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Full Title: **A review of nano-based materials used as flocculants for water treatment**

Running Title: **Nano-flocculants for water treatment: A review**

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Abstract

In recent years, the development of nanoparticle materials for water treatment has received great attention. From an industrial technological view point, the application of nanomaterials in the 21st Century for water treatment will be the focal point of advanced materials design, processing and progress. In this context, the potential utilisation of different types of flocculants to clean up contaminated water becomes important to address the tremendous increase of water pollution resulting from continued high level global industrialisation. A number of researchers have investigated the effectiveness of various nano-flocculants for this purpose. Although, these nano-flocculants have been reported as successfully treating contaminated water, their flocculation performances are different. To the best of our knowledge, there is no review article which summarises the application and performance of nano-flocculants in the treatment of water containing various types of contaminants. This review summarises recent development of a wide range of nano-flocculants for the treatment of water polluted particularly by heavy metals, dyes and bacteria. The influence of physicochemical properties of nano-flocculants upon their performance and optimum flocculation conditions are discussed in detail. This review will provide a useful source of information for researchers working on the advancement of cost-effective and environmentally friendly nano-flocculants.

Keywords Water pollution; Water treatment; Flocculation; Nano-flocculants; Nanomaterials

Introduction

A country's development, population growth and concomitant change in consumption patterns can significantly affect the globalisation process, and lead to serious environmental problems especially including water pollution (UNWWDR 2019). It is undeniable that urbanisation is of utmost importance for the development of a country. However, an urbanisation process that does not consider environmental aspects will not contribute to success of meeting the sixth Sustainable Development Goal target by 2030 and in particular to enhance water quality by minimising the pollution issues, eliminating dumping and reducing the release of toxic substances and wastes. Based on the AQUASTAT database, it is estimated that 56 % (2,212 km^3 per year) of 3,928 km^3 of the global freshwater withdrawal annually is discharged directly into the environment as wastewater in the form of municipal, industrial effluent and agricultural drainage water (FAO 2016). According to the Water Operational Plan 2011-2020 developed by the Asian Development Bank (ADB), it has been estimated that more than 20-25 billion USD will be required to sustain the momentum and continuity of water development in the Asia-Pacific region by 2020 (ADB 2012).

Up to the present day, a number of commonly applied treatment methods have been developed and employed for water treatment such as coagulation/flocculation (Hargreaves et al. 2018; Yusoff et al. 2018), adsorption (Li et al. 2018; Yang et al. 2018), oxidation (Nidheesh et al. 2018; Boczkaj and Fernandes 2017), membrane filtration (You et al. 2018; Rezakazemi et al. 2018) and evaporation (Higgin et al. 2018; Yang et al. 2018). Table 1 gives the cost, the advantages and the disadvantages of several common treatment methods for water treatment. Among these techniques, flocculation is one of the most widely used strategies for solid-liquid separation, mainly due to its cost effectiveness, ease of operation with the generation of lower quantities of sludge when compared to other conventional treatment methods. The total number of citations for the topic of flocculation has increased based on a Scopus citation report from 32,077 in 2014 to 49,376 in 2018.

Generally, flocculation is a physical process to separate solid particles from a liquid that cause particles to combine together to form larger aggregations of flocs (Muralikrishna and Manickam 2017). There are two methods of flocculation treatment which are (i) direct flocculation and (ii) indirect flocculation. Indirect flocculation is the combination of coagulation and the flocculation process. The flocs produced in the coagulation process tend to be small and fragile and so to overcome these issues, flocculants are used to form large flocs and increase their density and solidity. Direct flocculation is the fastest process treatment without requiring pH adjustment and it presents advantages in terms of cost, less sludge formation, lower requirements for chemical use and process simplicity compared to indirect flocculation (Lee et al. 2014).

The flocculation mechanisms for the contaminant removal can be categorised into four types, namely: (1) charge neutralisation (the reduction of net electrical charge due to adsorption of polyelectrolytes on oppositely charged sites of colloidal particles), (2) electrostatic charge patching (the interaction of positively and negatively charged particle surfaces), (3) bridging (connection of a polymer molecule with another particle, thereby linking the particles together), and (4) sweep flocculation (colloidal contaminants are entrained or swept down by precipitates as they settle in suspension) (Yang et al. 2016; Zhou and Franks 2006). Although flocculation has been confirmed to be able to reduce the contamination level of polluted water, the tendency of the existing flocs to break resulting from destructive forces is possible. It is known that, at high mixing strength the collision efficiency of the particles is increased so the flocs are vulnerable to breakage due to the rate of fluid shear (Rui et al. 2012; Jarvis et al. 2005).

A number of researchers have investigated the effectiveness of various nano-flocculants for water treatment. Although, these nano-flocculants were reported successfully treated contaminated water, their flocculation performances are technically different. As the interest in application of flocculation strategy for water treatment has grown gradually, a number of review articles related to the flocculation process have been published in recent years. Table 2 lists selected review articles with their focus related to the flocculation process in water treatment. From Table 2, it is clear that to the present day there is no review article that focusses on application of nano-based materials as flocculants to treat contaminated water. Therefore, the current manuscript aims to review advanced nanomaterials used as flocculants to treat water contaminated by a number of contaminants.

In recent years, the application of nanotechnology in various fields has significantly increased, and nanomaterials have presented great potential to be used in water treatment. The key feature that makes nanomaterials attractive for water treatment is that they have a large surface area to volume ratio, which enhances their chemical activity and adsorption capacity towards target contaminants (Anjum et al. 2016) as compared to non-nanomaterials. The advantages and disadvantages between nano and non-nanomaterials are summarised in Table 3. It can be seen from Table 3 that they are some drawbacks that will affect the flocculation efficiency. For example, nanomaterials are difficult to handle and recover due to the size. However, a study conducted by Akbulut et al. (2012) found that up to 99% of nanorod has been separated using benchtop centrifuge in less than 10 mins on the separation of gold nanorod in aqueous multiphase system.

In addition, alum has been proven as one of an effective conventional flocculants since ancient times, its application in water treatment generate secondary by-products that are non-Newtonian and gelatinous that complicate sludge disposal by waste treatment plants (Nadella et al. 2020; Albrecht 1972). While in the case of non-nanobiopolymer flocculants, even though they are normally considered as not toxic and environmentally friendly however there are limitations regarding their short shelf life and moderate operational performance. This is due to the active components on the natural polymer that will biodegrade with time which shorter the shelf life of the material (Okaiyeto et al. 2016; Pivarčiová et al. 2014). For example, pristine chitosan has been found to biodegrade more rapidly than modified chitosans in both uncontaminated and contaminated environments (Kamari et al. 2015).

To overcome the drawbacks of non-nanomaterials, flocculants in the nanoscale size have been explored widely by environmental scientists in recent years which highlight the innovation in integrating various key properties of nanoparticles for water treatment application (Gehrke et al. 2015). In recent published papers, heavy metals (Alqadami et al. 2017), organic pollutants (Jun et al. 2018), inorganic pollutants (Bharath et al. 2017) and bacteria (Song et al. 2018) have been reported to be successfully removed with different kinds of nanomaterials by flocculation. The most extensively studied nanomaterials as flocculants for water treatment are mainly based on carbon nanotubes, cellulose, chitosan, metals and metal oxides.

In this review article, we have focused on the performance and optimum experimental conditions of flocculation process as affected by physicochemical characteristics of several nano-flocculants used to treat water contaminated by toxic metals, dyes and bacteria.

Carbon nanotubes

Carbon nanotubes (CNTs) can be divided into two general types, namely single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) with diameters of about 1-2 nm and 2-30 nm, respectively (Aqel et al. 2012). The atoms in CNTs are arranged in hexagonal rings in a similar manner to the graphite arrangement and the structures of CNTs are similar to those of cylindrical shells formed by rolling single or multiple graphene sheets into a seamless cylinder that can be open ended or capped (Zhang & Li 2009). CNTs possess several unique physicochemical properties such as high surface area, strong mechanical and chemical stability and as well can be functionalised with various chemical groups to increase enhance their attraction towards target compounds. Due to these characteristics, CNTs possess great potential for environmental applications especially in water and wastewater treatment (Rocha et al. 2017; Savage and Diallo 2005). A summary of studies based of the use of CNTs as flocculants for water treatment is presented in Table 4.

The potential of CNTs as flocculants to separate corrosive waste acid has been investigated by Lei (2013). The effectiveness of CNTs for flocculation strategy was compared with three common separation methods, namely dialysis, membrane filtration and high-speed centrifugation. It was noted that the addition of small amount of 3-(trimethoxysilyl)propyldimethyl octadecylammonium chloride (DC5700) along with CNTs to the flocculation system introduced covalently bound moieties to the sidewalls of the CNTs thereby significantly changing the flocculants from hydrophilic to hydrophobic. Following the introduction of DC5700, a floc was observed to appear within 10 minutes of stirring and the total time for separation of the corrosive waste acid was reported to be 30 minutes as compared to dialysis (10 h), membrane filtration (2.5 h) and high-speed centrifugation (1 h). It was also noted that the combination of CNTs and the flocculation method could be a green nanoseparation approach because the waste acid can be recycled or reused.

Meanwhile, Simate et al. (2012) evaluated the performance of HCl functionalised CNTs as heterogeneous flocculants in the pretreatment of brewery wastewater. The effectiveness of HCl functionalised CNTs was compared with the pristine CNTs and ferric chloride, a commercial flocculant. Based on the reduction in turbidity and chemical oxygen demand (COD) values, the overall flocculation performance was reported in the order of ferric chloride > HCl functionalised CNTs (surface area 601 m^2/g, pore volume 0.93 cm^3/g) > pristine CNTs (surface area 499 m^2/g, pore volume 0.64 cm^3/g). The introduction of functional groups onto the surface of CNTs changed the point of zero charge (PZC), which is an important characteristic which describes the pH for colloidal particle at which the net electrical charge density on its surface is zero. The PZC for the acid functionalised CNTs was determined as 7.3, which indicated that at pH values < PZC the H^+ ions were absorbed onto the surface of CNTs making their net surface charge positive. The positively charged functionalised CNTs contributed to the agglomeration of the negatively charged colloidal particles with a zeta potential of -38 mV from brewery wastewater. This study revealed that CNTs and ferric chloride had no synergetic effect, and therefore combining them in a flocculation process would not improve wastewater treatment.

The feasibility of the integration of treatment systems and devices for reducing turbidity and COD values in brewery wastewater has been assessed by Simate (2015). This study was conducted applying a semi-continuous laboratory scale water treatment plant using several treatment schemes. There were three modes of operation involved, namely: (i) conventional filtration (coagulation, flocculation, sedimentation and filtration), (ii) direct filtration (sedimentation is excluded) and (iii) in-line filtration (flocculation and sedimentation are excluded). The removal of turbidity and COD were reported to be in the order of operation mode (i) > (ii) > (iii). Besides that, the effect of CNTs addition to either coagulation/flocculation or the filter bed, or to both was also investigated. The application of CNTs to both coagulation/flocculation and the filter bed resulted in a higher loss of turbidity and COD up to 95.9% and 96.0%, respectively as compared to in-line filtration treatment method which was reported to be 58.3 and 66.7% for turbidity loss and COD removal, respectively.

Özdemir (2016) studied the removal of natural organic matter (NOM) using SWCNTs and MWCNTs as flocculants for water obtained from Ulutan Lake in Zonguldak, Turkey which is a source of drinking water. The influence of seasonal variation on such lake water treatment was evaluated during the period of September 2014 to July 2015. The NOM concentrations were characterised by applying ultraviolet absorbance at 254 nm (UV_{254}) and determination of dissolved organic carbon (DOC). It was noted that the seasonal variation played a key role in reducing the NOM concentration as SWCNTs showed higher removal of the hydrophobic portion in winter, while the MWCNTs exhibited a higher removal of the hydrophilic portion in summer. This observation was attributed to the larger surface area of the SWCNTs (1-2 nm diameter) as compared to the MWCNTs (50-80 nm diameter). The combination of SWCNTs and MWCNTs with commercial alum and $FeCl_3$ was reported to increase the percentage removal of NOM by approximately 10 and 15 %, respectively. It was also emphasised that the pH and ionic strength of the lake water significantly contributed to NOM removal.

Joseph et al. (2013) investigated the removal of two endocrine disrupting chemicals (EDCs), namely bisphenol A (BPA) and 17α-ethinyl estradiol (EE2) using SWCNTs and MWCNTs to treat natural surface water, synthetic seawater, brackish water and synthetic land fill leachates. They obtained a similar pattern of EDCs removal to that of findings reported by other researchers, whereby SWCNTs with diameter 1-2 nm showed a higher removal percentage (more than 90%) as compared to MWCNTs with diameter 100-170 nm. They discussed that the larger outer diameter of the MWCNTs is associated with a significant lower specific surface area thereby limiting the overall number of adsorption sites available. They also noted that the agglomeration of BPA and EE2 was affected by ionic strength, of which contaminated water with high ionic strength showed higher removal of EDCs due to the screening effect of the surface charge produced by high salt content. Additionally, they observed no significance effect of pH and this was attributed to all the solutions being below the pKa and thus no electrostatic repulsion occurred.

The flocculation performance of three materials, namely SWCNTs, graphene oxide (GO) and polyacrylamide (PAM) on methylene blue (MB) in aqueous solution was studied by Liu et al. (2015). They noted that MB was best removed by GO, followed by PAM and SWCNTs. They performed PIXEL energy calculations and revealed that London dispersion forces were the dominant forces for the interaction between GO and MB. Their findings indicated that the electrostatic interaction and other noncovalent interactions between MB and GO are weak. This proposal was in contradiction to previous speculation that the electrostatic attraction may be responsible for the interaction between GO and MB molecules. SWCNTs were reported to be the worst flocculation agent to remove MB from aqueous solution since no visible floc formed at any pH value. This observation was related to the low solubility of SWCNTs in water resulting in weak interaction of SWCNTs and MB.

Cellulose

There are two types of nanocellulose that are commonly used in water treatment, namely cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) (Blanco et al. 2018). Nanocellulose has received significant attention from researchers mainly due to its unique properties such as large surface area, high mechanical strength and the presence of abundant hydroxyl groups that can attach to many functional groups. These characteristics as well as widespread availability make nanocellulose suitable for diverse applications (Mohammed et al. 2018). In fact, it has been frequently applied in water treatment studies. Table 5 lists CNCs and CNFs that have been used as flocculants for water treatment.

A study by Akhlaghi et al. (2015) has shown that amine functionalised CNCs exhibited promising results as a flocculating agent in water treatment due to the presence of a high number of amine groups. At low pH, the zeta potential of the CNCs was reported to change from negative to positive. It was explained that the protonation of amine group resulted in effective flocculation as a consequence of strong electrostatic interaction. It was also found that the application of sodium dodecyl sulfate (SDS), an anionic surfactant, together with CNCs successfully formed a floc after 9 minutes due to the interaction of oppositely charged systems.

In a study to remove organic colloidal latex particles present in an industrial wastewater, Zhou (2016) examined the potential of three types of modified cationic CNCs, namely: (i) PDMA-g-CNCs (tertiary amine), (ii) P4VP-g-CNCs (pyridine amine) and (iii) amine-CNCs (primary amine) as flocculants. The flocculation performance of modified cationic CNCs was compared based on the type of amine, optimal dosage, flocculation efficiency and floc size formation. The study revealed that amine-CNCs at pH 4 showed the best flocculation performance with the lowest optimal ratio of 0.07 and 100% flocculation efficiency due to a strong intermolecular force that induced charge neutralisation to restabilise the latex. It was also noted that P4VP-g-CNCs at pH 4 formed a larger floc agglomeration due to the bridging effect, or insertion, of the hydrophobic ring into the flocculant. All cationic CNCs did not form flocs when they were used at pH 10 indicating that this pH value should be avoided.

The effects of five different hydrolysis times on the production of anionic carboxylated CNCs were evaluated by Yu et al. (2016). The applicability of anionic carboxylated CNCs as flocculants to treat methylene blue dye, dye effluent and kaolin suspension was studied in detail. A novel citric/hydrochloric acid hydrolysis method was used in the study to prepare the carboxylated CNCs. The CNCs with high carboxyl content at a hydrolysis time of 4 h (CNCs-4H) with 1.39 ± 0.10 mmol/g showed the highest turbidity reduction and flocculation efficiency for all Özdemir (2016)he contaminant targets studied. It was also mentioned that the charge of the zeta potential of the CNCs played an important role in the charge neutralisation mechanism whereby more active flocculation sites of the sample were produced for agglomeration with the suspended particles. An effectiveness study was conducted using CPAM commercial flocculant on a real industrial dye effluent. It was found that that CNCs-4H which possessed -46.6 mV zeta potential assisted with coagulant $CaCl_2$ gave a higher reduction of turbidity, COD and BOD_5 with 80.9%, 36.5 % and 37%, respectively. Meanwhile, for CPAM the reduction was 40.8%, 5.1% and 5.0 % for turbidity, COD and BOD_5, respectively.

Liu et al. (2017) grafted polyacrylamide (PAM) and poly(*N,N*-dimethylacrylamide) (PDAM) on CNCs which they applied as flocculants to treat a kaolin suspension. The flocculation experiment for 0.1 wt% of kaolin suspension was carried out at pH 7, settling time 2 minutes, and with the assistance of 300 mg/L of $CaCl_2$ as coagulant. They found that the turbidity removal of CNC-g-PDMA was slightly lower than CNC-g-PAM under the same dosage with turbidity reductions from 200 NTU to 17.7 NTU and 62.3 NTU, respectively. This observation was explained as relating to the absence of intermolecular hydrogen bonding that would affect the agglomeration ability of the PDMA and colloidal particles. The floc size of both CNCs was measured as being similar under 7 ppm dosage, but up to 10 ppm, PDMA was reported to form a larger floc than PAM. This finding was related to the flexibility of grafted PDMA chains that might have increased aggregation tendency. They also noted that the settling time for flocculation was optimised at 2 minutes.

The potential of CNCs grafted imidazole and the effects of CO_2 application to induce *Chlorella vulgaris* flocculation were evaluated by Eyley et al. (2015). The noted that the adjustment of CO_2 saturation within the medium was a key strategy to reduce the pH for inducing the flocculation. In their study, imidazole was used as a functional group mainly due to the proximity of the pKa of the substituted imidazoles to the apparent pKa of CO_2 in solution. They observed a significant trend when the pH was increased from pH 4 to 9 over which the flocculation efficiency was decreased from 90% to 20%. At pH 6-8, the zeta potential of ImBnOO-g-CNCs was reported to change from negative to positive causing a sharp decrease in flocculation performance. They also pointed out that by increasing the CO_2 saturation, the pH would be reduced and therefore ImBnOO-g-CNCs will be protonated and flocculation will be activated. They concluded that increasing the degree of substitution (DS) of ImBNOO-g-CNCs will increase the flocculation effectiveness and thus reducing the amount of flocculants required for the treatment.

Two types of modified CNCs with 4-(bromomethyl)benzoic acid and 4-(1-bromoethyl)benzoic denoted as [Br][PyBnOO]-g-CNCs and [Br][PyMeBnOO]-g-CNCs, respectively, were used by Vandamme et al. (2015) as flocculants for harvesting *C. vulgaris*. Based on a comparison study, they reported that no floc was obtained for unmodified CNCs while the modified CNCs successfully achieved 100% flocculation efficiency at the same dosage. In the pH range of 4 to 11, both [Br][PyBnOO]-g-CNCs and [Br][PyMeBnOO]-g-CNCs were reported to exhibit positive zeta potential values between 9 and 27 mV, while the degrees of saturation were determined as 0.21 and 0.38, respectively. They suggested that the presence and absence of algal organic matter (AOM) significantly affects the flocculation efficiency. In their earlier work (Vandammen et al. 2012), they had noted that AOM contains extracellular polysaccharides with negatively charged carboxyl groups that might interact with the positively charged flocculants making them unavailable for microalgae flocculation and thus resulting a higher flocculant demand.

CNF prepared from ginger fibre waste was synthesised by Wang et al. (2018) using three different ratios of a mixture of $C_6H_8O_7$/HCl acid (9/1, 7/3 and 5/5) in a hydrolysis method and a traditional sulfuric acid method to assess the potential of carboxylated CNF aerogesl for turbidity removal in kaolin suspension and removal of Methyl Orange dye. They indicated that CNF can be a adsorption–flocculation agent as it has high surface charge (resulting from the carboxyl groups) that would lead to a large surface charge density and absolute zeta potential value that has charge neutralisation ability to stabilise the dye particle. They reported that 7-CNF aerogel with the length of 3,690 nm and diameter of 25.6 nm possessed was very robust mechanically with the highest compressive stress of 241.77 kPA at 90% strain. It also had a higher thermal stability compared to other CNFs produced from ginger fibre wastes. 7-CNF showed the highest removal of turbidity due to the charge neutralisation between CNF, kaolin and $CaCl_2$ particles. This was attributed to the higher carboxyl content and zeta potential of 7-CNF with 1.18 ± 0.10 mmol/g and -36.0 ± 3.0 mV, respectively whereas S-CNF showed zero carboxyl content with -21.7 ± 5.2 mV of zeta potential.

In another study conducted by He et al. (2016), CNFs were synthesised with three varying degrees of fibrillation, namely CNF-15p, CNF-25p and CNF-35p. The CNFs were then used to agglomerate precipitated calcium carbonate (PCC). In the one-component treatment system studied, they conducted an experiment at low (1%) and high (5%) CNFs dosage. They observed no significant difference in flocculation performance between the three degrees of fibrillation at both dosage levels. This observation was attributed to weak interaction between PCC and CNFs. The imperceptible change of CNFs during the fibrillation process was explained to be the main factor for the aforementioned observation. In a two-component treatment system, the combination of cationic starch (C-starch) and CNFs was reported to improve the flocculation of PCC. It was also noted that in the reflocculation process the floc was easily broken under a high shear level due to weak interaction between the PCC particles and CNFs.

Quinlan et al. (2015) modified CNFs with glycidyltrimethylammonium chloride using three different degrees of quaternization (quaternary ammonium content), namely 0.44 (QCNF-1), 1.47 (QCNF-2) and 2.28 (QCNF-3) meq/g. These materials were used as flocculants for the removal of anionic Reactive Orange 16 dye. Based on conductometric titration, the quaternary ammonium content was reported to increase from QCNF-1 to QCNF-3 proportionally to the zeta potential. They obtained a complete charge reversal, from negative to positive, for quaternized CNFs. This scenario favoured the dispersion stability of quaternized CNFs in water. They observed a significant change in the internal morphology of CNFs of which the tightly intertwined bundles of unmodified CNFs unravelled after the quaternization. This was explained as being due to strong electrostatic repulsion between quaternary ammonium moieties on CNFs. It was observed that tangled bundles decreased with increasing quaternary ammonium content. In the flocculation test, after the addition of QCNF-3 to dye solution, the flocs were observed to form instantaneously and within 1 h larger flocs were seen in the solution, while finer flocs were obtained following 12 h of sedimentation. The best flocculation treatment (highest removal efficiency of 295.1 mg/g) was obtained when QCNF-3 was applied as a flocculant.

Suopajärvi et al. (2013) evaluated the potential of five anionic dicarboxylic acid nanocelluloses (DCCs) with different charge densities to treat municipal wastewater. Their flocculation performance in the perspective of the coagulation-flocculation was examined by measuring the residual turbidity and COD. The flocculation efficiency of the DCCs correlated well with the charge density and nanofibril content of the DCCs. Moreover, the best flocculation performance was observed for DCCs type IV and V which possessed a higher number of both carboxyl and aldehyde groups as well as containing highly nanofibrillated materials at 1.31 and 1.68 mmol/g respectively. The content of aldehyde and carboxyl groups of the cellulose increased with the increase of the charge density. The authors also emphasised that the right coagulant dose for charge neutralisation was important in order to obtain effective coagulation and flocculation because flocculation will not occur in municipal wastewater without the presence of cationic coagulant. Based on a comparison study, they reported that the all five DCCs were effective to flocculate contaminants in wastewater possessing a similar performance to that of commercial flocculants, examined under similar optimised experimental conditions.

Chitosan

Chitosan is the second most abundant polymer on the earth after cellulose. It is generally obtained from chitin by deacetylation (H.P.S et al. 2016). Chitosan has a long chain structure that consists of large amounts of free amino and hydroxyl groups along its polymer chain backbone (Kumari et al. 2017). In acidic media, chitosan will be protonated and typically behave as a cationic polyelectrolyte. The protonated chitosan will interact with negatively charged surfaces of target pollutants via charge neutralisation and bridging mechanisms to achieve maximum flocculation performance (Yang et al. 2016). Therefore, there have been a number of research studies on the treatment of wastewater by applying chitosan and its derivatives as flocculants (Table 6).

The flocculation efficiency of three different types of chitosan, namely raw chitosan, nanoparticle chitosan and chitosan magnetite as flocculants in harvesting microalgae *Chlorella* sp. was evaluated by Sari et al. (2016). They compared their performance at four different concentrations (25, 50, 75 and 100 mg/L) and emphasised that the three flocculants exhibited a similar flocculation efficiency performance of about 90% removal within 60 minutes. They observed that under acidic conditions, a lower dosage of chitosan-based flocculants was required due to the protonation of the amino groups of chitosan and a higher charge density of the flocculants to destabilise the particle. The flocculation was explained to occur due to charge density and the charge neutralisation mechanism between the flocculants and target particles. Overall, the combination of chitosan and magnetic material with diameter < 30 nm was reported to yield a high flocculation performance of 98% and 92 ± 0.4% of harvesting efficiency at optimum dosage 100 mg/L followed by chitosan nanoparticle with diameter range between 23.08 – 61.54 nm shows 85% floc rate.

The prediction and optimisation of flocculation of *Microcystis aeruginosa* (MA) using chitosan-modified nano-sized montmorillonite (CTS/NMMT) with the application of Box-Behnken experimental design assisted with surface methodology and the quadratic statistical model was reported by Wang et al. (2015). They assessed the influence of three experimental parameters, namely dosage of CTS/NMMT with particle size less than 0.2 mm, weight ratio of NMMT to CTS and agitation time, on the flocculation of MA. They reported that the maximum removal of 94.7% of MA cells was observed with the content of CTS/NMMT of 300-320 mg/L, weight ratio of NMMT to CTS of 14:16, and agitation time of 16–50 minutes. They noted that CTS/NMMT was able to act as a protection shield for MA cell, preventing the cell damage and the leakage of the microcystins, which is one of the harmful cyanobacterial blooms. However, the cell leakage observed during the study was related to mechanical action from continuous stirring during the flocculation that removed the chitosan protection function. For that reason, removal of the flocs within 12 h of stirring to prevent leakage was recommended.

In a study by Sami et al. (2017), starch was used to assist the function of chitosan in attracting the anionic commercial dye molecules. The application of chitosan–starch based nanocomposites as flocculant was reported to remove 90% of Congo Red (CR) dye at an initial concentration of 0.015 mM, low pH value and 12 h of flocculation. The high removal of this anionic dye was explained as being due to the attraction of anionic dye to the protonated amino groups of chitosan. It was also noted that the presence of amylose chains in starch are helpful in attracting anionic CR dye species via electrostatic interaction. Following the flocculation of dye, a significant change to the surface of the nanocomposite of which it became coloured with a smooth morphology was noted. The potential of chitosan–starch based nanocomposites to flocculate commercial dyes in a wastewater collected from a textile factory was investigated. Due to high NaCl concentration in the wastewater, they noted that the commercial dyes also contained a considerable amount of salt. They emphasised this increased the molar ratio of salt, thus facilitating the coagulation of charged dyes.

Ma et al. (2016) synthesised polyacrylamide-grafted chitosan nanoparticles (NCS-*g*-PAM) through an ultraviolet-assisted polymerisation technique using 2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone as a photo-initiator. In their preparation study, the factors affecting the intrinsic viscosity and the yield of copolymer were evaluated. The optimum conditions for the synthesis of NCS-g-PAM were reported as: mAM:mNCS = 8:1, 0.15 g of initiator dosage, mCS:mTPP= 4.5:1, 1 minute of ultrasonication time, 4 h of illumination time, and 30 minutes of stirring. The flocculation performances of nanoparticles for both kaolin suspension and Cu^{2+} simulated wastewater were evaluated under various dosages of flocculants at certain pH values according to the zeta potential. The results showed that at an initial Cu^{2+}concentration of 2 mg/L, NCS-*g*-PAM with a diameter of 22 .36 nm and zeta potential of 59.7 mV was able to remove 70.5% of Cu^{2+} and the turbidity removal efficiency was found to be improved from 11.5% to 23.8% by replacing CS with NCS. In the case of kaolin suspension, the optimum removal was obtained when the NCS-*g*-PAM and polyaluminium chloride (PAC) were applied at the rate of 1 mg/L and 5 mg/L, respectively. They noted that the application of PAC as a coagulant successfully assisted NCS-*g*-PAM in the treatment of kaolin suspension.

Quaternized chitosan/organic montmorillonite (QCS/OMMT) nanocomposites have been reported for the removal of cellulose in a chemical pulp suspension by Lai et al. (2016). They synthesised the nanocomposites at five different mass ratios of QCS to OMMT, namely 1:2, 1:1, 2:1 4:1 and 8:1. The study indicated that the flocculants with a higher QCS content, a higher zeta potential, a larger distance, a lower beating degree and a more hydrophobic layer exhibited stronger flocculation between the flocculants and the cellulose particles. This was stated to be an important aspect contributing to a better retention and drainage-aid performance. It was noted that both flocculants and cellulose particles showed a charged patch interaction. The flocculation performance of QCS/OMMT nanocomposites with the assistance of $CaCO_3$ was also studied. The flocculation process between $CaCO_3$ particles and QCS or QCS/OMMT nanocomposites was considered in terms of electrostatic interaction.

Farid et al. (2013) investigated the flocculation of *Nannochloropsis* sp., a marine microalga, using sodium tripolyphosphate (STPP) modified nanochitosan. They reported that under optimised conditions, an increase of 9% in biomass recovery and a decrease of 40% in flocculant consumption were obtained when modified nanochitosan with diameter 13.7 nm was used as a flocculant agent for harvesting microalgae *Nannochloropsis* sp. Both pH and cell concentration were found to significantly influence the flocculation performance. In alkaline solutions, the flocs were observed to have a larger size compared to flocs produced in acidic solutions, which was related to the changes in the conformation and structure of the macromolecules caused by the protonation of the amine groups of chitosan. Meanwhile, the removal efficiency was reported to increase at high microalgae cell concentration. They recommended an initial cell density of 665×10^6 cells/mL in order to attain a maximum biomass recovery and minimum flocculation dosage consumption. It was also noted that the estimated cost for harvesting process of *Nannochloropsis* sp. using STPP modified nanochitosan was \$0.0246 per kg dry biomass, a relatively lower than a cost estimation of \$0.4 to \$0.75 per kg dry biomass made by William and Laurens (2010).

Metals and metal oxides

Metal and metal oxide nanoparticles have attracted researchers' interest due to their unique characteristics such as their electrical, optical, magnetic and catalytic properties (Nguyen et al. 2018; Xu. 2015). They are the most diverse class of materials in water and wastewater treatment. A summary of studies of the use of metal and metal oxide nanoparticles as flocculants for water treatment is presented in Table 7. For example, the use of titanium for water treatment has been investigated by Nyzhnyk (2017). They found that the Ti(IV) nanoparticle required less dosage and sedimentation time compared to other metal nanoparticle such as Al(III) and Fe(II). This was due to ion charge of the element, which affected the zeta potential of the nanoparticle and water sample. Ti(IV) was reported to work effectively at medium with pH less than 3.0, where flock appeared at a shorter time (1-2 mins) and a larger size (10-15 mm).

A study in a coagulation and flocculation process of water samples collected from River Nile Rosetta Branch at Basyoun City, Egypt by Almarasy et al. (2018) found that hematite nanoparticles (diameter of 9 nm) application at 30 mL with concentration of 2.98×10^{-6} M at pH 7.55 reduced the highest turbidity of 93.8 ± 0.005%. The effects of hematite nanoparticle application on several water quality parameters, namely total dissolved solids, conductivity, phosphate concentration, nitrate concentration, ammonia concentration, iron(II) concentration, pH and alkalinity were evaluated. Based on a comparison study with commercial alum, it was noted that hematite nanoparticles had an excellent ability to treat water samples, particularly for phosphate concentration. Hematite nanoparticles were reported to interact with phosphate ions to form insoluble iron(III) phosphate showing a significant reduction from 0.10 ± 0.005 to 0.005 ± 0.0003 mg/L.

Meanwhile, separation of TiO_2 by magnetic nanoparticls flocculants of $Fe_3O_4@SiO_2$ coating with different polymers as the outermost layer was studied by Leshuk et al. (2018). The surface of $Fe_3O_4@SiO_2$ was coated with poly(diallyldimethylammonium chloride) (PDADMAC) and chitosan (CS) as positively charged polyelectrolytes (PEs), and poly(sodium 4-styrenesulfonate) (PSS) and poly(acrylic acid) (PAA) as negatively charged PEs. A significant difference in flocculation performance between positively and negatively charged Pes was noted, which was discussed in terms of the electrostatic interaction of magnetic flocculants with the TiO_2 particles. The Fe_3O_4@SiO_2@PDADMAC with a positive zeta potential of 29 mV was reported to exhibit strong interaction with negatively charged TiO_2 nanoparticles, which resulted in a higher removal of 52% compared to that obtained for Fe_3O_4@SiO_2@CS (12% removal). In contrast, the suspended TiO_2 nanoparticles showed a repulsion mechanism toward Fe_3O_4@SiO_4@PAA and Fe_3O_4@SiO_4@PSS because the three flocculants have a negative potential above pH 4.0. A three-cycle flocculation and deflocculation experiment was conducted and it was found that the flocculation performance remained the same over the course of the experiment ($p > 0.1$). They concluded that the properties of the flocculants remain intact over three cycles of flocculation and deflocculation.

Lü et al. (2018) modified quaternized chitosan QC-grafted magnetic nanoparticles (MNPs) with Fe_3O_4 nanoparticles through a combination of methods, namely coprecipitation, surface coating and grafting. The Fe_3O_4@SiO_2-QC was used for demulsification with several experimental parameters such as dosage, QC grafting ratio (G_{q}), pH and magnetic field. It was noted that the magnetic flocculants with a higher QC grafting ratio showed a greater demulsification performance of more than 95% at the dosage of 15 mg/L under acidic conditions, 17 mg/L under neutral conditions and 19 mg/L under alkaline conditions. For the deflocculation process, the QC-grafted MNPs with magnetisation substitution of 25–35 emu/g produced about 90% water transmittance after 8 cycles under acidic conditions and 7 cycles under neutral and alkaline conditions. They explained that the Fe_3O_4@SiO_2-QC endowed the hybrid MNPs with permanent positive surface charges, thus allowing them to flocculate negatively charged oil droplets via electrostatic patching with a separation capacity of more than 105 g/g.

Ma et al. (2018) evaluated the flocculation performance of coated Fe_3O_4 with cationic polyacrylamide (CPAM) as a novel flocculant for highly turbid water. It was noted that the cationic degree played an important role in the experiment, of which a low cationic degree provides more contact with Fe_3O_4 in the synthesis process and which is not easily washed away, while at high methacryloyloxyethyl trimethyl ammonium chloride (DMC) content, the intrinsic viscosity will decrease, and this condition is unfavourable for synthesis. The optimal transmittance and residual turbidity were measured as 92.4% and 17.93 NTU, respectively, when Fe_3O_4-CPAM was used at a dosage rate of 0.24 g/L in 500 mg/L of simulated kaolin wastewater at neutral pH with stirring speed of 300 rpm, fast stirring time of 20 minutes and slow stirring time of 25 minutes, respectively. They obtained higher transmittance at lower pH. At acidic pH, the surface of Fe_3O_4-CPAM becomes positively charged, and moreover, repulsion between H^+ ions and cationic functionalities enhance,the adsorption percentage of kaolin. The effect of shear force was studied and at optimum dosage it was found that the strength factor and recovery factor were 36.75 and 8.47%, respectively. The floc size was reported to increase with increasing flocculant dosage. Smaller flocs were obtained at pH 5 as compared to those formed at pH 7 and 9.

Noor et al. (2018) evaluated the potential of magnetic cellulose as an effective flocculant for anaerobically treated palm oil mill effluent (AnPOME) that was collected from Adela Palm Oil Mill, Johor, Malaysia. They noted that magnetic cellulose synthesised at a weight ratio of 1:1 (cellulose : magnetite powder) with 1.5 mL of glutaraldehyde as a crosslinking agent produced the highest removal efficiency for all AnPOME samples studied in terms of turbidity, total suspended solids, colour and COD at 74.60%, 77.20%, 63.90% and 55.80%, respectively. They found that a high amount of magnetite powder in the production of magnetic cellulose led to a significant reduction in flocculation efficiency, which was attributed to the low degree of protonation giving rise to $\equiv Fe\text{-}O^-$ surface moieties repelling the negatively charged AnPOME. Meanwhile, an excessive amount of glutaraldehyde crosslinker was considered to affect the polarity attraction between the glutaraldehyde and magnetite reducing the number of active sites for adsorption of pollutant.

The functionalisation of magnetic iron oxide nanoparticles to *Moringa oleifera* (Mo) seed extract with the presence of oleic acid (AO) was undertaken by Santos et al. (2016). The applicability of magnetic flocculant to treat contaminated water was assessed in terms of removal of colour, turbidity and organic matter. It was found that different amounts of AO has resulted in different compatibility between inorganic and organic molecules. Treatment with MoFeAO was reported to achieve a maximum removal not exceeding 40% for all parameters studied, a lower percentage of removal than those obtained following treatment with MoFe. It was discussed that although AO played an important role as a compatibilising agent between inorganic iron oxide surface and organic molecules, the presence of this fatty acid increased the amount of organic matter in the treated water, which was unfavourable for water treatment. MoFe flocculant with a particle size between 10-20 nm was reported successfully to remove turbidity, colour and UV_{254nm} absorption compounds at percentage removal rates of 90%, 85% and 50%, respectively. The flocs were formed within 30 minutes of settling under the influence of applied magnetic field. An Mo content of 400 mg/L was recommended in order to obtain the best performance of removal in accordance with previous studies for water treatment using flocculation.

In a study conducted by Wang et al. (2016) prepared amino-riched polyamidoamine (PAMAM) dendrimer coated magnetic iron oxide (Fe_3O_4) nanoparticles. The Fe_3O_4@PAMAN was used as a flocculant to harvest an oleaginous *Chlorella* sp. HQ and the influence of several parameters such as dosage, pH and the thickness of PAMAM on the magnetic material upon flocculation performance was investigated. The harvesting efficiency for microalgae was reported to increase as the thickness of PAMAN was increased from G0-dMNPs to G3-dMNPs with a maximum removal of 95%, at a dosage of 80 mg/L for G3-dMNPs and within 2 minutes of stirring. The high removal of *Chlorella* sp. HQ was attributed as being due to the presence of abundant active groups (-CO-NH and $–NH_2$) on the surface of Fe_3O_4@PAMAN following surface coating. It was stated that these groups were able to promote electrostatic attraction between algae cells and nanoparticles. It was also found that the optimum conditions for harvesting can be achieved at the natural pH of the *Chlorella* sp. HQ at pH 8.0, where no significant effect for magnetic polymeric flocculants G0-dMNPs to G3-dMNPs was obtained in the pH range of 9.0 to 4.0. In addition, it was noted that the harvesting efficiency showed a slight reduction from 97.0% to 75.5% following 5 cycles of regeneration and reuse.

Abbott Chalew et al. (2013) investigated the optimal alum dose assisted with each Ag, TiO2 and ZnO nanoparticles as flocculants to determine the percentage removal of turbidity and TOC from five water samples, namely: (i) Maryland groundwater source (GW), (ii) suburban surface water source (SW), (iii) synthetic freshwater with NOM (SFW), (iv) synthetic freshwater without NOM (SFW_NOM) and (v) tertiary wastewater effluent (WWeff). From their observation the performance of ZnO nanoparticles had shown a significant difference in SFW with $p < 0.05$ of optimal dosage of alum as compared to Ag and TiO2 (Table 7). Their findings indicated that the NOM was the key factor for optimal alum dosage and not the addition of nanoparticles to the target. The combination of alum and nanoparticles affected only the stability of nanoparticles by producing positively charged hydrolytic species that neutralise negative surface charged on nanoparticles, which caused the aggregation of nanoparticles due to mitigation of electrostatic repulsion of nanoparticles in aquatic environment. Besides that, they also highlighted a concern on possible toxicity effects on the environmental and human health due to the decomposition of each Ag, TiO2 and ZnO nanoparticle. Ag and TiO2 nanoparticles were reported to exhibit the lowest breakthrough, with approximately 20% and < 10%, respectively, for all water samples studied. While ZnO had the highest breakthrough, with > 60% in most water samples and shown a complete breakthrough in SFW.

Other nanomaterials

Table 8 presents a summary of studies of the use of other nanomaterials as flocculants for water treatment. Yin et al. (2018) investigated the performance of lignin nanoparticles (L-NPs) and a L-NPs-gelatin complex for flocculation of two bacteria, namely *Staphylococcus aureus* and *Escherichia coli* in wastewater treatment in terms of dosage, pH value, initial cell concentration and settling time. They reported that at pH 4.5, approximately 86% of *S. aureus* and 89% of *E. coli* were settled in the first 5 minutes and the flocculation efficiency was increased to 95% at 30 minutes. At pH 5.0, 76.8% of *S. aureus* and 76.6% of *E. coli* were settled within 15 minutes and the flocculation efficiency reached 90% at 60 minutes. Above pH 5.0, they measured the zeta potentials of both L-NPs and L-NPs-gelatin complex as negative, which caused electrostatic repulsion between the strains and therefore reduced the flocculation performance. They emphasised that gelatin had no obvious flocculation effect in their study.

Modified carbon black/cationic polyacrylamide (*m*-CB/CPAM) nanocomposites were synthesised and used by Tian et al. (2018) as flocculants for oil sludge suspension treatment. Several factors such as the total monomer concentration, the dosage of the complex initiator, the mass ratio of acrylamide (AM) to dimethyldiallylammonium chloride (DMDAAC) [*m*AM:*m*DMDAAC] and the

UV irradiation time were found to affect the molecular weight of CPAM. They reported that the optimum condition of the molecular weight of CPAM was achieved at the total monomer concentration of 25%, the *m*AM:*m*DMDAAC of 5:1 and the UV irradiation time of 75 minutes. The 1-CB/CPAM was reported to have a porous structure, rough morphology and large surface area. Due to these properties, it was chosen in the flocculation of oil sludge suspension of which it performed very well for bridging adsorption mechanism. They noted that the optimum flocculation conditions of 1-CB/CPAM were reached at pH lower than 7.0, *m*CB:*m*CPAM of 2.5:1 and dosage of 0.2 g/L at 40 °C, which successfully attained transmittance with 89.6–94.1% of removal.

New flocculant-coagulant aluminum-silicon (ASFC) and iron-silicon (ISFC) nanocomposites have been used by Pavel et al. (2017) for cleaning three industrial oil-containing wastewaters, namely oil depot, carwash and oil refining factory wastewaters. It was found that both flocculant-coagulant agents played an important role for the purification of oil effluent, of which ASFC was reported to be effective in reducing the colour of industrial effluent while ISFC treatment showed a great reduction in oil content. Based on a comparison study, they found that ISFC required a two times lower dosage than ASFC for wastewater treatment. The maximum reduction of colour in oil refining factory wastewater treated with ASFC and ISFC was reported as 37.8% and 28.7%, respectively. However, they noted that the ASFC nanocomposite had a short shelf life whereby it turned into gel form and lost its coagulation-flocculation properties. Therefore, they developed a method to produce ASFC with a longer shelf life of more than 6 months.

Manafi et al. (2016) synthesised a nanocomposite based on polyacrylamide/graphene oxide (PAM/GO) and it was applied as a flocculating agent for purification of solvent phase water. They also studied the impact of PAM/GO concentration on the flocculation and retention properties. They reported that the amount of GO was proportional to the removal of ground calcium carbonate (GCC). In addition, the floc size was observed to increase with increasing amount of GO, which was related to dispersion between GO, amide and carboxylic groups on the polymer chain. They also found that the GO addition showed a significant reduction in intrinsic viscosity and supernatant turbidity. The main aspects of GO that are involved in retention mechanism were discussed as micro particle size and shape, while PAM was reported to be less effective for retention.

The development and application of a modified guar gum/SiO2 (g-GG/SiO_2) nanocomposite as flocculant for synthetic and industrial wastewaters were investigated by Pal et al. (2015). The flocculation performance was compared using three flocculants, namely g-GG/SiO_2 [IV=47.9 dL/g], polyacrylamide grafted guar gum (g-GG) [IV=11.7 dL/g] and unmodified guar gum (GG) [IV= 5.8 dL/g]. The potential of the flocculants was examined at three levels of pH and investigated in Fe ore/Mn ore suspension. The optimum dosage of flocculant required was found to increase as the pH level was increased from pH 4.0 to 7.0 and the removal of turbidity was reported to be higher in acidic condition (15.4 NTU for Fe ore and 20.2 NTU for Mn ore) than at neutral condition (25.7 NTU for Fe ore and 27.2 NTU for Mn ore). Under optimum experimental parameters, the flocculation effectiveness was reported to be in the order of g-GG/SiO_2 > *g*-GG > GG. The great performance of g-GG/SiO_2 was discussed due to interaction of H-bonding between the modified GG and the matrix-silica nanofiller, which has shown a great synergistic effect and increase in viscosity. They concluded that the flocculation efficiency of industrial wastewater using g-GG/SiO_2 greatly depends on hydrodynamic radius, hydrodynamic volume and molecular weight of the nanocomposites.

Conclusions and future perspectives

This review summarises the application of nano-flocculants based on carbon nanotubes, cellulose, chitosan, metal and metal oxide, and other materials that have been used for the removal of contaminants such as heavy metals, dyes and bacteria from contaminated water. In this review, we have highlighted several important physical and chemical characteristics, as well as optimum experimental parameters that significantly affect the flocculation performance. We have also discussed the issues and challenges, as well as suggestions and recommendations by researchers related to flocculation process. Based on this review, it is obvious that nano-flocculants have outstanding properties with respect to conventional materials such as small size with large surface area and being sustainable flocculants making them attractive for application in water treatment processes. As the utilisation of nano-based materials for flocculation has received great attention from environmental scientists worldwide and is being progressively developed, this review is a timely reference for further evolution of nano-flocculants.

Despite the fact that many studies has shown the nanomaterial flocculants can improve the quality of contaminated water but there is a need for further studies on advanced nanomaterial flocculants, which may be helpful in enhancing the performance of the flocculation and induce long term the life cycle of the flocculants material. A deep study on the possibilities for recycling the waste organics materials such as chitosan from crab/shrimp shell as flocculants is needed to reduce shell waste dumped in landfill. The development of fundamental knowledge on understanding is also important to improve the water cleaning strategies with low energy and investment requirements. Thus identifying the synergy effect between the technology, materials used and operation condition is essential to get a high efficiency of contaminant removal.

Last but not least, a great public concern related to application of nanomaterials in water and wastewater treatment was the potential of toxicity/ecotoxicity to the human health and environment. Although a number of assessments on toxicity effects of nanomaterials have been carried out, information on comprehensive evaluation of such toxicity possibilities and effects particularly on human and environment is relatively insufficient at present. For example, the toxicity analysis of nanomaterials for flocculant application should consider flora and fauna tolerance study, as well as antimicrobial activity. In this context, we would like to suggest the involvement of regulatory authorities to set up a framework and policy related to toxicity evaluation and application of nanomaterials for water treatment.

Disclosure statement

The authors declare no conflict of scientific and financial interest.

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Table Caption:

Table 1

Advantages and disadvantages of common methods for water treatment

Table 2

List of selected review articles with their focus related to flocculation process in water treatment

Table 3

The advantages and disadvantages of nano and non-nanomaterials used as flocculants in water treatment

Table 4

Carbon nanotubes used as flocculants for water treatment

Table 5

Cellulose-based nanomaterials used as flocculants for water treatment

Table 6

Chitosan-based nanomaterials used as flocculants for water treatment

Table 7

Metal and metal oxide nanoparticles used as flocculants for water treatment

Table 8

Other nanomaterials used as flocculants for water treatment

Table 1 Advantages and disadvantages of common methods for water treatment

Treatment	Description	Cost	[f]Advantages	[f]Disadvantages
Coagulation /flocculation	Contaminants particle will collide and bind together form flocs, then followed by sedimentation	[a]Operating cost (chemical, energy and sludge disposal): USD 0.3805 per m^3	• Easy and simple technique • Efficient treatment method to separate much kind of particles.	• Produce toxic sludge • Low removal of arsenic
Adsorption	Contaminants particle adhere to the surface of adsorbent or trapped in the small pores of the adsorbent	[b]The global activated carbon market size is expected to reach USD 14.66 billion by 2025	• Simplicity and ease of operation • Wide variety of target contaminants	• Require several types of adsorbent • Rapid saturation • Not applicable for large effluent
Oxidation	The production of very reactive oxygen species will be able to destroy a wide range of organic compounds	[c]The cost for removal of phenol was USD 308.482 per 1000 gallons for UV/H_2O_2 process [c]The cost for removal of reactive azo dyes was USD 74.613 per 1000 gallons for UV/H_2O_2 process [c]The cost for removal of trichloroethylene was USD 3.3266 per 1000 gallons for UV/H_2O_2 process	• Not producing any secondary by-products • No sludge formation	• Require of hazardous oxidizing chemical • High energy input
Membrane filtration	Membrane acts as a barrier to retain larger particles, and allowing smaller molecules to pass through the membrane into permeate	[d]The membrane filtration market is estimated to be valued at USD 12.66 billion in 2018, and is projected to reach USD 17.34 billion by 2023	• Small footprint • No chemicals required • Higher separation efficiency to retain small molecular weight organic micropollutants	• High operational cost and maintenance • Membrane fouling • High energy demand
Evaporation	Evaporator or solar light	[e]Operating system: USD 4200	• Efficient process	• High operational cost

	converts the wastewater to water vapour, while leaving the higher boiling contaminants behind.	[e]Operating expenses: USD 226/year	and main

Source: [a]Yoo (2018), [b]Business Wire (2018), [c]Mahamuni and Adewuyi (2010), [d]Business Wire (2019), [e]Pankratz (2000), [f]Crini and Lichtfouse (2019)

Table 2 List of selected review articles with their focus related to flocculation process in water treatment

No.	Title	Review Focus	Reference
1.	A critical review on flocculants and flocculation	Classification, mechanism and application of graft copolymers applied dynamically as polymeric flocculants for wastewater treatment	Bharti (2019)
2.	Water soluble polymer flocculants: Synthesis, characterization, and performance assessment	Methods used for characterisation of particle-polymer force measurement and flocculation/dewatering assessment with attention to the characterisation of aggregate structures	Vajihinejad et al. (2018)
3.	A review of wastewater treatment using natural material and its potential as aid and composite coagulant	Various types of natural-based coagulants used in the coagulation-flocculation of wastewater treatment	Salleh et al. (2019)
4.	Microbial flocculant as an alternative to synthetic polymers for wastewater treatment: a review	Bioflocculants derived from microororganisms used for wastewater depollution	Ben Rebah et al. (2018)
5.	Coagulation/flocculation in dewatering of sludge: a review	The prospects and technical developments of coagulation/flocculation in sludge dewatering	Wei et al. (2018)
6.	Understanding and optimization of the flocculation process in biological wastewater treatment processes: a review	The current state of sludge flocculation in terms of factor and strategies for intervention sludge flocculation and deflocculation process	Suresh et al. (2018)
7.	Potential of natural flocculant in coagulation-flocculation wastewater treatment process	Application and challenges of natural flocculant based on plant source in wastewater treatment	Zaman (2018)
8.	Plants extracts as coagulants-flocculant for wastewater treatment: a short review	The potential of natural based coagulants-flocculants used in wastewater treatment	Othamani & Khadharaoui (2018)
9.	Applications of natural coagulants to	The application of natural coagulants (non-plant based and plant-based) to	Kumar et al. (2017)

	treatwastewater - a review	treat wastewater	
10.	Research progress in bioflocculants from bacteria	Various bioflocculants from natural sources used for water and wastewater treatment	Abdullah et al. (2017)
11.	A review of the application of bioflocculants in wastewater treatment	The implication of actinobacteria application in flocculation and its mechanisms	Agunbiade et al. (2016)
12.	Recent advancement of coagulation – flocculation and its application in wastewater treatment	Elaborate the influence of process parameters on treatment efficiency and with recommendations for improvements and new directions for wastewater treatment	Teh et al. (2016)
13.	A review on chitosan-based flocculants and their applications in water treatment	Describe several flocculation mechanisms, the influence of structural elements of the chitosan-based flocculants on their flocculation properties and their applications in the treatment of various wastewaters containing different pollutants	Yang et al. (2016)
14.	Treatment of palm oil mill effluent (POME) by coagulation-flocculation using different natural and chemical coagulants: a review	Chemical and natural coagulant/flocculant used to treat POME	Jagaba (2016)
15.	A review on application of flocculants in wastewater treatment	Development of different types of flocculants in terms of flocculation performance and flocculation mechanisms	Lee et al. (2014)
16.	A review on applications of coagulation-flocculation and ballast flocculation for water and wastewater	Describe the coagulation and ballast flocculation, parameter affecting the coagulation-flocculation process, coagulant material, advantage of coagulation-flocculation and ballast flocculation and their application of water and wastewater	Borchate et al. (2014)
17.	A review on development and application of plant-based bio-flocculants and grafted bio-flocculants	Development and flocculating efficiencies of plant-based bio-flocculants and grafted bio-flocculants, the processing methods, flocculation mechanism and the current challenges	Lee et al. (2014)
18.	Current review on the	Coagulant/flocculant used for treatment of lignin	Yaser et al. (2014)

	coagulation/flocculation of lignin containing wastewater		
19.	Coagulation/flocculation of anaerobically treated palm oil mill effluent (AnPome): a review	Characterisation of AnPome by anaerobic digestion and coagulation/flocculation treatment	Yaser et al. (2013)
20.	A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewater	Various chemical and natural coagulant/flocculants used in textile wastewater	Verma et al. (2012)
21.	Development, characterization and the application of hybrid material in coagulation/flocculation of wastewater: a review	Application of hybrid materials in treating wastewater under different conditions, through coagulation and flocculation method. Step of preparation and characterisation of hybrid coagulant/flocculant	Lee et al. (2012)
22.	Algae and cyanotoxins removal by coagulation/flocculation: a review	Examines the character of freshwater algal populations and algogenic organic matter from a coagulation/flocculation context.	Ghernaout et al. (2010)
23.	Chitosan for coagulation/flocculation processes- an eco-friendly approach	The effects of the chitosan with different characteristic and the conditions of solution in the coagulation/flocculation performance from various suspensions and solutions	Renault et al. (2009)

Table 3 The advantages and disadvantages of nano and non-nanomaterials used as flocculants in water treatment

Source: Laux et al. (2018), Shak et al. (2018), Leshuk et al. (2018), Ajao et al. (2018), Schwaminger et al. (2017), Vlasova et al. (2016), Lu et al. (2016), Lee

Nanomaterials		Non-nanomaterials	
Advantages	Disadvantages	Advantages	Disadvantages
• Large surface area to mass ratio • High porosity Mechanically strong • Chemically reactive • Strong adsorption capacity	• Tend to aggregate or agglomerate in the application of cellulose nanocrystal due to the H-bond networks arising from the –OH groups on the cellulose nanocrystal surface • Exhibit toxic effects in terms of metal oxide nanoparticle • Difficult to handle and recover nanomaterials from aqueous due to the size particle excluding magnetic nanomaterial. • Easily oxidise, change the composition and properties of metal oxide nanoparticle	*Chemical Flocculants (organic and inorganic)* • High flocculation efficiency • Require low dosage	• Lack of biodegradability • Generate toxic products, (e.g., acrylamide from polyacrylamide) that lead to neurotoxic or carcinogenic effects • Produce fragile flocs
		Natural Flocculants • Safe and biodegradable • Renewable resources	• Short shelf-life • Require higher dosage relatively due to low molecular weight • Low flocculation efficiency

et al. (2014), Misha et al. (2012), Biener et al. (2009)

Table 4 Carbon nanotubes used as flocculants of water treatment

No.	Flocculants	Characteristics of flocculants	Contaminant/Effluent	Optimum flocculation conditions	Flocculation performance	Reference
1.	CNTs	NR	Corrosive wasted acid	Dosage: 2 g Settling time: 30 min	Treatment time: 30 min	Lei (2013)
2.	CNTs	Acid functionalised CNTs Surface area: 601 m^2/g Pore volume: 0.93 cm^3/g PZC: 7.3	Brewery wastewater	Dosage: 50 mg/L Settling time: 30 min	Turbidity removal: 57% COD removal: 61%	Simate et al. (2012)
3.	CNTs	NR	Brewery wastewater	Dosage: 40-50 mg/L Settling time: 30 min	CNTs ‘sandwiched’ in filter bed Turbidity removal: 89.2% COD removal: 94.2% CNTs in coagulation/flocculation tanks Turbidity removal: 91.7% COD removal: 95.4% CNTs in coagulation/flocculation tanks and ‘sandwiched’ in filter bed Turbidity removal: 95.9% COD removal: 96.0%	Simate (2015)
4.	SWCNTs	Diameter: 1-2 nm Length: 5-30 µm Purity: >90%	NOM	Dosage: 50 mg/L	DOC removal: 81.13% (winter), 63.5% (fall), 69.08% (spring) and 56.23% (summer) Residual UV_{254}: 82% (winter), 76% (spring), 71% (fall) and 65% (summer)	Özdemir (2016)

	MWCNTs	Diameter: 50-80 nm Length: 5-9 µm Purity: >90%			DOC removal: 73.4% (winter), 66.44% (fall), 76.54% (spring) and 61% (summer) Residual UV_{254}: 72.2% (winter), 80.2% (spring), 76.61% (fall) and 68.29% (summer)	
5.	SWCNT	Diameter: 1-2 nm Length: 5-30 µm Purity: >90%	EDCs	Dosage: 20 mg/L for BW, SW, and BRW and 50 mg/L for YL and OL.	EE2 removal: YL (>99%), BW (96.4%), SW (92.0%), BRW (86.1%) and OL (59.6%) BPA removal: YL (91.0%), BW (76.3%), SW (75.8%), OL (71.9%) and BRW (70.6%).	Joseph et al. (2013)
	MWCNT	Diameter:100-170 nm Length: 5-9 µm Purity: >90%			EE2 removal: YL (91.4%), BRW (68.5%), SW (35.4%), BW (30.4%) and OL (7.9%) BPA removal: YL (16.1%), BW (13.3%), BRW (13.0%), OL (10.3%) and SW (8.1%)	
6.	SWCNTs	NR	Methylene blue	Dosage: 150 mg/L pH: 10 Settling time: 1 hour	MB removal: 20% (pH 4), 20% (pH 7) and 31% (pH 10)	Liu et al. (2015)

NR not reported, *BW* brackish water, *SW* seawater, *BRD* broad river water, *YL* young leachate and *OL* old leachate

Table 5 Cellulose-based nanomaterials used as flocculants for water treatment

CELLULOSE NANOCRYSTALS						
No.	Flocculants	Characteristics of flocculants	Contaminant/Effluent	Optimum flocculation conditions	Flocculation performance	Reference
1.	Amine functionalised cellulose nanocrystal	NR	Fine dispersions in water	pH: 4	Settling time: 30 min (CNC-NH_2), and ~9 min (CNC-NH_2 + SDS)	Akhlaghi et al. (2015)
2.	PDMA-g-CNCs	NR	Latex colloids	Settling time: overnight Ratio optimal: ~0.2 pH: 4	Flocculation window: 0.26-1.05 Flocculation efficiency: 97.8-98.2 % Floc size range: 1043-1486 nm	Zhou (2015)
	P4VP-g-CNCs				Flocculation window: 0.15-0.30 Flocculation efficiency: 97.6-91.7 % Floc size range: 614-6112 nm	
	Amine-g-CNCs				Flocculation window: 0.07-0.15 Flocculation efficiency: 98.2-100 % Floc size range: 1193-3125 nm	
3.	Anionic carboxylated CNCs	Length: 200-250 nm Diameter: 15-22 nm Carboxyl content: 1.0-1.5 mmol/g Zeta potential: -33 to -47 mV	Kaolin suspension Methylene blue dye	pH: 7 Dosage: 20 mg/mL	Turbidity removal: 98% Dye removal: 92.3%	Yu et al. (2016)

4.	CNC-g-PDMA	NR	Kaolin suspension	Dosage: 10 ppm pH: 7 Settling time: 2 min	Turbidity removal: 91% Sedimentary floc size: 87 µm	Liu et al. (2017)
	CNC-g-PAM				Turbidity removal: 69% Sedimentary floc size: 72 µm	
5.	Imidazole-g-CNCs	Degree of substitution: 0.06 Crystallinity index: 0.81 Crystallite size: 6.7 nm Specific surface area: 370 m^2/g Surface coverage: 0.52 nm^2	Microalgae *Chlorella vulgaris*	Dosage: 200 mg/L pH: 43.5 Settling time: 10 min	Flocculation efficiency: 90.4 ± 0.4 %	Eyley et al. (2015)
6.	[Br][PyBnOO]-g-CNCs [Br][PyMeBnOO]-g-CNCs	Degree of substitution: 0.21 [PyBnOO] and 0.38 [PyMeBnOO] Zeta potential: 9-27 mV	Microalgae *Chlorella vulgaris*	Dosage: 70 mg/L for [PyBnOO] and 40 mg/L for [PyMeBnOO] Settling time: 30 min	Flocculation efficiency: 89% [PyBnOO] and 97% [PyMeBnOO]	Vandamme et al. (2015)

CELLULOSE NANOFIBRILS

No.	Flocculants	Characteristics of flocculants	Contaminant/Effluent	Optimum flocculation conditions	Flocculant performance	Reference
1.	Carboxylated CNFs aerogels	Length: 3800-2500 nm Diameter: 35-25 nm Carboxyl content: 1.13-1.18 mmol/g Zeta potential: -21 to -36 mV	Kaolin suspension	Dosage: 6 mg/L pH: 7	Turbidity removal: 87.64 %	Wang et al. (2018)
			Methyl Orange Dye		Dye Removal: 38-47 %	
2.	Cellulose nanofibril	Viscosity at 1% (w/w) dosage CNF-15p: 293 mPA s CNF-25p: 610 mPA s CNF-35p: 795 mPA s Zeta potential	PCC	NR	Maximum flocculation time at 1% (w/w) dosage of PCC CNF-15p: 90 s CNF-25p: 88 s CNF-35p: 85 s At 5 % dosage of PCC	He et al. (2016)

		CNF-15p: -33.6 mV CNF-25p: -34.8 mV CNF-35p: -36.1 mV Charge density CNF-15p: -94.2 µeq/g CNF-25p: -101.3 µeq/g CNF-35p: -126.9 µeq/g Degree of crystallinity CNF-15p: 62.3% CNF-25p: 60.3% CNF-35p: 59.5%			CNF-15p: 92 s CNF-25p: 98 s CNF-35p: 95 s Average ratio of maximum flocculation at 1% (w/w) dosage of PCC CNF-15p: 1.39 CNF-25p: 1.47 CNF-35p: 1.44 At 5 % dosage of PCC CNF-15p: 2.82 CNF-25p: 2.97 CNF-35p: 2.80	
3.	Quaternised cellulose nanofibrils	Quaternary ammnonium content QCNF-1: 0.44 QCNF-2: 1.47 QCNF-3: 2.28 Zeta potential QCNF-1: +29.9 mV QCNF-2: +32.4 mV QCNF-3: +39.9 mV	Reactive Orange 16	Dosage: 150 mg/L Settling time: 12 hour	Flocculation efficiency QCNF-1: 71.1 ± 2.3 % QCNF-2: 76.3 ± 1.2 % QCNF-3: 79.4 ± 0.9 %	Quinlan et al. (2015)
4.	Nanofibrillar dicarboxyl acid cellulose	Aldehyde content: 0.30-1.70 mmol/g Carboxyl content: 0.35-1.80 mmol/g	Municipal wastewater	Dosage: 2.5-5.0 mg/dm^3 pH: 8 Settling time: 30 min	COD removal: 40-60% Turbidity removal: 40-80%	Suopajärvi et al. (2013)

NR not reported

Table 6 Chitosan-based nanomaterials used as flocculants for water treatment

No.	Flocculants	Characteristics of flocculants	Contaminant/Effluent	Optimum flocculation conditions	Flocculation performance	Reference
1.	Chitosan nanomagnetite	Diameter: < 30 nm	Microalgae *chlorella* sp.	Dosage: 100 mg/L pH: 4.5 Settling time: 3 min	Flocculation efficiency: 98%	Sari et al. (2016)
	Nano chitosan	Diameter: 23.08-61.54 nm			Flocculation efficiency: ~87%	
2.	Chitosan/montmorillonite nanocomposite	Particle size: < 0.2 mm	*Microcystis aeruginosa*	Dosage: 300-320 mg/L Settling time: 16-50 min Ratio NMMT to CTS (14:16)	Removal efficiency: 94.7%	Wang et al. (2015)
3.	Chitosan-starch based nanocomposite	NR	Congo red dye	pH: 4 Settling time: 12 hour	Dye removal: 90%	Sami et al. (2016)
4.	Polyacrylamide-grafted nano-chitosan (NCS-g-PAM)	Diameter: 22.36 nm Polydispersity index: 0.533 Zeta potential: 59.7 mV	Cu^{2+} simulated wastewater	pH: 4 Settling time: 40 min Stirring time: 30 min	Cu^{2+} removal: 70.5% at dosage of 2 mg/L Turbidity removal: 23.8%	Ma et al. (2016)
5.	Quarenised chitosan/organic montmorillanite (QCS/OMMT)	Zeta potential OMMT-1: 45.0 mV OMMT-2: 61.0 mV OMMT-3: 61.5 mV OMMT-4: 61.0 mV OMMT-5: 64.0 mV Particle size OMMT-1: 4 µm OMMT-2: 4 µm OMMT-3: 4 µm OMMT-4: 4.8 µm OMMT-5: 5.3 µm	$CaCO_3$	Settling time: 30 min	Absorbance of $CaCO_3$ at UV_{550nm} QCS: 0.030 at 15 mg/kg QCS/OMMT-1: 0.034 at 40 mg/kg QCS/OMMT-2: 0.030 at 30 mg/kg QCS/OMMT-3: 0.029 at 20 mg/kg QCS/OMMT-4: 0.028 at 15 mg/kg QCS/OMMT-5: 0.025 at 10 mg/kg	Lai et al. (2015)

6.	Nano-chitosan	Diameter: 13.7 nm	Microalga *Nannochloropsis* sp.	Dosage: 60 mg/L pH: 8 Settling time: 1 hour	Turbidity removal: 98% Removal efficiency: 97%	Farid (2013)

NR not reported

Table 7 Metal and metal oxide nanoparticles used as flocculants for water treatment

No.	Flocculants	Characteristics of flocculants	Contaminant/Effluent	Optimum flocculation conditions	Flocculation performance	Reference
1.	Hematite (α-Fe_2O_3)	Diameter: 9 nm	Nile river water	pH: 7.55 Settling time: 30 min Concentration: 2.98×10^{-6} M	Turbidity removal: 93.8 ± 0.005%	Almarasy et al. (2018)
2.	Fe_3O_4@SiO_2@PDADMAC Fe_3O_4@SiO_2@CS Fe_3O_4@SiO_2@PSS Fe_3O_4@SiO_2@PAA	Hydrodynamic diameter PDADMAC: 272 nm PSS: 278.1 nm PAA: 462 nm CS: 1180.3 nm Zeta potential PDADMAC: 29 mV PSS: -56.2 mV PAA: -52.1 mV CS: -35.9 mV	TiO_2 nanoparticles	pH: 7 Dosage: 0.1 g/L	TiO_2 removal: PDADMAC: ~70% CS: ~13% PSS: ~2% PAA: ~2%	Leshuk et al. (2018)
3.	QC-grafted MNPs	Magnetisation saturation: 25-35 emu/g	Emulsified oil droplet	Dosage: ~13 mg/L Settling time: 30 min	Water transmittance: ~ 85%	Lu et al. (2018)
4.	CPAM	Magnetisation saturation: ~59 emu/g	High turbid water	Dosage: 0.24 g/L Settling time: 30 min Stirring speed: 300 rpm Stirring time: 20 min	Water transmittance: 98.3% Turbidity removal: 99.6%	Ma et al. (2018)
5.	Magnetic cellulose (m_{cel}:m_{mag}) 1:2 as Magcell 1 1:1 as Magcell 2 2:1 as Magcell 3	NR	AnPOME	Settling time: 30 min	Turbidity removal Magcell 1: 36.20% Magcell 2: 74.60% Magcell 3: 59.10% Colour removal Magcell 1: 17.20%	Noor et al. (2018)

					Magcell 2: ~51% Magcell 3: 33% TSS removal Magcell 1: 17.20% Magcell 2: 71.1% Magcell 3: 50.30% COD removal Magcell 1:30% Magcell 2: 52% Magcell 3: 40.70%	
6.	Magnetic functionalised Mo	Size: 10-20 nm Magnetisation saturation: 43 emu/g	Raw water	Dosage: 10 mg/L of γ-Fe_2O_3 and 400 mg/L of Mo Settling time: 30 min	Colour removal: 85% Turbidity removal: 90% Residual UV_{254nm}: 50%	Santos et al. (2016)
7.	Fe_3O_4@PAMAM	Nitrogen content (wt. %) G0: 0.4 G1: 2.0 G2: 5.0 G3: 10.6	Oleaginous *Chlorella* sp. *HQ*	Dosage G0-dMNPs: 200 mg/L G1-dMNPs: 150 mg/L G2-dMNPs: 120 mg/L G3-dMNPs: 80 mg/L Settling time: 10 min	Harvesting efficiency: 95%	Wang et al. (2016)
8.	Ag NP TiO_2 NP ZnO NP	Averarage size particles Ag: 83.6nm TiO_2: 33.7 nm ZnO: 35.6 nm	Synthetic and natural water from central Maryland	Settling time: 60 min	Optimum alum dosage for Ag nanoparticle Turbidity: 4.36 (GW), 3.41 (SW), 2.62 (SFW), 3.32 (SFW_NOM), and 10.2 (WWeff) TOC: 3.98 (GW), 3.79 (SW), 2.84 (SFW), 3.70 (SFW_NOM), and 10.64 (WWeff)	Abbott Chalew et al. (2013)

TiO_2 nanoparticle
Turbidity: 4.55 (GW), 3.22 (SW), 2.66 (SFW), 3.05 (SFW_NOM), and 9.40 (WWeff)

TOC: 3.55 (GW), 3.27 (SW), 2.78 (SFW), 3.41 (SFW_NOM), and 9.95 (WWeff)

ZnO nanoparticle
Turbidity: 3.98 (GW), 2.75 (SW), 1.21 (SFW), 3.36 (SFW_NOM), and 8.36 (WWeff)

TOC: 3.22 (GW), 2.84 (SW), 1.42 (SFW), 3.84 (SFW_NOM), and 9.10 (WWeff)

NR not reported

Table 8 Other nanomaterials used as flocculants for water treatment

No.	Flocculants	Characteristics of flocculants	Contaminant/Effluent	Optimum flocculation conditions	Flocculation performance	Reference
1.	Lignin nanoparticles - gelation complex	Average size: 955.3 nm Zeta potential: -19.8 mV	*S. aures* and *E. coli*	Dosage: 3 g/10^{12} cell pH: 4.5 Settling time: 30 min	Flocculation efficiency: ~99%	Yin et al. (2018)
2.	*m*-CB/CPAM (*m*=1,2,3)	NR	Oil sludge suspension	Dosage: 0.2 g/L pH: 2-7 Temperature: 40°C	Transmittance: 89.6-94.1%	Tian et al. (2018)
3.	ASFC and ISFC	NR	Oil-containing industrial wastewater	Dosage ISFC: 5 mg/L ASFC: 10 mg/L pH: 8.3-8.7 (ISFC)	1) Oil refining factory wastewater Turbidity removal: 48.3% (ASFC) & 74.4% (ISFC) Oil products: 58.3% (ASFC) & 53.4% (ISFC) 2) Carwash wastewater Turbidity removal: 67.5% (ASFC) & 30.0% (ISFC) Oil products: 98.2% (ASFC) & 96.3% (ISFC) 3) Oil depot wastewater Turbidity removal: 30.2% (ASFC) & 63.0% (ISFC) Oil products: 40.1% (ASFC) & 32.2% (ISFC)	Pavel et al. (2017)
4.	PAM/GO	Intrinsic viscosity: 328-1351 cm^3/g Surface charge: 0.40-1.09 meq/g	GCC	Dosage: 75 mg	Turbidity removal PG0: 410 NTU PG0.1: 305 NTU PG0.3: 270 NTU PG0.5: 225 NTU	Manafi et al. (2016)

4.	PAM/GO	Intrinsic viscosity: 328-1351 cm^3/g Surface charge: 0.40-1.09 meq/g	GCC	Dosage: 75 mg	Turbidity removal PG0: 410 NTU PG0.1: 305 NTU PG0.3: 270 NTU PG0.5: 225 NTU PG0.7: 190 NTU	Manafi et al. (2016)
5.	Modified guar gum/SiO$_2$ nanocomposite	Intrinsic viscosity: 40.0-46.0 dL/g Polydispersity index : 1.10-1.45 Molecular weight : 2.44-4.12 (x 10^6) g/mol Hydrodynamic radius: 2.0-3.1 nm	Paper industry effluent and mine process water	Dosage: 9 ppm Agitation time: 15 min Agitation speed: 75 rpm	1) Paper effluent Turbidity removal: 84.38% TS: 59.54% TDS: 40.60%, TSS: 77.74% COD: 49.23% Fe^{3+} removal: 86.40% Pb^{2+} removal : 68.42% Zn^{2+} removal: 84.62% 2) Mine process water Turbidity removal: 89.18% TS: 51.82% TDS: 28.57% TSS: 67.90% Mn^{2+} removal: 99.27% Fe^{3+} removal: 95.00%	Pal et al. (2015)