anions and surfactants is then easily affected. In operational terms, however, the anionic removal process is similar to the cationic removal process, and with equally rapid kinetics. The general effects of the length of surfactant carbon chain on the PSA treatment performance were also investigated for removing dilute metallic anions from aqueous solutions [183]. The hydrophobicity of the surfactant can be enhanced by increasing the length of its carbon chain, along with other means such as branching and the addition of functional groups. The results of this work showed that an extended chain surfactant could decrease the concentration of chromate after treatment from 7 ppm to 0.5 ppm and the concentration of residual surfactant from 1 mM to 0.02 mM, using the same polymer. It was thus demonstrated that the PSAs formed with a longer chain surfactant enhanced the effectiveness of treating dilute metallic anions, and at the same time led to much less surfactant residue in the treated water. This is clearly an advantage when the quality of the treated water is important.

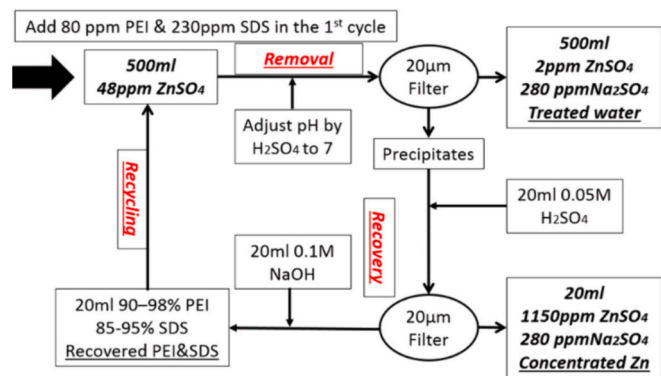


Fig. 5. Flow sheet diagram for the whole treatment process of the PSA (complexation and flocculation) process [182].

3.4.3. Recovery of metals and recycle of the PSAs

After the metal ion removal step, recovery of the metal ion, surfactant and polyelectrolyte were attempted. In subsequent studies by Shen et al. [182,186], the process was divided into three key steps: removal of metal ions, recovery of metal ions and recycle of polyelectrolytes and surfactants. The metal ions were recovered from the flocs within minutes as simple salts by acid leaching at pH 1. The concentration factor from the original effluent ranged from 20 to 50. An attempt was also made to recycle the polyelectrolyte and surfactant substrates by basification at pH 13 and reintroduction of the dissolved substrates to the upstream process. The overall process cycle was repeated in this way multiple

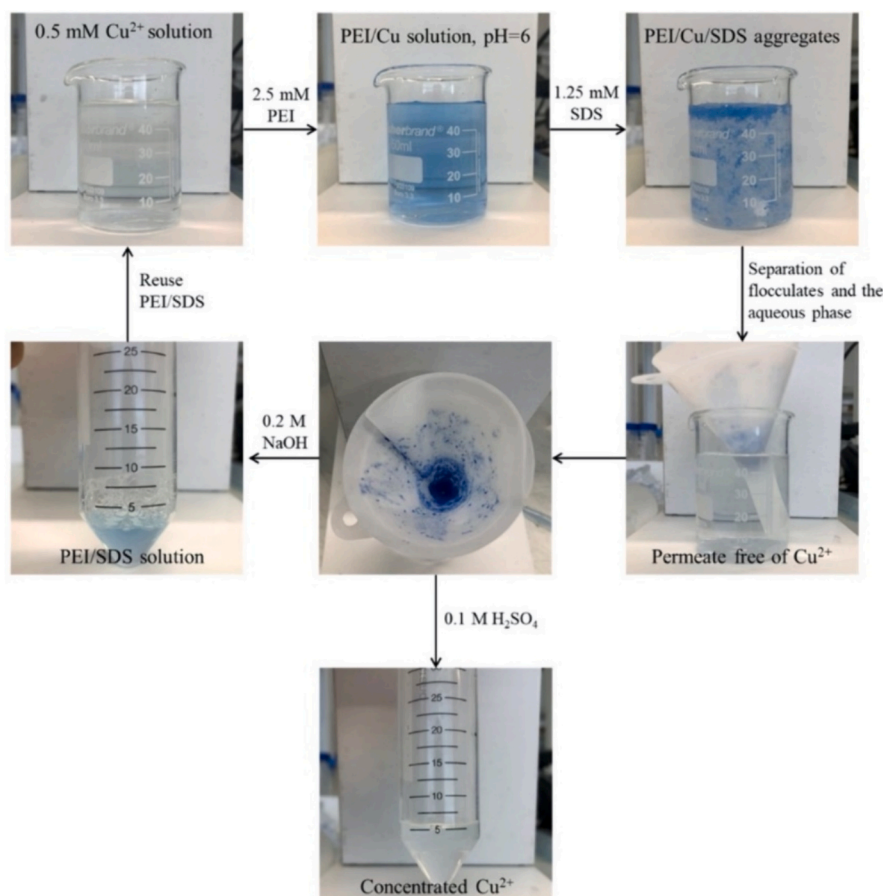


Fig. 6. Copper removal and recovery during 3 cycles using the PSAs process.

times, with little deterioration of removal ability. Fig. 5 presents a schematic of the overall process cycle.

The importance of pH adjustment was also demonstrated in the work by Chen and Hankins [9], as shown in Fig. 6. It was observed that the flocs on the filter paper turned white after acidification, since Cu^{2+} was then released, and the PEI and SDS could then be dissolved by basification and reused in a new cycle. Copper removal and recovery were up to 98 % and 88 % after 3 cycles of reuse, respectively.

4. Challenges and future opportunities

As shown in this review, polyelectrolytes have myriad potential applications in water and wastewater treatment processes, due to their varied and specialized properties. However, except for use as coagulants or flocculants during water and sludge treatment, other polyelectrolyte related processes have not yet been adopted as standard water treatment technologies. Thus, at present, there are no reported industrial-scale water treatment plants applying PEUF, polyelectrolyte modified membranes and adsorbents, or the PSA process. In order to reach such a milestone, it is clear that some key challenges need to be addressed or overcome to better promote polyelectrolyte related technologies in the field of water and wastewater treatment.

The loss of polyelectrolytes, the fouling of membranes caused by polyelectrolyte aggregation, and the need for the reuse of polyelectrolytes during PEUF are some of the current constraints of PEUF technology. The balance between membrane separation efficiency (i.e., flux) and the polyelectrolyte MW/membrane MWCO ratio needs more research.

Although attempts to recycle polyelectrolytes have been made in some investigations, more reliable and convenient recycling methods such as electrochemical techniques still need to be developed. The physical and chemical stability of membrane materials or adsorbents modified with polyelectrolytes is also an important concern.

Another obvious short-fall in previously published work in this field was the fact that studies were only performed on the removal of metal ions from single metal ion systems or the removal of all the metals together, with no studies on selective recovery of metal ions from streams which contain mixtures of them. This issue can usually be addressed by modifying the polyelectrolyte with functional groups to selectively capture target metals, e.g., the separation of precious metals from complex and competitive metal ion water matrices. In our latest work (as yet unpublished), a functionalized PEI was synthesized and applied with SDS for Cu (II) selective recovery from Fe (III) in highly acidic aqueous streams, such as occur in acid mine drainage. In this work, the removal performance was compared with unfunctionalized PEI as well as with conventional ion exchange resins, including functionalized (grafted) silica beads. Using the functionalized PEI polymer at low pH, the PSA process selectively removed Cu (II) from Fe (III) in a short time, removing in a matter of seconds up to 90 % of 100 mg/L Cu (II) from a mixture with 500 mg/L Fe (III). On the other hand, the unfunctionalized amino groups in PEI were non-chelating and protonated and were thus non-selective. Whenever such a modified PEI is to be used for the selective removal of copper from iron and other ions, further study is required on the metal recovery and polyelectrolyte/surfactant recycle. In future work, it may be necessary to tune the strength of chelation through functionalization, or change the polymer backbone, to achieve the best balance between metal removal and subsequent recovery. Potentially, this implies that the level of metal removal may need to be sacrificed to facilitate the recovery and recycle steps.

5. Summary

Polyelectrolytes are a type of water-soluble polymer with a multitude of ionizable groups and are used in various industrial fields, because the combination of their polymeric characteristics and electrolytic behaviour confers on them various useful properties. Polyelectrolytes have

been introduced into water and wastewater treatment due to their potential as functional materials to remove contaminants from aqueous solutions, and to enhance the technical efficiency of water processing. The most common and mature existing application of polyelectrolytes is where they are used in the coagulation and flocculation process, as well as in sludge dewatering. Polyelectrolytes can also be used directly as water treatment materials or indirectly as additives or modifiers to improve existing water treatment processes, based in both cases on their interaction with contaminants. Polyelectrolytes generally operate in this context via bonding or capturing contaminants during the water treatment process, and (especially for ionic contaminants) due to two dominant interactions in particular; coordination complexation, and electrostatic association. The different applications of polyelectrolytes for contaminant removal from water are reviewed in the current paper, including PEUF, the application of polyelectrolytes to efficiently or functionally modify membranes and adsorbents, and the formation of polyelectrolyte-surfactant aggregates to recover metals from water. Some key challenges need to be addressed or overcome to better promote these polyelectrolyte related technologies, such as membrane fouling mitigation, the simple and steady recycle of polyelectrolytes, and the modification of polyelectrolytes to enhance the selectivity of contaminant removal.

CRediT authorship contribution statement

Ming Chen: Conceptualization, Project administration, Supervision, Writing – original draft. **Ruibo Xu:** Data curation, Software, Validation, Writing – original draft. **Yichen Wu:** Conceptualization, Writing – original draft. **Jianglei Xiong:** Funding acquisition, Project administration, Writing – original draft. **Seda Zeynep Keleş:** Investigation, Validation, Writing – original draft. **Nicholas P. Hankins:** Conceptualization, Supervision, Writing – review & editing, Formal analysis, Writing – original draft.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Dr. Ming Chen serves in the Early Career Editorial Board of the journal. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

- [1] W.P. Cheng, A.I. Gray, L. Tetley, T.L.B. Hang, A.G. Schätzlein, I.F. Uchegbu, Polyelectrolyte nanoparticles with high drug loading enhance the oral uptake of hydrophobic compounds, *Biomacromolecules* 7 (2006) 1509–1520.
- [2] S. Llamas, E. Guzman, F. Ortega, N. Baghdadli, C. Cazeneuve, R.G. Rubio, G. S. Luengo, Adsorption of polyelectrolytes and polyelectrolytes-surfactant mixtures at surfaces: a physico-chemical approach to a cosmetic challenge, *Adv. Colloid Interface Sci.* 222 (2015) 461–487.
- [3] V.S. Meka, M.K. Sing, M.R. Pichika, S.R. Nali, V.R. Kolapalli, P. Kesharwani, A comprehensive review on polyelectrolyte complexes, *Drug Discov. Today* 22 (2017) 1697–1706.

- [4] M. Veisi, S. Johnson, K. Shafer-Peltier, J.T. Liang, C. Berkland, M. Chen, R. Barati, Controlled release of poly (vinyl sulfonate) scale inhibitor to extend reservoir treatment lifetime, *J. Appl. Polym. Sci.* 136 (2019) 47225.
- [5] K. Shafer-Peltier, C. Kenner, E. Albertson, M. Chen, S. Randtke, E. Peltier, Removing scale-forming cations from produced waters, *Environ. Sci.: Water Res. Technol.* 6 (2020) 132–143.
- [6] H. Strathmann, Selective removal of heavy metal ions from aqueous solutions by diafiltration of macromolecular complexes, *Sep. Sci. Technol.* 15 (1980) 1135–1152.
- [7] B.Y. Spivakov, K. Geckeler, E. Bayer, Liquid-phase polymer-based retention—the separation of metals by ultrafiltration on polychelators, *Nature* 315 (1985) 313–315.
- [8] D.A. Palacio, B.F. Urbano, B.L. Rivas, Application of nanocomposite polyelectrolytes for the removal of antibiotics as emerging pollutants in water, *Journal of Water Process Engineering* 46 (2022) 102582.
- [9] M. Chen, N.P. Hankins, Interaction among branched polyethylenimine (PEI), sodium dodecyl sulfate (SDS) and metal cations during copper recovery from water using polymer-surfactant aggregates, *Journal of Water Process Engineering* 34 (2020) 101170.
- [10] S. Ilyas, S.M. Abtahi, N. Akkiliç, H.D.W. Roesink, W.M. de Vos, Weak polyelectrolyte multilayers as tunable separation layers for micro-pollutant removal by hollow fiber nanofiltration membranes, *J. Membr. Sci.* 537 (2017) 220–228.
- [11] B. Bolto, J. Gregory, Organic polyelectrolytes in water treatment, *Water Res.* 41 (2007) 2301–2324.
- [12] B. Bolto, Z. Xie, The use of polymers in the flotation treatment of wastewater, *Processes* 7 (2019) 374.
- [13] S. Jabin, J. Kapoor, Role of polyelectrolytes in the treatment of water and wastewater, in: *Sustainable Green Chemical Processes and Their Allied Applications*, 2020, pp. 289–309.
- [14] S. Jabin, P. Gupta, M. Sharma, Polyelectrolytes as a material of value in water treatment: a review, *Asian Journal of Water, Environment and Pollution* 18 (2021) 109–115.
- [15] Y. Qi, K.B. Thapa, A.F. Hoadley, Application of filtration aids for improving sludge dewatering properties—a review, *Chem. Eng. J.* 171 (2011) 373–384.
- [16] A. Neitzel, G. Hoe, M. Tirrel, Expanding the structural diversity of polyelectrolyte complexes and polyzwitterions, *Curr. Opin. Solid State Mater. Sci.* 25 (2021) 100897.
- [17] S.M.R. Shaikh, M.S. Nasser, I. Hussein, A. Benamor, S.A. Onaizi, H. Qiblawey, Influence of polyelectrolytes and other polymer complexes on the flocculation and rheological behaviors of clay minerals: a comprehensive review, *Sep. Purif. Technol.* 187 (2017) 137–161.
- [18] M.E. Elhalwagy, A.S. Elsherbiny, A.H. Gemeay, Amine-rich polymers for water purification applications, *Materials Today Chemistry* 27 (2023) 101344.
- [19] W. Jaeger, J. Bohrisch, A. Laschewsky, Synthetic polymers with quaternary nitrogen atoms synthesis and structure of the most used type of cationic polyelectrolytes, *Prog. Polym. Sci.* 35 (2010) 511–577.
- [20] A. Laschewsky, Recent trends in the synthesis of polyelectrolytes, *Curr. Opin. Colloid Interface Sci.* 17 (2012) 56–63.
- [21] M. Chen, K. Shafer-Peltier, M. Veisi, S. Randtke, E. Peltier, Complexation and precipitation of scale-forming cations in oilfield produced water with polyelectrolytes, *Sep. Purif. Technol.* 222 (2019) 1–10.
- [22] J. Bratby, Coagulation and flocculation in water and wastewater treatment - second edition, *Water Intelligence Online* 5 (2006).
- [23] J.S. Wang, J.C. Liu, D.J. Lee, Dual conditioning of sludge utilizing polyampholyte, *J. Environ. Eng.* 131 (2005) 1659–1666.
- [24] F.K. Katrivesis, A.D. Karela, V.G. Papadakis, C.A. Paraskeva, Revisiting of coagulation-flocculation processes in the production of potable water, *Journal of Water Process Engineering* 27 (2019) 193–204.
- [25] J.D. Roach, D. Tush, Equilibrium dialysis and ultrafiltration investigations of perchlorate removal from aqueous solution using poly (diallyldimethylammonium) chloride, *Water Res.* 42 (2008) 1204–1210.
- [26] K. Geckeler, G. Lange, H. Eberhardt, E. Bayer, Preparation and application of water-soluble polymer-metal complexes, *Pure Appl. Chem.* 52 (1980) 1883–1905.
- [27] Y. Huang, X. Feng, Polymer-enhanced ultrafiltration: fundamentals, applications and recent developments, *J. Membr. Sci.* 586 (2019) 53–83.
- [28] P. Teyssie, C. Decoene, M.T. Teyssie, Structure and properties of polymeric chelates. 4. Structure and shape of polyvinylamine chelates in aqueous solution, *Makromolekulare Chemie* 84 (1965) (51–8).
- [29] L. Besra, D.K. Sengupta, S.K. Roy, P. Ay, Influence of surfactants on flocculation and dewatering of kaolin suspensions by cationic polyacrylamide (PAM-C) flocculant, *Sep. Purif. Technol.* 30 (2003) 251–264.
- [30] M. Chen, K. Shafer-Peltier, S.J. Randtke, E. Peltier, Competitive association of cations with poly(sodium 4-styrenesulfonate) (PSS) and heavy metal removal from water by PSS-assisted ultrafiltration, *Chem. Eng. J.* 344 (2018) 155–164.
- [31] A. Tabatabai, J.F. Scamehorn, S.D. Christian, Economic-feasibility study of polyelectrolyte-enhanced ultrafiltration (PEUF) for water softening, *J. Membr. Sci.* 100 (1995) 193–207.
- [32] A. Tabatabai, J.F. Scamehorn, S.D. Christian, Water softening using polyelectrolyte-enhanced ultrafiltration, *Sep. Sci. Technol.* 30 (1995) 211–224.
- [33] J.H. Zhu, J.C. Shu, X.J. Yue, Y.P. Su, Hollow and porous octacalcium phosphate superstructures mediated by the polyelectrolyte PSS: a superior removal capacity for heavy metal and antibiotics, *J. Mater. Sci.* 55 (2020) 7502–7517.
- [34] J.J. Beh, B.S. Ooi, J.K. Lim, E.P. Ng, H. Mustapa, Development of high water permeability and chemically stable thin film nanocomposite (TFN) forward osmosis (FO) membrane with poly(sodium 4-styrenesulfonate) (PSS)-coated zeolitic imidazolate framework-8 (ZIF-8) for produced water treatment, *Journal of Water Process Engineering* 33 (2020).
- [35] C.J. Dong, R.R. He, S.S. Xu, H.L. He, H. Chen, Y.B. Zhang, T. He, Layer-by-layer (LBL) hollow fiber nanofiltration membranes for seawater treatment: ion rejection, *Desalination* 534 (2022).
- [36] V. Khutoryansky, Hydrogen-bonded interpolymer complexes as materials for pharmaceutical applications, *Int. J. Pharm.* 334 (2007) 15–26.
- [37] Z.S. Nurkeeva, V.V. Khutoryanskiy, G.A. Mun, M.V. Sherbakova, A.T. Ivaschenko, N.A. Aitkhodzina, Polycomplexes of poly(acrylic acid) with streptomycin sulfate and their antibacterial activity, *Eur. J. Pharm. Biopharm.* 57 (2004) 245–249.
- [38] J. Miao, R. Zhang, R.B. Bai, Poly (vinyl alcohol)/carboxymethyl cellulose sodium blend composite nanofiltration membranes developed via interfacial polymerization, *J. Membr. Sci.* 493 (2015) 654–663.
- [39] P.M. Pakdel, S.J. Peighambari, Review on recent progress in chitosan-based hydrogels for wastewater treatment application, *Carbohydr. Polym.* 201 (2018) 264–279.
- [40] U. Upadhyay, I. Sreedhar, S.A. Singh, C.M. Patel, K.L. Anitha, Recent advances in heavy metal removal by chitosan based adsorbents, *Carbohydr. Polym.* 251 (2021).
- [41] H. Karimi-Maleh, A. Ayati, R. Davoodi, B. Tanhaei, F. Karimi, S. Malekmohammadi, Y. Orooji, L. Fu, M. Sillanpaa, Recent advances in using of chitosan-based adsorbents for removal of pharmaceutical contaminants: a review, *J. Clean. Prod.* 291 (2021).
- [42] B. Rivas, C. Espinosa, J. Sánchez, Application of the liquid-phase polymer-based retention technique to the sorption of molybdenum(VI) and vanadium(V), *Polym. Bull.* 76 (2019).
- [43] X. Zhang, D. Lin, W. Chen, Nitrogen-doped porous carbon prepared from liquid carbon precursor for CO₂ adsorption, *RSC Adv.* 5 (2015).
- [44] Z. Tong, W.S.W. Ho, New sterically hindered polyvinylamine membranes for CO₂ separation and capture, *J. Membr. Sci.* 543 (2017) 202–211.
- [45] D.M. Reurink, E. te Brinke, I. Achterhuis, H.D.W. Roesink, W.M. de Vos, Nafion-based low-hydration polyelectrolyte multilayer membranes for enhanced water purification, *ACS Applied Polymer Materials* 1 (2019) 2543–2551.
- [46] B. Xiong, R.D. Loss, D. Shields, T. Pawlik, R. Hochreiter, A.L. Zydney, M. Kumar, Polyacrylamide degradation and its implications in environmental systems, *npj Clean Water* 1 (2018) 17.
- [47] M. Abdel Khalek, H. Ahmed, A. El-Midany, High molecular weight poly(sodium 4-styrene sulfonate) - bentonite interaction, *Journal of Ore Dressing* 17 (2015) 12–17.
- [48] S. Vats, L. Honaker, M. Frey, F. Basoli, J. Lagerwall, Electrospinning ethanol-water solutions of poly(acrylic acid): non-linear viscosity variations and dynamic Taylor cone behavior, *Macromol. Mater. Eng.* 307 (2021).
- [49] M. Saiful, M.S.A. Rani, S. Che Balian, A. Ahmad, N.S. Mohamed, Biopolymer electrolyte based on derivatives of cellulose from kenaf bast fiber, *Polymers* 6 (2014) 2371–2385.
- [50] B. Teixeira-Costa, C. Andrade, Chitosan as a valuable biomolecule from seafood industry waste in the design of green food packaging, *Biomolecules* 11 (2021) 1599.
- [51] B.L. Rivas, E.D. Pereira, I. Moreno-Villoslada, Water-soluble polymer-metal ion interactions, *Prog. Polym. Sci.* 28 (2003) 173–208.
- [52] C.F. Couto, L.C. Lange, M.C.S. Amaral, A critical review on membrane separation processes applied to remove pharmaceutically active compounds from water and wastewater, *Journal of Water Process Engineering* 26 (2018) 156–175.
- [53] S. Al Aani, T.N. Mustafa, N. Hilal, Ultrafiltration membranes for wastewater and water process engineering: a comprehensive statistical review over the past decade, *Journal of Water Process Engineering* 35 (2020) 101241.
- [54] M. Chen, C.T. Jafvert, Application of cross-linked stearic acid nanoparticles with dialysis membranes for methylene blue recovery, *Sep. Purif. Technol.* 204 (2018) 21–29.
- [55] M. Chen, C.T. Jafvert, Anion recovery from water by cross-linked cationic surfactant nanoparticles across dialysis membranes, *Environmental Science: Nano* 5 (2018) 1350–1360.
- [56] E.M. Wilts, J. Herzberger, T.E. Long, Addressing water scarcity: cationic polyelectrolytes in water treatment and purification, *Polym. Int.* 67 (2018) 799–814.
- [57] M. Schwarze, Micellar-enhanced ultrafiltration (MEUF)—state of the art, *Environmental Science: Water Research & Technology* 3 (2017) 598–624.
- [58] M. Chen, C.T. Jafvert, Y. Wu, X. Cao, N.P. Hankins, Inorganic anion removal using micellar enhanced ultrafiltration (MEUF), modeling anion distribution and suggested improvements of MEUF: a review, *Chem. Eng. J.* 398 (2020) 125413.
- [59] M. Chen, K. Shafer-Peltier, S.J. Randtke, E. Peltier, Modeling arsenic (V) removal from water by micellar enhanced ultrafiltration in the presence of competing anions, *Chemosphere* 213 (2018) 285–294.
- [60] T.T.H. Dang, C.-W. Li, K.-H. Choo, Comparison of low-pressure reverse osmosis filtration and polyelectrolyte-enhanced ultrafiltration for the removal of Co and Sr from nuclear plant wastewater, *Sep. Purif. Technol.* 157 (2016) 209–214.
- [61] S. Santoro, P. Timpano, A.H. Avci, P. Argurio, F. Chidichimo, M. De Biase, S. Straface, E. Curcio, An integrated membrane distillation, photocatalysis and polyelectrolyte-enhanced ultrafiltration process for arsenic remediation at point-of-use, *Desalination* 520 (2021) 115378.
- [62] Q.T. Nguyen, P. Aptel, J. Neel, Investigation of the amylose-iodine complexation in aqueous solution by ultrafiltration, *Biopolymers: Original Research on Biomolecules* 15 (1976) 2097–2100.
- [63] K.J. Sasaki, S.L. Burnett, S.D. Christian, E.E. Tucker, J.F. Scamehorn, Polyelectrolyte ultrafiltration of multivalent ions. Removal of copper (2+) by sodium poly (styrenesulfonate), *Langmuir* 5 (1989) 363–369.

- [64] B. Chaufer, A. Deratani, Removal of metal ions by complexation-ultrafiltration using water-soluble macromolecules: perspective of application to wastewater treatment, *Nuclear and Chemical Waste Management* 8 (1988) 175–187.
- [65] D. Gallo, E.J. Acosta, J.F. Scamehorn, D.A. Sabatini, Pilot-scale study of polyelectrolyte-enhanced UF for arsenic removal, *Journal American Water Works Association* 98 (2006) 106–116.
- [66] J.F. Scamehorn, S.D. Christian, E.E. Tucker, B.I. Tan, Concentration polarization in polyelectrolyte-enhanced ultrafiltration, *Colloids Surf.* 49 (1990) 259–267.
- [67] M. Hammami, D.J. Ennigrou, K. Horchani-Naifer, M. Ferid, Comparative study of neodymium recovery from aqueous solutions by polyelectrolytes assisted-ultrafiltration, *Korean J. Chem. Eng.* 35 (2018) 518–525.
- [68] N.B. Kraiem, D.J. Ennigrou, K. Zlaoui, K. Horchani-Naifer, Lanthanum recovery from aqueous solutions by polyelectrolytes assisted ultrafiltration, *Desalin. Water Treat.* 204 (2020) 348–355.
- [69] Y. Uludag, H.Ö. Özbelge, L. Yilmaz, Removal of mercury from aqueous solutions via polymer-enhanced ultrafiltration, *J. Membr. Sci.* 129 (1997) 93–99.
- [70] J. Muslehiddinoglu, Y. Uludag, H.O. Ozbelge, L. Yilmaz, Effect of operating parameters on selective separation of heavy metals from binary mixtures via polymer enhanced ultrafiltration, *J. Membr. Sci.* 140 (1998) 251–266.
- [71] C.-W. Li, C.-H. Cheng, K.-H. Choo, W.-S. Yen, Polyelectrolyte enhanced ultrafiltration (PEUF) for the removal of Cd(II): effects of organic ligands and solution pH, *Chemosphere* 72 (2008) 630–635.
- [72] Y. Huang, D. Wu, X. Wang, W. Huang, D. Lawless, X. Feng, Removal of heavy metals from water using polyvinylamine by polymer-enhanced ultrafiltration and flocculation, *Sep. Purif. Technol.* 158 (2016) 124–136.
- [73] M.A. Barakat, E. Schmidt, Polymer-enhanced ultrafiltration process for heavy metals removal from industrial wastewater, *Desalination* 256 (2010) 90–93.
- [74] Y.-H. Chou, K.-H. Choo, S.-S. Chen, J.-H. Yu, C.-Y. Peng, C.-W. Li, Copper recovery via polyelectrolyte enhanced ultrafiltration followed by dithionite based chemical reduction: effects of solution pH and polyelectrolyte type, *Sep. Purif. Technol.* 198 (2018) 113–120.
- [75] S. Tang, Y. Qiu, Removal of Zn (II) by complexation-ultrafiltration using rotating disk membrane and the shear stability of PAA-Zn complex, *Korean J. Chem. Eng.* 35 (2018) 2078–2085.
- [76] Q. Meng, J. Nan, Y. Mu, X. Zu, M. Guo, Study on the treatment of sudden cadmium pollution in surface water by a polymer enhanced ultrafiltration process, *RSC Adv.* 11 (2021) 7405–7415.
- [77] J.D. Roach, R.F. Lane, Y. Hussain, Comparative study of the uses of poly(4-vinylpyridine) and poly(diallyldimethylammonium) chloride for the removal of perchlorate from aqueous solution by polyelectrolyte-enhanced ultrafiltration, *Water Res.* 45 (2011) 1387–1393.
- [78] X. Tan, W.K. Teo, K. Li, Removal of chromate ions from water using the polyelectrolyte-enhanced ultrafiltration process, *Sep. Sci. Technol.* 43 (2008) 477–489.
- [79] S. Sriratana, J.F. Scamehorn, S. Chavadej, C. Saiwan, K.J. Haller, S.D. Christian, E.E. Tucker, Use of polyelectrolyte-enhanced ultrafiltration to remove chromate from water, *Sep. Sci. Technol.* 31 (1996) 2493–2504.
- [80] K. Roa, A. Boulett, E. Oyarce, J. Sánchez, Removal of Cr(VI) by ultrafiltration enhanced by a cellulose-based soluble polymer, *Journal of Water Process Engineering* 51 (2023) 103478.
- [81] X.S. Zhu, K.H. Choo, J.M. Park, Nitrate removal from contaminated water using polyelectrolyte-enhanced ultrafiltration, *Desalination* 193 (2006) 350–360.
- [82] C.O. Doganay, H.O. Ozbelge, L. Yilmaz, N. Bıçak, Removal and recovery of metal anions via functional polymer based PEUF, *Desalination* 200 (2006) 286–287.
- [83] S. Tangvijitsri, C. Saiwan, C. Soponvuttikul, J.F. Scamehorn, Polyelectrolyte-enhanced ultrafiltration of chromate, sulfate, and nitrate, *Sep. Sci. Technol.* 37 (2002) 993–1007.
- [84] P. Pookrod, K.J. Haller, J.F. Scamehorn, Removal of arsenic anions from water using polyelectrolyte-enhanced ultrafiltration, *Sep. Sci. Technol.* 39 (2004) 811–831.
- [85] H.P. Huq, J.-S. Yang, J.-W. Yang, Removal of perchlorate from groundwater by the polyelectrolyte-enhanced ultrafiltration process, *Desalination* 204 (2007) 335–343.
- [86] C. Haktanır, H.Ö. Özbelge, N. Bıçak, L. Yılmaz, Removal of hexavalent chromium anions via polymer enhanced ultrafiltration using a fully ionized polyelectrolyte, *Sep. Sci. Technol.* 52 (2017) 2487–2497.
- [87] R.S. Juang, C.H. Chiou, Feasibility of the use of polymer-assisted membrane filtration for brackish water softening, *J. Membr. Sci.* 187 (2001) 119–127.
- [88] J. Dasgupta, J. Sikder, T. Mandal, U. Adhikari, Reactive red 120 retention through ultrafiltration enhanced by synthetic and natural polyelectrolytes, *J. Hazard. Mater.* 299 (2015) 192–205.
- [89] C. Cojocaru, L. Clima, Polymer assisted ultrafiltration of AO7 anionic dye from aqueous solutions: experimental design, multivariate optimization, and molecular docking insights, *J. Membr. Sci.* 604 (2020) 118054.
- [90] E. Oyarce, P. Santander, B. Butter, G.D.C. Pizarro, J. Sánchez, Use of sodium alginate biopolymer as an extracting agent of methylene blue in the polymer-enhanced ultrafiltration technique, *J. Appl. Polym. Sci.* 138 (2021) 50844.
- [91] E. Oyarce, K. Roa, A. Boulett, S. Sotelo, P. Cantero-López, J. Sánchez, B.L. Rivas, Removal of dyes by polymer-enhanced ultrafiltration: an overview, in: *Polymers*, 2021.
- [92] G. Chakraborty, A. Bhattarai, R. De, Polyelectrolyte–dye interactions: an overview, in: *Polymers*, 2022.
- [93] T. Izumi, K. Takahashi, M. Hirata, Interactions of water-soluble polymers with small molecules I: poly(2-diethylaminoethyl methacrylate)-orange II and ethyl orange systems, *Colloid Polym. Sci.* 264 (1986) 748–755.
- [94] Y. Yu, Y.Y. Zhuang, Q.M. Zou, Interactions between organic flocculant PAN-DCC and dyes, *Chemosphere* 44 (2001) 1287–1292.
- [95] E. Oyarce, B. Butter, P. Santander, J. Sánchez, Polyelectrolytes applied to remove methylene blue and methyl orange dyes from water via polymer-enhanced ultrafiltration, *J. Environ. Chem. Eng.* 9 (2021) 106297.
- [96] X. Tan, N.N. Kyaw, W.K. Teo, K. Li, Decolorization of dye-containing aqueous solutions by the polyelectrolyte-enhanced ultrafiltration (PEUF) process using a hollow fiber membrane module, *Sep. Purif. Technol.* 52 (2006) 110–116.
- [97] H. Ouni, M. Dhahbi, Spectrometric study of crystal violet in presence of polyacrylic acid and polyethylenimine and its removal by polyelectrolyte enhanced ultrafiltration, *Sep. Purif. Technol.* 72 (2010) 340–346.
- [98] A.B. Fradj, S.B. Hamouda, H. Ouni, R. Lafi, L. Gzara, A. Hafiane, Removal of methylene blue from aqueous solutions by poly(acrylic acid) and poly(ammonium acrylate) assisted ultrafiltration, *Sep. Purif. Technol.* 133 (2014) 76–81.
- [99] M. Schwarze, D. Seo, B. Bibouche, R. Schomäcker, Comparison of positively charged polymer species and cationic surfactants for methyl orange removal via polyelectrolyte and micellar enhanced ultrafiltration, *Journal of Water Process Engineering* 36 (2020) 101287.
- [100] E.N. Durmaz, S. Sahin, E. Virga, S. de Beer, L.C. de Smet, W.M. de Vos, Polyelectrolytes as building blocks for next-generation membranes with advanced functionalities, *ACS Applied Polymer Materials* 3 (9) (2021) 4347–4374.
- [101] B. Ladewig, M.N.Z. Al-Shaeli, Fundamentals of membrane processes, in: *Fundamentals of Membrane Bioreactors*, Springer, 2017, pp. 13–37.
- [102] F. Meng, F. Song, Y. Yao, G. Liu, S. Zhao, Ultrastable nanofiltration membranes engineered by polydopamine-assisted polyelectrolyte layer-by-layer assembly for water reclamation, *ACS Sustain. Chem. Eng.* 8 (2020) 10928–10938.
- [103] W. Cheng, C. Liu, T. Tong, R. Epsztein, M. Sun, R. Verduzco, J. Ma, M. Elimelech, Selective removal of divalent cations by polyelectrolyte multilayer nanofiltration membrane: role of polyelectrolyte charge, ion size, and ionic strength, *J. Membr. Sci.* 559 (2018) 98–106.
- [104] M. Elshof, W. de Vos, J. de Grooth, N. Benes, On the long-term pH stability of polyelectrolyte multilayer nanofiltration membranes, *J. Membr. Sci.* 615 (2020) 118532.
- [105] B. Wu, X.-D. Weng, N. Wang, M.-J. Yin, L. Zhang, Q.-F. An, Chlorine-resistant positively charged polyamide nanofiltration membranes for heavy metal ions removal, *Sep. Purif. Technol.* 275 (2021) 119264.
- [106] Q. Zhao, Q.F. An, Y. Ji, J. Qian, C. Gao, Polyelectrolyte complex membranes for pervaporation, nanofiltration and fuel cell applications, *J. Membr. Sci.* 379 (2011) 19–45.
- [107] G. Decher, J.D. Hong, Buildup of ultrathin multilayer films by a self-assembly process, 1 consecutive adsorption of anionic and cationic bipolar amphiphiles on charged surfaces, in: *Makromolekulare Chemie. Macromolecular Symposia*, Wiley Online Library, 1991, pp. 321–327.
- [108] J. de Grooth, D.M. Reurink, J. Ploegmakers, W.M. de Vos, K. Nijmeijer, Charged micropollutant removal with hollow fiber nanofiltration membranes based on polycation/polyzwitterion/polyanion multilayers, *ACS Appl. Mater. Interfaces* 6 (2014) 17009–17017.
- [109] C. Liu, L. Shi, R. Wang, Crosslinked layer-by-layer polyelectrolyte nanofiltration hollow fiber membrane for low-pressure water softening with the presence of SO4²⁻ in feed water, *J. Membr. Sci.* 486 (2015) 169–176.
- [110] J.M. Thomas, V. Radhakrishnan, C. Aravindakumar, U.K. Aravind, Polyelectrolyte functional bilayers for the removal of model emerging contaminants, *Ind. Eng. Chem. Res.* 56 (2017) 13874–13884.
- [111] Z. Ouyang, Z. Huang, X. Tang, C. Xiong, M. Tang, Y. Lu, A dually charged nanofiltration membrane by pH-responsive polydopamine for pharmaceuticals and personal care products removal, *Sep. Purif. Technol.* 211 (2019) 90–97.
- [112] Y. Wang, I. Zucker, C. Boo, M. Elimelech, Removal of emerging wastewater organic contaminants by polyelectrolyte multilayer nanofiltration membranes with tailored selectivity, *ACS ES&T Engineering* 1 (2020) 404–414.
- [113] S.M. Abtahi, L. Marbelia, A.Y. Gebreyohannes, P. Ahmadiannamini, C. Joannis-Cassan, C. Albasi, W.M. de Vos, I.F. Vankelecom, Micropollutant rejection of annealed polyelectrolyte multilayer based nanofiltration membranes for treatment of conventionally-treated municipal wastewater, *Sep. Purif. Technol.* 209 (2019) 470–481.
- [114] D. Scheepers, B. Chatillon, Z. Borneman, K. Nijmeijer, Influence of charge density and ionic strength on diallyldimethylammonium chloride (DADMAC)-based polyelectrolyte multilayer membrane formation, *J. Membr. Sci.* 617 (2021) 118619.
- [115] L.Y. Ng, A.W. Mohammad, C.Y. Ng, A review on nanofiltration membrane fabrication and modification using polyelectrolytes: effective ways to develop membrane selective barriers and rejection capability, *Adv. Colloid Interface Sci.* 197 (2013) 85–107.
- [116] E. Virga, J. de Grooth, K. Žvab, W.M. de Vos, Stable polyelectrolyte multilayer-based hollow fiber nanofiltration membranes for produced water treatment, *ACS Applied Polymer Materials* 1 (2019) 2230–2239.
- [117] R. Malaissamy, A. Talla-Nwafo, K.L. Jones, Polyelectrolyte modification of nanofiltration membrane for selective removal of monovalent anions, *Sep. Purif. Technol.* 77 (2011) 367–374.
- [118] C.V. Gherasim, T. Luelf, H. Roth, M. Wessling, Dual-charged hollow fiber membranes for low-pressure nanofiltration based on polyelectrolyte complexes: one-step fabrication with tailored functionalities, *ACS Appl. Mater. Interfaces* 8 (2016) 19145–19157.
- [119] W. Lau, A. Ismail, N. Misdan, M. Kassim, A recent progress in thin film composite membrane: a review, *Desalination* 287 (2012) 190–199.

- [120] C. Liu, L. Cheng, Y. Zhao, L. Zhu, Interfacially crosslinked composite porous membranes for ultrafast removal of anionic dyes from water through permeating adsorption, *J. Hazard. Mater.* 337 (2017) 217–225.
- [121] S.P. Sun, T.A. Hatton, T.-S. Chung, Hyperbranched polyethyleneimine induced cross-linking of polyamide-imide nanofiltration hollow fiber membranes for effective removal of ciprofloxacin, *Environ. Sci. Technol.* 45 (2011) 4003–4009.
- [122] S. Zhao, C. Ba, Y. Yao, W. Zheng, J. Economy, P. Wang, Removal of antibiotics using polyethylenimine cross-linked nanofiltration membranes: relating membrane performance to surface charge characteristics, *Chem. Eng. J.* 335 (2018) 101–109.
- [123] L. Shan, H. Guo, Z. Qin, N. Wang, S. Ji, G. Zhang, Z. Zhang, Covalent crosslinked polyelectrolyte complex membrane with high negative charges towards anti-natural organic matter fouling nanofiltration, *RSC Adv.* 5 (2015) 11515–11523.
- [124] C. Qiu, S. Qi, C.Y. Tang, Synthesis of high flux forward osmosis membranes by chemically crosslinked layer-by-layer polyelectrolytes, *J. Membr. Sci.* 381 (2011) 74–80.
- [125] Z. Yang, Y. Zhou, Z. Feng, X. Rui, T. Zhang, Z. Zhang, A review on reverse osmosis and nanofiltration membranes for water purification, *Polymers* 11 (2019) 1252.
- [126] G. Han, T.-S. Chung, M. Weber, C. Maletzko, Low-pressure nanofiltration hollow fiber membranes for effective fractionation of dyes and inorganic salts in textile wastewater, *Environ. Sci. Technol.* 52 (2018) 3676–3684.
- [127] R.W. Baker, *Membrane Technology and Applications*, John Wiley & Sons, 2012.
- [128] R.M. Rajendran, S. Garg, S. Bajpai, Study of transport models for arsenic removal using nanofiltration process: recent perspectives, in: *Emerging Technologies in Environmental Bioremediation*, Elsevier, 2020, pp. 391–405.
- [129] E. te Brinke, I. Achterhuis, D.M. Reurink, J. de Groot, W.M. de Vos, Multiple approaches to the buildup of asymmetric polyelectrolyte multilayer membranes for efficient water purification, *ACS Applied Polymer Materials* 2 (2020) 715–724.
- [130] Z. Abbasi, M. Alikarami, Kinetics and thermodynamics studies of acetic acid adsorption from aqueous solution by peels of banana, *Biochemistry and Bioinformatics* 1 (2012) 1–7.
- [131] A.C. Sadiq, A. Olasupo, W.S.W. Ngah, N.Y. Rahim, F.B.M. Suah, A decade development in the application of chitosan-based materials for dye adsorption: a short review, *Int. J. Biol. Macromol.* 191 (2021) 1151–1163.
- [132] S. Sadaf, H.N. Bhatti, S. Nausheen, S. Noreen, Potential use of low-cost lignocellulosic waste for the removal of direct violet 51 from aqueous solution: equilibrium and breakthrough studies, *Arch. Environ. Contam. Toxicol.* 66 (2014) 557–571.
- [133] S. Sadaf, H.N. Bhatti, S. Ali, K.U. Rehman, Removal of Indosol Turquoise FBL dye from aqueous solution by bagasse, a low cost agricultural waste: batch and column study, *Desalin. Water Treat.* 52 (2014) 184–198.
- [134] T.M.V. Ngo, T.H.L. Nguyen, X.T. Mai, T.H.N. Pham, T.T.T. Nguyen, T.D. Pham, Adsorptive removal of cationic dyes using hybrid material-based polyelectrolyte modified laterite soil, *J. Environ. Chem. Eng.* 9 (2021) 105135.
- [135] S. Deng, Y.-P. Ting, Characterization of PEI-modified biomass and biosorption of Cu(II), Pb(II) and Ni(II), *Water Res.* 39 (2005) 2167–2177.
- [136] Y. Wen, S. Pan, X. Luo, X. Zhang, W. Zhang, M. Feng, A biodegradable low molecular weight polyethyleneimine derivative as low toxicity and efficient gene vector, *Bioconjug. Chem.* 20 (2009) 322–332.
- [137] Y. Zhou, N. Zhu, N. Kang, Y. Cao, C. Shi, P. Wu, Z. Dang, X. Zhang, B. Qin, Layer-by-layer assembly surface modified microbial biomass for enhancing biorecovery of secondary gold, *Waste Manag.* 60 (2017) 552–560.
- [138] R. Verma, P.K. Maji, S. Sarkar, Removal of hexavalent chromium from impaired water: polyethylenimine-based sorbents – a review, *J. Environ. Chem. Eng.* 11 (2023) 109598.
- [139] A. Bhattacharya, B.N. Misra, Grafting: a versatile means to modify polymers: techniques, factors and applications, *Prog. Polym. Sci.* 29 (2004) 767–814.
- [140] Z.M. Ayalew, X. Guo, X. Zhang, Synthesis and application of polyethyleneimine (PEI)-based composite/nanocomposite material for heavy metals removal from wastewater: a critical review, *Journal of Hazardous Materials Advances* 8 (2022) 100158.
- [141] P. Madhusudhana Reddy, C.-J. Chang, J.-K. Chen, C.-F. Huang, C.-Y. Chou, M.-C. Lee, Polymer-coated gauze as efficient, reusable and economically viable adsorbents for the removal of Ni²⁺ ion, *React. Funct. Polym.* 134 (2019) 1–9.
- [142] X. Zeng, Y. Wang, X. He, C. Liu, X. Wang, X. Wang, Enhanced removal of Cr(VI) by reductive sorption with surface-modified Ti3C2Tx MXene nanocomposites, *J. Environ. Chem. Eng.* 9 (2021) 106203.
- [143] S. Zhang, S. Yi, S. Yang, D. Chen, Novel montmorillonite/jute composites functionalized with polyethyleneimine and cetyltrimethylammonium bromide for Cr(VI) adsorption, *Appl. Clay Sci.* 249 (2024) 107235.
- [144] A.A. Aryee, E. Dovi, Q. Li, R. Han, Z. Li, L. Qu, Magnetic biocomposite based on peanut husk for adsorption of hexavalent chromium, Congo red and phosphate from solution: characterization, kinetics, equilibrium, mechanism and antibacterial studies, *Chemosphere* 287 (2022) 132030.
- [145] Y. Nie, S.B. Deng, B. Wang, J. Huang, G. Yu, Removal of clofibrac acid from aqueous solution by polyethylenimine-modified chitosan beads, *Front. Environ. Sci. Eng.* 8 (2014) 675–682.
- [146] Y.G. Mishaal, P.L. Dubin, Uptake of organic pollutants by silica-polycation-immobilized micelles for groundwater remediation, *Environ. Sci. Technol.* 39 (2005) 8475–8480.
- [147] Y.L. Wang, J. Banziger, P.L. Dubin, G. Filippelli, N. Nuraje, Adsorptive partitioning of an organic compound onto polyelectrolyte-immobilized micelles on porous glass and sand, *Environ. Sci. Technol.* 35 (2001) 2608–2611.
- [148] D. Zadaka, Y.G. Mishaal, T. Polubesova, C. Serban, S. Nir, Modified silicates and porous glass as adsorbents for removal of organic pollutants from water and comparison with activated carbons, *Applied Clay Science* 36 (2007) 174–181.
- [149] T.D. Pham, T.T. Bui, T.T. Trang Truong, T.H. Hoang, T.S. Le, V.D. Duong, A. Yamaguchi, M. Kobayashi, Y. Adachi, Adsorption characteristics of beta-lactam cefixime onto nanosilica fabricated from rice HUSK with surface modification by polyelectrolyte, *J. Mol. Liq.* 298 (2020) 111981.
- [150] T.D. Pham, T.T. Bui, V.T. Nguyen, T.K.V. Bui, T.T. Tran, Q.C. Phan, T.D. Pham, T. H. Hoang, Adsorption of polyelectrolyte onto nanosilica synthesized from rice husk: characteristics, mechanisms, and application for antibiotic removal, *Polymers* 10 (2018).
- [151] M. Anbia, S. Salehi, Adsorption of methyl-orange from aqueous solution onto nanoporous silica materials, *Scientia Iranica* 21 (2014) 2036–2048.
- [152] H.-S. Hsieh, J.J. Pignatello, Modified carbons for enhanced nucleophilic substitution reactions of adsorbed methyl bromide, *Appl. Catal. Environ.* 233 (2018) 281–288.
- [153] M. Anbia, S. Salehi, Synthesis of polyelectrolyte-modified ordered nanoporous carbon for removal of aromatic organic acids from purified terephthalic acid wastewater, *Chem. Eng. Res. Des.* 90 (2012) 975–983.
- [154] Z.A. Jamiu, S.A. Ali, Construction of a double-layered polyelectrolyte-coated mesoporous silica containing residues of biogenic aspartic acid and its utilization for cadmium (II) removal, *J. Sol-Gel Sci. Technol.* 89 (2019) 830–843.
- [155] T.A. Oyeahan, F.A. Olabemiwo, B.S. Tawabini, T.A. Saleh, The capacity of mesoporous fly ash grafted with ultrathin film of polydiallyldimethyl ammonium for enhanced removal of phenol from aqueous solutions, *J. Clean. Prod.* 263 (2020) 121280.
- [156] H. Karimi-Maleh, A. Ayati, R. Davoodi, B. Tanhaei, F. Karimi, S. Malekmohammadi, Y. Orooji, L. Fu, M. Sillanpää, Recent advances in using of chitosan-based adsorbents for removal of pharmaceutical contaminants: a review, *J. Clean. Prod.* 291 (2021) 125880.
- [157] I.O. Saheed, W.D. Oh, F.B.M. Suah, Chitosan modifications for adsorption of pollutants – a review, *J. Hazard. Mater.* 408 (2021) 124889.
- [158] J. Ma, Y. Lei, M.A. Khan, F. Wang, Y. Chu, W. Lei, M. Xia, S. Zhu, Adsorption properties, kinetics & thermodynamics of tetracycline on carboxymethyl-chitosan reformed montmorillonite, *Int. J. Biol. Macromol.* 124 (2019) 557–567.
- [159] Z. Li, Y. Liu, S. Zou, C. Lu, H. Bai, H. Mu, J. Duan, Removal and adsorption mechanism of tetracycline and cefotaxime contaminants in water by NiFe₂O₄-COF-chitosan-terephthalaldehyde nanocomposites film, *Chem. Eng. J.* 382 (2020) 123008.
- [160] J. Liu, B. Zhou, H. Zhang, J. Ma, B. Mu, W. Zhang, A novel Biochar modified by Chitosan-Fe/S for tetracycline adsorption and studies on site energy distribution, *Bioresour. Technol.* 294 (2019) 122152.
- [161] W. Phasuphan, N. Praphairaksit, A. Imyim, Removal of ibuprofen, diclofenac, and naproxen from water using chitosan-modified waste tire crumb rubber, *J. Mol. Liq.* 294 (2019) 111554.
- [162] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, *J. Hazard. Mater.* 97 (2003) 219–243.
- [163] U. Upadhyay, I. Sreedhar, S.A. Singh, C.M. Patel, K.L. Anitha, Recent advances in heavy metal removal by chitosan based adsorbents, *Carbohydr. Polym.* 251 (2021) 117000.
- [164] S.-P. Wu, X.-Z. Dai, J.-R. Kan, F.-D. Shilong, M.-Y. Zhu, Fabrication of carboxymethyl chitosan-hemicellulose resin for adsorptive removal of heavy metals from wastewater, *Chin. Chem. Lett.* 28 (2017) 625–632.
- [165] A. Saad, A. Azzam, S. El-Wakeel, B. Mostafa, M. El-latif, Industrial wastewater remediation using Hematite@Chitosan nanocomposite, *Egyptian Journal of Aquatic Biology and Fisheries* 24 (2020) 13–29.
- [166] V.T. Le, V.D. Doan, D.D. Nguyen, H.T. Nguyen, Q.P. Ngo, T.K.N. Tran, H.S. Le, A novel cross-linked magnetic hydroxyapatite/chitosan composite: preparation, characterization, and application for Ni(II) ion removal from aqueous solution, *Water Air and Soil Pollution* 229 (2018).
- [167] S. Peng, Y. Liu, Z.Y. Xue, W.Y. Yin, X.C. Liang, M. Li, J. Chang, Modified nanoporous magnetic cellulose-chitosan microspheres for efficient removal of Pb (II) and methylene blue from aqueous solution, *Cellulose* 24 (2017) 4793–4806.
- [168] V.V. Dev, G. Baburaj, S. Antony, V. Arun, K.A. Krishnan, Zwitterion-chitosan bed for the simultaneous immobilization of Zn(II), Cd(II), Pb(II) and Cu(II) from multi-metal aqueous systems, *J. Clean. Prod.* 255 (2020) 120309.
- [169] X. Wang, X. Liu, C. Xiao, H. Zhao, M. Zhang, N. Zheng, W. Kong, L. Zhang, H. Yuan, L. Zhang, J. Lu, Triethylenetetramine-modified hollow Fe₃O₄/SiO₂/chitosan magnetic nanocomposites for removal of Cr(VI) ions with high adsorption capacity and rapid rate, *Microporous Mesoporous Mater.* 297 (2020) 110041.
- [170] L. Zhang, S. Tang, F. He, Y. Liu, W. Mao, Y. Guan, Highly efficient and selective capture of heavy metals by poly(acrylic acid) grafted chitosan and biochar composite for wastewater treatment, *Chem. Eng. J.* 378 (2019) 122215.
- [171] M. Hossein Beyki, F. Shemirani, M. Shirkhodaei, Aqueous Co(II) adsorption using 8-hydroxyquinoline anchored γ -Fe₂O₃@chitosan with Co(II) as imprinted ions, *Int. J. Biol. Macromol.* 87 (2016) 375–384.
- [172] I.M.M. Kenawy, M.M. Eldefrawy, R.M. Eltabey, E.G. Zaki, Melamine grafted chitosan-montmorillonite nanocomposite for ferric ions adsorption: central composite design optimization study, *J. Clean. Prod.* 241 (2019) 118189.
- [173] H.C. Ge, T.T. Hua, J.C. Wang, Preparation and characterization of hollow (itaconic acid)-grafted crosslinked chitosan nanoadsorbent for high uptake of Hg₂⁺ and Pb₂⁺, *Int. J. Biol. Macromol.* 95 (2017) 954–961.
- [174] T. Jintakosol, W. Nitayaphat, Adsorption of silver (I) from aqueous solution using chitosan/montmorillonite composite beads, *Materials Research-Ibero-American Journal of Materials* 19 (2016) 1114–1121.

- [175] L. Xie, F. Lan, W. Li, Z. Liu, S. Ma, Q. Yang, Y. Wu, Z. Gu, Polyacrylic acid brushes grafted from P(St-AA)/Fe₃O₄ composite microspheres via ARGET-ATRP in aqueous solution for protein immobilization, *Colloids Surf. B Biointerfaces* 123 (2014) 413–418.
- [176] P. Zhao, Q. Zhou, C.J. Yan, W.J. Luo, Polyacrylic acid grafted kaolinite via a facile ‘grafting to’ approach based on heterogeneous esterification and its adsorption for Cu²⁺, *Materials Research Express* 4 (2017).
- [177] Q. Zhou, Y. Fu, X. Zhang, T. Luo, W. Luo, Light induced growth of polyelectrolyte brushes on kaolinite surface with superior performance for capturing valuable rare-earth Ce³⁺ from wastewater, *Mater. Sci. Eng. B* 227 (2018) 89–99.
- [178] T.H. Dao, N.T. Nguyen, M.N. Nguyen, C.L. Ngo, N.H. Luong, D.B. Le, T.D. Pham, Adsorption behavior of polyelectrolyte onto alumina and application in ciprofloxacin removal, *Polymers* 12 (2020).
- [179] W.W. Zhao, Y.X. Fan, H. Wang, Y.L. Wang, Coacervate of polyacrylamide and cationic gemini surfactant for the extraction of methyl orange from aqueous solution, *Langmuir* 33 (2017) 6846–6856.
- [180] S. Bao, W. Yang, Y. Wang, Y. Yu, Y. Sun, Highly efficient and ultrafast removal of Cr(VI) in aqueous solution to ppb level by poly(allylamine hydrochloride) covalently cross-linked amino-modified graphene oxide, *J. Hazard. Mater.* 409 (2021) 124470.
- [181] L.-C. Shen, X.-T. Nguyen, N.P. Hankins, Removal of heavy metal ions from dilute aqueous solutions by polymer–surfactant aggregates: a novel effluent treatment process, *Sep. Purif. Technol.* 152 (2015) 101–107.
- [182] L.C. Shen, A. Lo, X.T. Nguyen, N.P. Hankins, Recovery of heavy metal ions and recycle of removal agent in the polymer–surfactant aggregate process, *Sep. Purif. Technol.* 159 (2016) 169–176.
- [183] L.C. Shen, N.P. Hankins, Metallic anion removal from dilute aqueous solutions using polymer–surfactant aggregate process: effect of surfactant chain length, *Journal of Water Process. Eng.* 20 (2017) 243–248.
- [184] L.C. Shen, J. Wu, S. Singh, N.P. Hankins, Removal of metallic anions from dilute aqueous solutions by polymer–surfactant aggregates, *Desalination* 406 (2017) 109–118.
- [185] L. Shen, N.P. Hankins, Removal of metallic ions at the parts per billion level from aqueous solutions using the polymer–surfactant aggregate process, *Journal of Water Process Engineering* 30 (2019) 100486.
- [186] L.C. Shen, N.P. Hankins, Metallic anion recovery from aqueous streams and removal agent recycle in the polymer–surfactant aggregate process, *Desalination* 406 (2017) 67–73.