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The Use of Polymers in the Flotation Treatment of Wastewater

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Abstract: The use of flotation for the treatment of wastewaters in general, but especially for the removal of oil, grease, general organic matter, and suspended solids, is well established as a low energy process. Polyelectrolytes (PEs) can enhance performance without adding to the solids load that occurs with inorganic additives such as alum. The bridging of pollutants and the attachment of the resulting aggregates to the air-water interface can be effectively carried out with most wastewaters. Hydrophobic modification of the PEs can be useful for difficult species. It should be applied to the flotation of polyfluoroalkyl substances, for example, as they are not amenable to economical conventional treatment. Similarly, the removal of microplastic particles from sewage effluents by flotation could be enhanced.

Keywords: polymer; flotation; polyelectrolyte; wastewater; oil recovery; hydrophobic polymers

1. Introduction

Flotation methods have an important role in the removal from wastewaters of oil, grease, other hydrocarbons, and general organic matter, as well as suspended solids of diverse types, mainly because of the compact equipment and low energy requirements. The topic has been covered in wide-ranging reviews that contain excellent overall surveys of flotation processes that have been applied to many contaminated waters [1,2]. The present article focuses on the use of soluble polymers to enhance flotation. A general review of polymer use in wastewater treatment has been published [3], following an earlier article on drinking water treatment [4]. For flotation purposes, polyelectrolytes (PEs) can form bridges between the offending species to produce aggregates which attach to the surface of air bubbles.

2. Oil and Grease Removal

A summary [5] quotes early flotation systems that utilize PEs in systems treating low level oil refinery wastes and oily wastes from other industries, as shown in Table 1. Also shown are the findings from later studies. The treatment of a synthetic waste of mineral oil dispersed with the aid of sodium oleate has been examined [6]. It made use of cationic polyacrylamides, one of which was of hydrophobic character. The cationic polyacrylamide has the charged site linked to an acrylate unit via an ethylene link, as shown in Figure 1A. When a hydrophobic analogue, such as a copolymer of acrylamide and trimethylaminoethylacrylamide chloride (PDMAEMA), which has the charge linked to a methacrylamide unit via a propylene bridge (as shown in Figure 1B) was used, the required polymer dose was more than halved (15 mg/L versus 40 mg/L). This was interpreted as the hydrophobicity encouraging adsorbance at the air bubble surface.
Table 1. Separation of oil from wastewater by flotation methods.

<table>
<thead>
<tr>
<th>Oil Concn., mg/L</th>
<th>Additives, mg/L</th>
<th>Removal, %</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>PE, 2</td>
<td>79</td>
<td>[7]</td>
</tr>
<tr>
<td>1000–2000</td>
<td>Alum, 150</td>
<td>100</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>Cationic PE, 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>PE, dose unstated</td>
<td>60</td>
<td>[9]</td>
</tr>
<tr>
<td>220</td>
<td>Alum, 50</td>
<td>96</td>
<td>[10]</td>
</tr>
<tr>
<td></td>
<td>PE, 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>Alum, 35</td>
<td>40</td>
<td>[12]</td>
</tr>
<tr>
<td></td>
<td>Alum plus PE, 2</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>Alum, 200</td>
<td>99</td>
<td>[13]</td>
</tr>
<tr>
<td></td>
<td>Anionic PE, 1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>220</td>
<td>Alum, 10</td>
<td>89</td>
<td>[14]</td>
</tr>
<tr>
<td></td>
<td>PE, 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>280</td>
<td>Alum, 50</td>
<td>79</td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>PEI, 2.5</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PDMAEMA, 2.5</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>370</td>
<td>FeCl$_3$, 270</td>
<td>81</td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td>PE, 10–20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>810</td>
<td>Alum, 100</td>
<td>98</td>
<td>[17]</td>
</tr>
<tr>
<td></td>
<td>Anionic PE, 6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>Two cationic PEs, 1 and 1.5</td>
<td>92–94</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td>Cationic PE, 100</td>
<td>50–57</td>
<td>[19]</td>
</tr>
<tr>
<td>280–7600</td>
<td>Cationic PE, 50 at pH 7 plus ECH/DMA *, 500</td>
<td>85</td>
<td>[20]</td>
</tr>
<tr>
<td>1600</td>
<td>Cationic polymer, 40 Hydrophobically modified, 15</td>
<td>97–99</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cationic PE; Cationic and anionic PEs</td>
<td>More sludge; Better product water</td>
<td>[21]</td>
</tr>
<tr>
<td>20–77</td>
<td>Alum, 30–40 PE C-577, 7–14</td>
<td>53–86</td>
<td>22–96</td>
</tr>
<tr>
<td>1630</td>
<td>Alum, 100 Cationic polyacrylamides</td>
<td>95–99</td>
<td>Ineffuctual</td>
</tr>
<tr>
<td>5000</td>
<td>Alum, 25 Chitosan, 15–100</td>
<td>95</td>
<td>[24]</td>
</tr>
<tr>
<td>2000</td>
<td>Poly (aluminium chloride), 24 Anionic PE, 1.5. Two stages</td>
<td>99</td>
<td>[25]</td>
</tr>
<tr>
<td>820–1050</td>
<td>Ferric sulphate, 30 plus an anionic PE, 3</td>
<td>87</td>
<td>[26]</td>
</tr>
<tr>
<td>409–2650</td>
<td>Hydrophobically modified cationic polyacrylamide</td>
<td>Better than inorganics</td>
<td>[27]</td>
</tr>
<tr>
<td>500</td>
<td>Alcohol propoxylate sulphate* Na*, 0.3%</td>
<td>98</td>
<td>[28]</td>
</tr>
<tr>
<td>522</td>
<td>Cationic Superfloc C-572, 0.1 Alum, 200 plus C-572, 0.1</td>
<td>87</td>
<td>96</td>
</tr>
</tbody>
</table>

PE: polyelectrolyte; PEI: polyethyleneimine; PDMAEMA: poly (dimethylaminoethyl methacrylate). * ECH/DMA is a hydrophilic PE made from epichlorohydrin and dimethylamine.
In the treatment of oil refinery wastewaters, the weakly basic cationic PEs polyethyleneimine (PEI) and PDMAEMA have been applied before flotation [15]. The slight superiority of the more hydrophobic PDMAEMA over PEI is apparent (Table 1). The two PEs were also less sensitive to the concentration of oil in the raw water than alum, needing only 2.5 mg/L for wastewater containing 70–280 mg/L of oil, whereas the requirement for alum increased from 28 to 50 mg/L, with poorer pollutant removal as well.

Using commercially available cationic PEs comprising linear copolymers of acrylamide and trimethylaminoethyl acrylate chloride, another study showed that in the flotation of oil in water emulsions the process was more robust towards changes in PE dose when PEs of lower charge density were employed [30]. Generally, the optimum PE dose decreased as the charge density increased, but changes in the molecular weight (MW) had no effect on flotation over the range studied.

The possible advantages of hydrophobic cationic polyelectrolytes as flocculants for clarifying aqueous systems have been the subject of early patents [31,32]. Fundamental studies of chain conformation have been published [33], as well as descriptions of the polymer synthesis [34].

Dual PE addition schemes have been explored for the treatment of an oily wastewater by dissolved air flotation (DAF)—a double system of a cationic followed by an anionic polymer (Vaughan et al. 2000) [21]. The sludge produced by the single cationic polymer system was 2–3 times the volume of the dual one, and the chemicals and sludge disposal cost was almost twice as high. However, the single polymer system gave more stable operation and a better quality effluent.

Chitosan has been employed in the treatment of olive oil wastewater in conjunction with alum, with respective doses of 15 and 25 mg/L [24]. Flotation could achieve up to 95% removal.

A DAF system has been applied to the treatment of poultry slaughterhouse wastewater [25]. In a two-stage approach with the addition of 24 mg/L of poly (aluminium chloride) (PAC) and 1.5 mg/L of an anionic polymer it was possible to remove 99% of the oil and grease. There were also other operating advantages as well.

In the treatment of wastewater from meat processing by flotation, ferric salts in conjunction with four different polymers were tested. Ferric sulphate at 30 mg/L plus 3 mg/L of an anionic polyacrylamide gave the best performance, with 87% removal of oil and grease [26].

The aim of another recent study was to assess the effect of alum and cationic polyelectrolytes on the removal by DAF of hydrocarbons from petrochemical wastewater [22]. The best removal was by a cationic polyelectrolyte (Cyanamid C577) which could remove 22–96% of the total oil, versus a 53–86% removal by alum.

A comparison of alum versus four different cationic polyacrylamides of low and high MW and low and high charge density showed 95–99% removal of the oil from an emulsified aqueous system by DAF when using 100 mg/L of alum, but no enhanced performance with the polyacrylamides [23].
The very high hydrophilicity of the PEs was thought to be the reason for this behaviour, resulting in a deterioration of the hydrophobic attraction between oil droplets and air bubbles.

Flooding to enhance oil recovery from oil fields in China has been used with success with polymer loading of the water, usually with hydrolysed polyacrylamide, which is an anionic PE [27]. Separation of the oil from the water was facilitated by the addition of a cationic inorganic coagulant, a cationic polyelectrolyte, or a non-ionic polymer. Oil–water separation was effective by flotation, which was better with increasing amounts of inorganic additive, but had an optimum dose when a cationic PE was used. The preferred cationic polymer had a MW of $6-8 \times 10^6$ and a charge density of 80%. It was a hydrophobic copolymer of acrylamide and trimethylaminoethyl acrylate chloride.

A continuous multistage froth flotation column has been employed to remove motor oil at a low concentration of 500 mg/L from a wastewater [28]. An anionic extended surfactant was used which had a chain length of 14–15 carbon atoms and eight groups of propylene oxide (PO) units with sulphate as the hydrophilic site. It was defined as C$_{14-15}$(PO)$_8$SO$_4$Na$^-$ and is known commercially as Alfoterra®. The addition of NaCl enhanced the performance.

Eight cationic polyelectrolytes have been evaluated for the treatment of strong oily wastewater from commercial dishwashers [29]. They could destabilize colloids at much smaller doses than the usually employed alum. Only one, a poly(dimethylamine-co-epichlorohydrin) (DMA-ECH), sold commercially as Superfloc C-572, outperformed alum prior to the use of DAF. Even better results were obtained with a combination of 200 mg/L of alum and 0.1 mg/L of polymer.

Settling experiments have been performed with regards to palm oil mill effluent treatment with 50 mg/L of various PEs, aimed at coalescing 22,000 mg/L of total suspended solids [35]. With alum dosed at 10,000 mg/L, a total suspended solids (TSS) concentration of 250 mg/L was obtained. The dose of PE required was much lower at 50 mg/L, with the results for a range of PEs shown in Table 2. Charge was extremely important, with very high MW cationic PEs being the best performers.

**Table 2.** Effectiveness of PEs in settling 22,000 mg/L of total suspended solids (TSS) in palm oil effluent using 50 mg/L of PE (from [35]).

<table>
<thead>
<tr>
<th>Polyelectrolyte:</th>
<th>N-100</th>
<th>A-100</th>
<th>A-130</th>
<th>Z-32</th>
<th>Z-72</th>
<th>Z-92</th>
<th>C-983</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge type:</td>
<td>Neutral</td>
<td>Anionic</td>
<td>Anionic</td>
<td>Cationic</td>
<td>Cationic</td>
<td>Cationic</td>
<td>Cationic</td>
</tr>
<tr>
<td>Amount:</td>
<td>Medium</td>
<td>Medium</td>
<td>Small</td>
<td>Small</td>
<td>Medium</td>
<td>V. High</td>
<td>V. High</td>
</tr>
<tr>
<td>TSS, mg/L:</td>
<td>3280</td>
<td>2560</td>
<td>14,600</td>
<td>1440</td>
<td>1840</td>
<td>721</td>
<td>634</td>
</tr>
</tbody>
</table>

In a like manner, hydrophobic cationic terpolymers were made from acrylamide (AM), diallyldimethylammonium chloride (DADMAC), and butyl acrylate (BA), then tested as a flocculant in oil removal [36]. These were high charge (24.3%) cationic polymers, with a high MW of 2.6 M and hydrophobic unit contents of 0.5%, 1.0%, and 2.0%. To treat a wastewater containing 100 mg/L of oil, a dose of 50 mg/L of polymer was required to remove 93% of the oil. To reduce operating costs, a simple natural polymer was used conjointly with 30 mg/L of the hydrophobic polymer. With 20 mg/L of soluble starch as well, the oil removal was 93%. A similar effect could be obtained by pre-treatment with alum, when more rapid settling of flocs was observed.

New hydrophobically modified cationic PEs using stearyl methacrylate as a co-monomer at up to 8 wt% have recently been announced [37]. The other components are AM and methacryloylamino-propyltrimethylammonium chloride. These PEs were very promising in the flocculation of effluents from an olive oil mill, with 90% turbidity and 34% TSS removal achieved by settling at a dose of 53 mg/L. With a dose of only 13 mg/L there was 79% turbidity removal. This can be compared with the reference copolymer that was devoid of vinyl methacrylate, which removed a negligible amount of turbidity at a dose of 100 mg/L. Dual flocculants in the form of anionic tannin and cationic hemicellulose have been shown to have good performance in the removal of oily and surfactant residues in biodiesel wastewater [38]. A 25/75 mix removed 70–89% of turbidity particles by settling.
3. Algae Removal

The removal of *Scenedesmus quadricauda* by froth flotation can be enhanced by using the cationic surfactant cetyltrimethylammonium bromide (CTAB). A previous study showed that CTAB resulted in a high algal removal of 90%, whereas anionic sodium dodecylsulphate removed only 19% [39]. The results are summarized in Table 3.

Table 3. Removal of algae by dissolved air flotation.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Additive, mg/L</th>
<th>Dose, mg/L</th>
<th>Removal, %</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Scenedesmus quadricauda</em></td>
<td>CTAB</td>
<td>10</td>
<td>90</td>
<td>[39]</td>
</tr>
<tr>
<td></td>
<td>Alum</td>
<td>1.46–2.9</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CTAB</td>
<td>0.72</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chitosan at pH 7</td>
<td>0.9</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chitosan at pH 5</td>
<td>0.9</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PEI</td>
<td>0.66</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>Microcystis Aeruginosa</td>
<td>Magnafloc LT-31</td>
<td>0.9</td>
<td>76</td>
<td>[40]</td>
</tr>
<tr>
<td></td>
<td>Agefloc A-50</td>
<td>0.9</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PolyDADMAC</td>
<td>0.32–0.44</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>Chlorella sp.</td>
<td>CTAB</td>
<td>20–30</td>
<td>Less energy needed than conventional *</td>
<td>[41]</td>
</tr>
<tr>
<td>Cyanobacteria</td>
<td>CTAB</td>
<td>0.4</td>
<td>32</td>
<td>[42]</td>
</tr>
<tr>
<td></td>
<td>PolyDADMAC</td>
<td>0.2</td>
<td>90–99</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Poly(dimethylamino-ethyl methacrylate)</td>
<td>0.2</td>
<td>99</td>
<td></td>
</tr>
</tbody>
</table>

CTAB: cetyltrimethylammonium bromide; DADMAC: diallyldimethylammonium chloride. *Filtration, flocculation, or centrifugation processes.

A previous study considered the use of DAF for the treatment of water laden with the algae *Microcystis aeruginosa* [40]. Attempts were made to modify the air bubbles by adding either metal coagulant, surfactant, or PE. When using alum, 60% removal was achieved, whereas 63% removal was achieved when using only CTAB. However, an average of 95% removal was possible with the cationic polyDADMAC. An additive containing both a hydrophobic component to encourage adsorption at the air interface in addition to a highly positively charged hydrophilic polymer of high MW was thought to be the preferred option. A high molecular weight polymer has the advantage of increasing the swept volume or enmeshment area. PolyDADMAC was superior to polyamines such as PEI (78%), chitosan at pH 5 (80%) or pH 7 (65%), and the commercial polyamines Magnafloc LT-31 (76%) and Agefloc A-50 (87%), both supplied by CIBA UK.

Foam flotation has been applied to the harvesting of algae for biofuel extraction. As a surfactant with charge opposite to that of the algae, CTAB was able to facilitate the flotation step, as tested in trials using polystyrene latex beads to simulate the algae, and then with a *Chlorella* sp. of algae [41]. With a CTAB dose of 20–30 mg/L, energy consumption was less than that required by filtration, flocculation, or centrifugation.

DAF has been found to be an effective treatment method for clarifying algae/cyanobacteria-laden water [42]. The benefits of surfactants and polymers were obtained by combining surfactants and bridging PEs while using poly (dimethylaminoethyl methacrylate) as a hydrophobic species. This improved the adsorption of the PE to the bubble surface and reduced the amount of residual PE in the product water, but the removal of algae was about the same as that obtained with polyDADMAC. The bridging enhancement obtained with the hydrophobic PE is shown diagrammatically in Figure 2. The cationic PE bridges the negatively charged algal cells and the agglomerates become bound to the air bubbles via the hydrophobic segments of the PE.
coagulant, surfactant, or PE. When using alum, 60% removal was achieved, whereas 63% removal 

Figure 2. Charge neutralization effects of a hydrophobic cationic PE, followed by its binding to 

air bubbles.

4. Removal of Surfactants

4.1. Conventional Surfactants

Foam fractionation has been used to recover surfactants from water. In a study by Tharapiwattananon et al. [43], three surfactants were studied, one cationic and two anionic. It was found that the cetylpyridinium chloride (CPC) concentration in water could be reduced by 90% in one stage. It was easier to remove than when the anionic surfactants were used.

Another foam fractionation study simulated the recovery of three surfactants present at low concentrations [44]. They were CPC, sodium dodecyl sulphate (SDS), and sodium n-hexadecyldiphenyloxide disulphonate (SHDD). To avoid the formation of micelles, the surfactant concentration in the feed was kept at 80% of the critical micelle concentration. The enrichment ratio was in the order SDS > CPC > SHDD and increased with temperature, but the rate of recovery was unaltered except for SDS, when it decreased with rising temperature. Generally, the recovery diminished with increasing salt levels.

A previous study has shown that it was possible to selectively remove surfactants and anionic dyes with a modified membrane comprising a membrane onto which catechol-PEI was deposited [45]. The dual functioning system can be used to treat surfactant-stabilized oil in water emulsions and water-soluble dyes at the same time.

The association between surfactants and oppositely charged PEs that contain long alkyl side chains has been the subject of several studies [46]. These PEs can have good water solubility, and in dilute solutions they form micellar-like aggregates, resulting in networks of associative polymers. These can involve non-ionic surfactants and even those that have the same charge. It was felt by Iliopoulos [46] that a deeper understanding of the association mechanism was needed.

4.2. Polyfluoroalkyl Substances (PFAS)

PFAS are akin to surfactants in that they have a charged sulphonate or carboxylate group at one end of a polyfluorinated main chain and a -CF₃ group at the other. They are highly stable products that have been used in coating additives and fire-fighting foams for over sixty years and are thought to cause adverse human health effects. These were reviewed recently in an article that quotes 85 studies from many countries, including China, Japan, and the United States [47]. Immunotoxicity and carcinogenicity now appear to be relevant risks at existing exposure levels, and there is a comment that drinking water limits may be 100 times too high.

However, adequate removal of PFAS from water supplies is difficult to achieve [48–52]. Previously published works point out that PFAS are not fully removed by the usual drinking water treatment processes such as coagulation, flocculation, sedimentation, filtration, biofiltration, oxidation, UV irradiation, flotation, and low-pressure membranes. Granulated activated carbon and high-pressure membranes are the most common treatment methods for long-chain PFAS removal [52]. The latter treatments are not ideal because of the need for frequent regenerative procedures, which makes them expensive.

In the Australian context, studies on PFAS removal were carried out at two water reclamation plants in Queensland [49]. The first plant used adsorption, flotation, and filtration methods, followed
by ozonation. The influent concentrations of various PFAS were from 3.7 to 16 ng/L and were lowered to 0.7 and 12 ng/L after ozonation. Throughout the plant the concentrations of most of the PFAS remained relatively unchanged after each treatment step. Polyfluorooctane sulphonate was an exception, with some removal after coagulation and DAF, followed by sand filtration. At both plants the observed concentrations were well below provisional drinking water guidelines. The lack of effectiveness of DAF generally was ascribed to the low volatility of PFAS, but the surfactant nature of the compounds suggests that PEs, especially of the hydrophobic variety, would assist in aggregating PFAS on the air/water interface, and thus improve performance. More work should be carried out on this approach.

5. Sewage Effluents

Flotation may be used in municipal wastewater treatment plants to enhance the removal of colloidal and suspended matter, as has been postulated some time ago [53]. It may replace sedimentation after coagulation and flocculation and lead to a very compact plant. Its use in combination with biofilm processes is attractive because of the usually small amount of TSS that needs to be removed.

DAF was tested on effluents from an anaerobic reactor that treated sewage, after coagulation with ferric chloride and/or a cationic PE [54]. Ferric chloride dosages ranging from 15 to 65 mg/L were employed, with tests involving 29 different polymers: cationic, anionic, and non-ionic. Cationic PEs at 7 mg/L produced good flotation performance, although not as good as ferric chloride. Also, these PEs could not remove phosphate. However, the use of cationic PEs at 1 mg/L, together with 15 mg/L of ferric chloride, allowed operation at higher rates, giving more compact units and greater economy. PEs of high charge density and high MW were preferred.

A study by Mels et al. showed that it was possible to remove 80% of TSS and turbidity from municipal wastewater by using cationic PEs prior to DAF [55]. Of the two commercial linear PEs tested, the higher MW version was the better; the charge density was the same for both at 24 wt%. More recently, a study was conducted using a combination of a high-rate membrane bioreactor and an enhanced flotation process in which low-density beads instead of air were used, thus saving the energy that would be required by air pressurization (Brosseau et al. 2016). Metallic-based green coagulants such as tannin derivatives were compared with PEs. A high MW, low charge density cationic polyacrylamide gave the best result, with 0–97% TSS removal, versus 58–85% for the green coagulant. With the latter, the binding of the solids to the beads appeared to be more fragile.

Of interest is a topical article which raises the possibility of synthesizing sodium polystyrene sulphonate from waste plastic cups and employing it for coagulation and flocculation in wastewater treatment, followed by flotation [56]. The article showed that this process provided better results than several commercial polyacrylamides of non-ionic and anionic character. Further work is under way on its application to drinking water treatment.

Of current concern is the removal of microplastics (MPs) < 5 mm in size from primary and secondary effluent. MPs are used in personal care products, industrial scrubbers used in abrasive cleaning agents, and plastic powders used for moulding; others result from the fragmentation of larger plastic particles. They are made up of 13 different polymers and have the potential to adsorb persistent organic pollutants. A pertinent removal study included several tertiary treatments: disc filter (DF), rapid sand filtration (RSF), DAF, and membrane bioreactor (MBR) [57]. The DAF system involved pre-treatment with PAC. DF removed 40–98.5%, RSF removed 97%, DAF removed 95%, and the MBR removed 99.9%. The treatments removed all size fractions and shapes of MPs. DAF lowered the particle content from 2.0 to 0.1 MP/L. A more appropriate pre-treatment for DAF with PEs should enhance the control of MP pollution.
6. Other Industrial Wastewaters

6.1. Tannery Effluents

The leather industry is well known for generating highly polluted wastewater, the main characteristics of which are elevated salinity, high organic loading, high levels of ammonia and organic nitrogen, and the presence of specific pollutants such as sulphides and chromium. In one study on the treatment of a chromium-laden tannery effluent, PAC was used [6]. The solids load was too high, so a high MW, medium charge density cationic polymer was employed. At a 25 mg/L dose, this gave better turbidity removal than 100 mg/L of PAC.

The largest Slovenian tannery for processing pig skins has been shown to have a good system of physicochemical pre-treatment of the wastewater, using coagulation and flocculation with alum and an anionic PE [58]. About 60% of the organic substances were removed and >95% of the sulphide and chromium were removed. A final biological treatment with activated sludge followed.

6.2. Papermaking Effluents

PEI can remove colour from paper mill effluents [59]. A branched chain version of MW 1800 was the preferred structure, removing 85–90% of the colour at pH 8.5 with doses of 550–800 mg/L.

A study by Miranda et al. [60] considered papermaking wastewaters that were treated with chitosan prior to DAF treatment [60]. A quaternary ammonium version was also tested, along with anionic bentonite microparticles, alone and in combination. Results showed that a low MW chitosan was more effective than a medium MW chitosan. The efficiency of treatment was enhanced by the combined system, with the optimum being 50 mg/L of chitosan and 100 mg/L of bentonite, with 83–89% of the turbidity was removed. The quaternary ammonium derivative did not improve on this. The low cost of bentonite compensated for the more expensive chitosan, but chitosan could be used in smaller amounts in the combination, which was the preferred choice.

In a study by Quartaroli et al. [61], chitosan and DAF were evaluated as a post-treatment of effluent from an activated sludge plant treating pulp and paper industry wastewater. Tests were made with cationic and anionic PEs, with the best performance being by a cationic PE, which removed 85% of the colour and 90% of the turbidity when used with a dose of 175 mg/L of PAC and 50 mg/L of the PE.

7. New Polyelectrolytes

Several different PEs are currently under study, several of them based on biopolymers. In the first of these, the lack of biodegradability of the synthetic PEs and the possible presence of residual monomers in these materials have been pointed out [3]. Because of their moderate flocculation efficiency, they need to be employed in larger doses. To combine the best properties of both types, it was suggested that synthetic PEs be grafted onto the backbone of natural polymers. A completely natural PE has been obtained from the cactus tree (Opuntia ficus-indica) [62,63]. Others have been reviewed [4]. Hydrophobically modified versions of these systems should be considered.

A review of temperature-responsive polymers as novel agents for solid-liquid separation and froth flotation of minerals carried out over the past decade has been published [64]. A lot of work has been done on this type of polymer on account of its potential use in the creation of drug carriers in the biopharmaceutical area, but less has been done on flotation in the mineral processing industry, which may be because of the cost of heating or cooling to induce any physical change. Polymers such as poly(N-isopropylacrylamide) remain hydrophilic in solution when below a specific temperature (the lower critical solution temperature), but on heating they undergo a reversible coil-to-globule transition into an insoluble state, displaying hydrophobic properties. A consequent reduction in pumping costs could be a good incentive for their use. The hope is that the fine mineral particles which are difficult to recover by flotation might be selectively trapped into larger hydrophobic flocs by the hydrophilic/hydrophobic change in the polymer. Several novel copolymers have been made which have enhanced collector performance to equal or better than conventional collectors.
Temperature responsive hydrogel nanoparticles have been made by the association of two different hydrophobically modified polymers in the form of a copolymer of poly(N-isopropylacrylamide) and N-[4-(1-pyrenyl)butyl]-N-n-octadecyacrylamide] (PNIPAM-C18Py) and one with a cholesterol-bearing microbial polysaccharide, pullulan [65]. Above 32 °C, the nanoparticles increased in diameter from 47 to 160 nm, but no aggregation could be detected. On cooling, they resumed their original size. It was speculated that such particles could be used as a thermal stabilizer of enzymes in biotechnology, as well as in drug carrier systems.

PEs based on polyacrylonitrile have been prepared from oxidized asphalt [66]. Included are cationic, anionic, and amphoteric varieties, all with hydrophilic acrylic structures. The cationic PEs were made by amination with ethylenediamine and 3-methylaminopropylamine. They exhibited stronger flocculating properties than the amphoteric PEs, and the anionic PEs behaved as stabilisers in dispersed systems of wastewater. It was suggested that the cationic PEs could be used in treating oil refinery and textile wastewaters.

8. Conclusions

The enhancement of flotation processes by using PEs has been successfully carried out for a wide range of industrial and domestic wastewaters. The use of flotation processes has the added benefit of a reduced solids load compared to that obtained with inorganic coagulants. Further improvements have been demonstrated with hydrophobically modified cationic PEs in the case of oil and grease removal, and in the treatment of algae/cyanobacteria-laden water. The PE needs to be designed to amalgamate specific contaminants. The challenge now is to apply additives like cationic surfactants, cationic PEs, and especially hydrophobically modified cationic PEs to the cleaning up of intractable wastes, such as those from PFAS-laden waters and microplastics from sewage effluents.

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