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Evaluation and removal of emerging nanoparticle contaminants in water treatment: a review

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ABSTRACT

Engineered nanoparticles (ENPs) are currently introduced into various consumer products. Numerous new applications and products containing nanoparticles are expected to increase in the future, and hence leading to the presence of nanoparticles in natural aquatic environment. The prominent concerns with the release of ENPs are their detrimental effects on ecosystem and human health. However, we are far from having appropriate analytical methods to acquire data on concentration, chemical characteristics, and transport of nanoparticles in aquatic environment. Moreover, there is no conventional treatment that can absolutely protect the consumer from exposure to ENPs. This paper discusses the characterization techniques that are used for identifying different types of nanoparticles, the status of current analytical methods, advantages of coagulation and ultrafiltration that can effectively remove contaminants from drinking water, future development of water analysis and treatment technologies for removing different nanoparticles from aquatic environment.

Keywords: Nanoparticles; Aquatic system; Coagulation; Ultrafiltration

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1. Introduction

Nowadays, nanotechnologies utilizing engineered nanoparticles (ENPs) (e.g. metal/metal oxide, carbon nanotubes, and fullerenes) have envisaged to become a flourishing industry and have significant influence on human everyday life for example by providing approaches for the production of novel material, clean energy, as well as a number of medicine application for serious human disease [1]. Moreover, they also showed potential to contribute to effective pollution control, treatment and environmental remediation because of their high surface area (surface-to-volume ratio) and their associated high reactivity [2–7]. However, along with the unique benefits of nanoparticles, there was also significant concern about the ecological and human health consequences stemming from exposure to ENPs that have proliferated in commercial products [8,9]. Recently, the toxicity of nanoparticles to a variety of organisms has been demonstrated in a number of recent studies. For example, the toxicity of nanoparticles has been observed for aquatic (*Lemna minor*) [10] and terrestrial (*Lolium multiflorum*) [11] plants, vertebrates (zebra fish) [12], microorganisms (*Escherichia coli*) [9,13], and human cells (skin keratinocytes, lung fibroblast cells, and glioblastoma cells) [14–18]. Consequently, determining the exposure of nanoparticles in the environment is crucial in evaluation of their potential risk to human health and ecosystem health.

Human exposure to nanoparticles is most likely during their manufacturing, but inhalation of nanoparticles released to the atmosphere, ingestion of drinking water or food (e.g. fish), dermal exposure from sunscreens and cosmetics that have accumulated nanoparticles may also be possible [19]. Oberdörster et al. [20] and Elder et al. [21] investigated that inhaled manganese oxide nanoparticles had an entry into the olfactory bundle under the forebrain via the axons of olfactory nerve in the nose and that they reached other parts of the brain also through systemic inhalation. Nurkiewicz et al. [22] demonstrated that inhalation of nano-sized titanium dioxide ENPs reached systemic circulation in rats. These findings revealed that different types of inhaled ENPs could reach systemic circulation and via this route be distributed to a number of different target organs including brain, liver, kidney, immunological system, and vessel walls. In addition, Metal-containing ENPs might cause toxicity to cells by releasing harmful trace elements or chemical ions in aqueous environment. For example, silver ENPs could release silver ions that interacted with proteins and inactivate vital enzymes. The lead and cadmium used in quantum dots (QDs) were known reproductive and developmental toxins [23,24].

Ingestion of drinking water, as an important route for human exposure to nanoparticles, is related to the fate, transport and transformation of nanoparticles in the aqueous environment. The fate of nanoparticles is largely depended on their physical, chemical, morphological characteristics and interaction with other substances in the aquatic environment. A crucial barrier in limiting human exposure to nanoparticles is the efficacy of water treatment processes, which generally include coagulation, flocculation, sedimentation, and filtration. However, the size, charge and surface properties and environmental conditions have significant effect on ENPs removal from water treatment processes [25–27]. Concomitantly, the presence of natural organic matter (NOM) plays a key role in the charge balance of ENPs, and thus determining the mobility and deposition behavior in natural aqueous matrices [28–30]. Moreover, environmental conditions such as pH, ionic strength and electrolyte type have a profound effect on surface charge and aggregation potential of nanoparticles [31]. It will be necessary to fully investigate the characteristics, dispersion and stability of ENPs in water as well as their removal by water treatment processes. Accordingly, the purpose of this article is to critically review analytical methodologies that are used for identifying transport, transformations and toxicity of nanoparticles in the aquatic environment and promising technology for developing new process for removing nanoparticles from the aquatic environment.

2. Classification and sources of nanoparticles

Nanoparticles are in the size range between 1 and 100 nm [32], and show unique physical and chemical properties as compared to bulk materials. Depending on the origin, a further distinction is made between three types of nanoparticles: natural, incidental and engineered particles. Natural nanoparticles such as volcanic dust, lunar dust and mineral composites have existed from the beginning of the earth and in the environment. Incidental nanoparticles, also defined as waste or anthropogenic particles, formed as the result of manmade industrial processes (e.g. diesel exhaust, coal combustion and welding fumes). ENPs can be grouped into two types, as depicted in Table 1.

ENPs have gained much attention because of their positive effects in improving many sectors of economy, including consumer products, pharmaceutics, cosmetics, transportation, energy and agriculture, and are being increasingly produced in large amounts

Table 1
Classification of nanoparticles [33]

Type	Formation			Example
Natural	C-containing	Biogenic	Organic colloids	Humic, fulvic acids
			Organisms	Viruses
		Geogenic	Soot	Fullerenes
		Atmospheric	Aerosols	Organic acids
	Inorganic	Biogenic	Oxides	Magnetite
			Metals	Ag, Au
		Geogenic	Oxides	Fe-oxides
			Clays	Allophane
		Atmospheric	Aerosols	Sea salt
Anthropogenic (manufactured, engineered)	C-containing	By-product	Combustion by-products	CNT, Nanoglobules, onion-shaped nanospheres
		Engineered	Soot	Carbon black, fullerenes, functionalized CNT
			Polymeric NP	Polyethyleneglycol (PEG) NP
	Inorganic	By-product	Combustion by-products	Platinum group metals
		Engineered	Oxides	TiO_2, SiO_2
			Metals	Ag, iron
			Salts	Metal-phosphates
			Aluminosilicates	Zeolites, clays, ceramics

[33,34]. This expansion in applications, and the incorporation of “nano” ingredients into products that may be released during the life cycle of those products, will increase the occurrence of ENPs in aquatic, terrestrial and atmospheric media environments. For this reason, the potential adverse organism- and ecosystem-level impacts have given rise to concerns by citizens, the scientific community and governmental agencies. Furthermore, sufficient knowledge of the fate, transformation and transport of ENPs in aquatic environmental and biological system is crucial to understand the environmental risks posed by these materials and to develop an effective removal process. Nanoparticles may follow a variety of pathways, whose ultimate destiny will be at the water/sediment interface, as depicted in Fig. 1 [35].

Moreover, the behavior, fate and transport of ENPs in natural environment depend on their surface properties, sizes, and environmental conditions, such as pH, ionic strength, electrolyte valence, and NOM components of natural aquatic environment. Aquatic chemistry dictates that formation or break-up of aggregates might result from interactions between natural water components and ENPs. Traditionally, the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory is dependent on solution properties such as ionic strength, electrolyte ion valence and pH [36], which determine the charge on the ENPs and the thickness of the electric double layer (EDL). As the pH of aquatic environment approaches the point of zero charge (PZC), the electrostatic repulsion between ENPs and the surrounding particles showed a notable decrease, which lead to fast aggregation, increased aggregate size, and increased rate of deposition onto soil and sediment particles. Ionic strength and valence of electrolyte ion also influence the EDL between ENPs and surrounding surfaces.

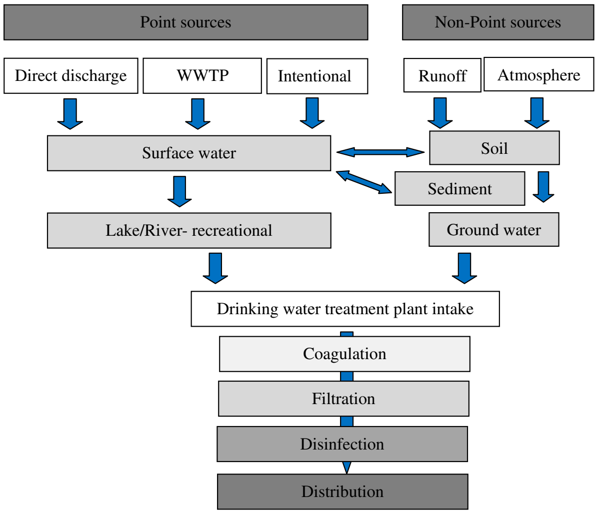

Fig. 1. Pathways by which nanoparticles enter the water column.

In addition, due to their high specific surface areas, ENPs are most likely to bind metals and other waterborne contaminants and the presence of these other natural species can also change the surface charge on the ENPs. Evidence from recent studies has shown that NOM had been observed to influence ENPs stability and aggregation for metal oxides [37,38], metals [39,40] and carbon-based ENPs [30]. Additionally, the charge screening and bridging are regarded as the aggregation mechanism between NOM, divalent ions and ENPs. These conclusions contribute to the full understanding of the fate and transport of ENPs in complex aquatic system.

At present, there is no single technique to extract and characterize nanoparticles from aquatic system, and a combination of analytical approaches for investigating the broad range of ENPs will have to be employed in the aquatic environment. Additionally, considering potential toxic effects on human health due to their unintended release into the environment, ENPs are becoming one of the most serious environmental issues. Therefore, it is critical to develop a more efficient and still economical potable water treatment unit processes to remove ENPs from the complex aquatic environment.

3. Analytical techniques

Test conditions have to be examined and optimized prior to analysis of nanoparticles. Aggregation, stabilization, dissolution as well as ecotoxicity of ENPs depend on experimental conditions and test medium to a large extent, and vary greatly across the aquatic system. For instance, humic substances present in water can stabilize ENPs by steric and electrostatic interaction [41,42]. The change in pH of test medium can alter the surface potential and thus very likely affect the behavior of ENPs. Variation of ionic strength can also cause change in the form of ENPs [43,44]. For certain ENPs such as TiO_2, light intensity may be an important experimental parameter [45]. Sample storage vessel should also be considered in the experiment. Au ENPs show stronger adherence to the wall of Teflon and plastic containers than glass vessels [46]. Consequently, the separation approaches of the nanoparticles have brought considerable attention in water industry recently.

3.1. Separation and size fractionation

Conventional methods to study size distribution include cross-flow ultrafiltration and size exclusion chromatography (SEC), hydrodynamic chromatography and field-flow fractionation (FFF). Cross-flow ultrafiltration separates particles into fractions according to membrane pore size. However, the resolution in size distribution is extremely limited even when fractioning goes through a few steps with different membrane pore sizes. SEC may suffer from irreversible adsorption of nanoparticles onto the column packing materials and the strong interaction between the stationary phase and nanoparticles, thus altering the characteristics of the environmental samples and misleading the interpretation of size distribution. HDC avoids phase interaction but experiences poor peak resolution.

FFF is a one phase chromatography technique, with the sub-technique asymmetric flow field-flow fractionation (AFFF) being most frequently employed. Size separation by AFFF is achieved due to differences in diffusion coefficients of particles or colloids. The whole separation process is gentle, rapid and non-destructive, without a stationary phase that may interact with the sample. The sample is eluted through a thin, flat channel (the channel flow). Within the flow channel, a parabolic flow profile is created due to the laminar flow of the liquid. A second flow (cross-flow) perpendicular to the channel flow is applied to force the sample particles or colloids towards the lower wall of the channel (accumulation wall). Diffusion associated with Brownian motion, in turn, produces a counteracting motion. Smaller particles with higher diffusion rates tend to reach an equilibrium position higher up in the channel, where the longitudinal flow is faster. Thus, different sizes of particles separate attributed to the velocity gradient in the channel, with smaller particles eluting earlier. The upper wall of the channel is impermeable. The accumulation wall covered with ultrafiltration membrane retains the particles larger than the cut-off value, but allows the solvent to pass through. Since the fractionation is based on simple physical properties, which can be theoretically described, the hydrodynamic diameter of the particle can be directly calculated from retention time and channel dimensions. Size separation of AFFF spans a wide range from 1 nm to 100 μm. The resolving power is such that the monomer and dimer of BSA can be baseline-separated.

3.2. Microscope technology

A wide range of analytical techniques are available for comprehensive as-synthesized materials, many of which can be potentially applied to analyze ENPs in the environmental samples. A review on the characterization of environmental nanoparticles enabled by various techniques has been published earlier [47]. The most confirmative and widely accepted technique for characterization of nanoparticles and other nanostructured materials is modern electron microscopy which includes transmission electron microscopy (TEM) and scanning electron microscopy (SEM), usually integrated with energy dispersive X-ray (EDX) analyzer. The imaging resolution of TEM is typically higher than SEM. Certain TEM configuration offers extremely high resolution down to 0.05 nm. However, TEM has its limitations. Extensive sample preparation procedures are required for many materials in order to get the sample film thin enough to be electron transparent, which is quite time-consuming and significantly reduces the throughput of sample analysis. In addition, sample must be dry and kept in a high vacuum (typically ~10^{-9} Torr), which makes it inconvenient for characterizing environmental samples. The structure of the materials may be altered during the sample preparation. Also, the field of view is relatively small, bringing up the possibility that the region analyzed may not be representative of the whole sample. On the other hand, SEM is capable of imaging a comparatively large area of the specimen and bulk materials instead of just thin films or foils. SEM can achieve the resolution of 1.0 nm, which is sufficient for nanoparticle characterization. Standard SEM also has the limitation of imaging artefacts upon drying environmental samples, whereas environmental SEM (ESEM) allows the samples to be observed in low-pressure gaseous environment (e.g. 1–50 Torr) and high relative humidity (up to 100%), sustaining the nature of the environmental sample and mitigating the load of sample preparation. In an attempt to obtain the images of fully undisturbed environmental samples, WetSEMTM technology employs stainless steel capsules equipped with an electron transparent membrane to contain wet samples, imaging in standard SEM [46,48,49]. Limitations of WetSEM such as possible blurring image due to the motion of particles in the medium, the lower detection limit than dried samples, different efficiency of adherence to capsule membrane, were identified, which make further development of this emerging technique absolutely necessary [47].

Atomic force microscopy (AFM) measures the forces of interaction between a sharp tip (radius of curvature usually ~10 nm) and the sample by rastering the tip over the sample surface or the sample beneath the tip. Particle size in 3-D with resolution of 1 nm, shape and topography can be obtained by AFM. The image can be measured in different environment including ambient air, liquid and vacuum, which is advantageous over TEM and standard SEM. However, the chemical information is difficult to obtain with AFM.

3.3. Scattering and spectroscopic techniques

Dynamic light scattering (DLS) determines particle size and size distribution for liquid samples [50]. The measurement is *in situ* and non-disturbing, suitable for environmental condition. However, this technique face challenges when dealing with polydispersed samples or in complex media [51]. Coupling with separation techniques helps mitigate the issue and thus enhances its applicability.

Laser induced breakdown spectroscopy (LIBS) is a type of atomic emission spectroscopy employing laser pulse as the excitation source to form plasma for atomizing and exciting samples. LIBD was applied to detect aquatic colloids including nanocolloids [52]. In theory and practice, breakdown probability is related to particle size and concentration. It is approximately proportional to particle diameter (sphere); LIBD is particularly much more sensitive for small particles (<70 nm) than LS. However, when particle size is above 70 nm, sensitivity of LS is better.

X-ray-based methods such as X-ray absorption (XAS), fluorescence (XRF), and photoelectron spectroscopy (XPS) as well as diffraction (XRD) are powerful tool for surface characterization. These methods can provide information on surface properties and coatings, crystallography structure or elemental composition [53].

3.4. Elemental analysis and characterization

Although SEM integrated with EDX is a suitable and powerful technique for the characterization of nanoparticles, it can only perform off-line detection with inefficient throughput of analysis. Alternatively, ICP-MS features low detection limits, high sensitivity, large dynamic range and ability to simultaneously characterize and measure a large number of elements, making it a super detector for metals. Coupling FFF with ICP-MS allows for the simultaneous determination of multielements at ppt level based on particle size and elements. Nanocomposites comprise more than one type of nanoparticles and contain metal elements in the compositions. Thus, this strategy can also be applied to nano-composites. ICP-MS is an element-specific detection technique, and the concentration of metal-based nanoparticles detected can be reported as the content of corresponding metal(s) contained, without the need of running standard nanoparticles. ICP-MS has already been used as an on-line detector for FFF in a number of geochemical and environmental applications such as study of size-based speciation of natural colloidal particles in a watershed system, investigation of trace metal distributions in colloidal organic matter from compost and municipal wastewater [54], multi-element determination of colloidal size distributions in natural water samples [55] and determination of composition and mineralogy of environmental colloidal samples [56]. The two techniques are well matched in terms of flow rates and liquid phase used.

Single particle ICP-MS has been found to be the practical technique for characterizing engineered metal-containing nanoparticle at environmentally relevant level [57]. Single particle ICP-MS can provide concentration of metal-containing ENPs in water sample as well as mass of analyte metal in each individual particle. Mass of single particle obtained can be used to estimate the size of nanoparticles. The analysis of one sample can be accomplished within 1 min. This technique is also extremely sensitive, being able to detect the concentration as low as a few hundred particles per mL. Coupling SP-ICPMS with AFFF can achieve separation of particles according to hydrodynamic diameters. The hyphenated method can help differentiate primary ENPs from nanoparticles associated with natural colloids or surface coating to a certain extent.

Quantitative analysis of fullerenes with high sensitivity can be accomplished by HPLC coupled with various mass spectrometers following sample extraction process [58]. Isaacson et al. [59] reported the determination of fullerenes in water samples with a detection limit of 0.4 μg/L by HPLC–ESI-MS following liquid–liquid extraction, while [60] applied HPLC coupled with tandem MS (HPLC–MS/MS) upon ultrasonic extraction to detect fullerenes at level as low as 0.2 ng/L. More recently, accurate mass screening liquid chromatography-hybrid linear ion trap Orbitrap mass spectrometry was explored to quantify fullerene nC_{60} and related transformation products in water and detection limit of 5 ng/L was achieved [61].

No reports can be found for the quantification of CNTs in environmental samples, probably due to their extremely low solubility in aqueous as well as organic system. This problem can be partially resolved by using surfactants [62], biopolymers [59], sonication and hydroxylation of the tubes ends and damaged regions. Separation and characterization of as-prepared carbon nanotubes by FIFFF-UV combined with TEM have been reported [63].

However, there is no single protocol to characterize the fate and the behavior of ENPs in complex environmental media, and it is likely that a combination of analytical methods will be required to investigate adequately the broad range of ENPs in aquatic matrices. Among the most promising on-line techniques are those integrating LIBD or FIFFF with subsequent spectroscopic, microscopic, or biosensor measurement for complete characterization [35].

4. Removal of nanoparticles via coagulation

4.1. Principle of coagulation

From the theoretical point of view, coagulation is a process where the repulsive potential of electrical double layers of colloids is reduced, which leads to microparticles w a mass large enough to settle or be trapped in the filter. Among several mechanisms of particle aggregate, two were referred frequently for the coagulation of particles or NOM: charge-neutralization and sweep-floc mechanism [64,65]. The charge neutralization would be accomplished over a narrow pH range (4–5.5), which results from a specific chemical reaction between positively charged coagulants and the negatively charged contaminants, thus leading to aggregation. On the other hand, sweep-floc mechanisms appear in the range of pH 6–8 where conditions can produce amorphous solid-phase. In the sweep-floc condition, removal of turbidity and NOMs occurs by adsorption on the precipitate of amorphous solid-phase. The characteristics of floc and treated water largely have been reported to highly depend on the coagulation conditions and mechanisms [66].

4.2. Coagulation application in water treatment

Historically, coagulation has been employed in water treatment to decrease turbidity and color and to remove a large amount of organic compounds, including some dissolved organic material, which is referred to as NOM or dissolved organic carbon (DOC), pathogens, and other contaminants, etc. A number of studies have reported that coagulation process can remarkably remove organic matter in surface water treatment [67–69].

Coagulation conditions are optimized for turbidity and organic matter removal including types, dose, mixing mode and pH conditions. Many coagulants are widely used in the conventional drinking water treatment processes such as aluminum sulfate ($Al_2(SO_4)_3$), ferric chloride ($FeCl_3$), polyferric sulfate (PFS) and polyaluminum chloride (PAC). A summary of recently published investigations regarding NOM removal in drinking water treatment with various coagulation conditions has been presented in Table 2.

Coagulation is also employed to remove heavy metal from wastewaters. Coagulation is the destabilization of colloids process, which results in the effective removal of wastewater particulates and impurities by charge neutralization of particles and by enmeshment of the impurities on the formed amorphous metal hydroxide precipitates. There are many reports on the removal of heavy metal by coagulation process.

Table 2
Overview of the different coagulation conditions used in recent research studies

Coagulant type	Features	Positive	Negative	
Alum, Aluminium	They are hydrolysed and form soluble complexes possessing high positive charges. During coagulation, the most effective range of pH is suggested to be about 5–6.5	Stable, easily handled, readily soluble. Better turbidity removal than with ferric salts in many cases. Higher colour removal efficiency	Relative high coagulant residuals and high alkalinity consumption. Sulphate and/or chloride in finished water increases corrosivity	[70–72]
Ferric chloride, Ferric sulphate	Ferric salts hydrolyse similarly as aluminium salts and formed different hydrolysis products during coagulation. The most effective range of pH is suggested to be pH 4.5–6	Especially the removal efficiency of middle size NOM fractions is noted to be higher. Not so sensitive to temperature changes compared to alum	Ferric-based coagulants have less buffering capacity and require greater chemical addition for stabilization and corrosion control	[69,73–75]
PACl	Made by partially neutralized (prehydrolyzed) aluminium chloride. Enhanced amounts of high-charged, moderate-molar-mass hydrolysis species e.g. Al^{13}	Better NOM removal efficiency than alum in many cases. Lower dose requirement and less sludge produced. Lower residual aluminium in treated water	Preformed Al species are stable and cannot be further hydrolysed during coagulation. The removing efficiency for HMM and highly hydrophobic is lower	[76–79]
PFS	Made by partially neutralized (prehydrolyzed) ferric sulphate. Enhanced amounts of high charged, moderate-molar-mass hydrolysis species	Wider pH range, lower sensitivity to temperature, reduced amounts of coagulants, lower residual iron concentration	Hydrolysis conditions have major impact on speciation of hydrolysis/polymeric species	[80,81]

Samrani et al. [82] studied that the excellent removal of heavy metal by coagulation of combined sewer overflow with two different coagulants, a $FeCl_3$ solution and a polyaluminium chloride (PAC), was achieved within a narrow range of coagulant around optimum coagulant dosage.

Coagulation is one of the most crucial methods for wastewater treatment, but the major objects of coagulation are only the hydrophobic colloids and suspended particles. In order to remove both soluble heavy metal and suspend particles efficiently by coagulation, an amphoteric polyelectrolyte was prepared, which contain sodium xanthogenate group grafted to polyethyleneimine [83]. Under lower pH, the colloidal substances with negative charges can be coagulated due to charge neutralization, but the cationic Ni^{2+} cannot be removed. In the case of higher pH, the turbidity removal decreases, and the Ni^{2+} removal increases. Hankins et al. [84] investigated that the binding of heavy metal by humic acid (HA) and then coagulation–flocculation with the cationic polyelectrolyte poly-diallyldimethylammonium chloride (Poly-DADMAC) can enhanced removal of heavy metal ions from solution, such as Pb^{2+} and Zn^{2+}. Chang et al. [85] prepared a macromolecule heavy metal coagulant mercaptoacetyl chitosan by reacting chitosan with mercaptoacetic acid. They found that this new coagulant could excellently remove turbidity and heavy metals from wastewater.

Coagulation of ENPs will likely be a major process that controls the ENP fate and the subsequent removal from the aqueous phase. Westerhoff et al. [86] investigated that alum could be employed to aggregate TiO_2 and CdTe QDs, and combined with membrane filtration to remove 90% of TiO_2 and CdTe (QDs). Experiments were carried out by Zhang et al. [87] suggested that coagulation with alum and sedimentation could remove metal oxides of titanium, iron, zinc, nickel and silica with initial concentration of 10 mg/L, removal efficiency of which was achieved 20–80%. Holbrook et al. [88] suggested that MWCNTs could be removed from the aqueous phase by coagulation using either $FeCl_3$ or alum. Hyung and Kim [89] reported that coagulant dose, presence of NOM, and ENPs surface properties played an important role in removal of nC_{60}. However, coagulation treatment has not been optimized for removal of ENPs because of the presence of NOM and negative zeta potential of ENPs, which induce the complexation of NOM and ENPs to occur and poor aggregately due to repulsion of ENPs like charges, respectively. ENPs haven't form stable flocs completely, which resulted in the incomplete removal of nanoparticles by sedimentation. In addition, ENPs may be present for a relatively long time even if they are in an aggregated state due to small concentrations of electrolytes containing in an aqueous environment.

Although coagulation and sedimentation as the conventional water treatment process can not remove ENPs completely, membrane filtration will be a promising technique because ENPs are aggregates and all larger nanoparticles flocs can be removed efficiently by membrane.

5. Potential of hybrid coagulation-ultrafiltration for removal of ENPs

As known to all for decades that NOM has significant effect on the biogeochemical cycling of trace metals and the mobility of colloidal particles in aquatic environments. In recent years, concerns about the ecological and human health effects of metal-based ENPs released into natural waters have increased efforts to better define the nature of NOM interactions with metals and surfaces. However, hybrid coagulation-ultrafiltration (UF)/microfiltration (MF) process or in-line coagulation (without settling) combined with direct UF/MF [67,90], which has become an attractive process for water treatment, can significantly enhance the removal of NOM (water quality), improving membrane flux (water production) and even mitigate irreversible membrane fouling. Many studies have addressed the integrated process composed of coagulation and UF/MF. Peuchot and Aim Ben [91] studied that coagulation-MF process using cross-flow mode tends to reduce the colloidal membrane fouling at the optimal concentration of coagulant. Leiknes et al. [92] suggested a coagulation-MF process could efficiently remove the contaminants from the typical water resources containing high concentration of NOM in Norway, and the MF metal membrane could be an alternative method for the sand filtration. Katsoufidou et al. [93] used three types of coagulants in a constant pressure in-line coagulation-UF (dead end filtration) system and found that alum and polyaluminum chloride can increase the removal of organic matter and mitigate a considerable membrane fouling, with no influence for sodium aluminates. Moon et al. [94] had carried out a pilot scale integrated process composed of MF and pre-coagulation and sedimentation to investigate the correlation between membrane flux, dissolved organic matter (DOM) removal and the influence on membrane fouling properties. Their results illustrated that pre-coagulation step prior to membrane filtration was a better performance in permeate quality and DOM control than the direct filtration system without pretreatment.

Recent studies also reported that the integrated process composed of MF or UF and coagulation is also effective for virus removal [95,96]. Fiksdal and Leiknes [95] investigated the removal of phage MS2 in drinking water by pre-coagulation using two commercial aluminum-based coagulants (ALG and PAX), and filtration through UF and MF membranes. They reported that low-pressure MF filtration in combination with pre-coagulation is an effective technology for removal of virus and color in drinking water.

As above mentioned, conjunctive use of coagulation and membrane filtration is becoming more attractive for water treatment because the coagulation is an opportunity to aggregate NOM with other particles present in water that contribute to fouling. In addition, membrane filtration can achieve the physical separation by rejecting aggregates formed in coagulation. There is a great amount of research on influence factor in hybrid coagulation-UF process, which is probably associated with coagulation conditions [93,97–100], properties (hydrophobicity, charge density, molecular weight) of the aquatic impurities, solution environment (solution pH and ion strength), and characteristics of the membrane (membrane charge, hydrophobicity, and surface morphology) [101,102].

Hybrid coagulation-UF drinking-water-treatment processes have been optimized for removal of NOM, bacteria and viruses (10–100 nm) but their effectiveness in removing ENPs has received little attention. During the hybrid of coagulation-MF/UF, coagulation was used to destabilize particulates suspended in water by adding chemicals that form flocs during mixing. However, solutions of nanoparticles with negative zeta potentials are unlikely to aggregate very rapidly due to repulsion of their charges. If the electrical double layer is compressed (e.g. by adding ions that can reduce the zeta potential to near zero), aggregation can be occurred and then removal is possible during subsequent membrane filtration.

6. Future research and outlook

With the accelerating introduction of ENPs into commercial products, it is inevitable that these materials will ultimately reside at some level in aquatic environment. Thereby the potential risks associated with nanoparticles indicate that water facilities may face a challenge of evaluation and removing nanoparticles in the future. Development of reference materials in nanotechnology is even more crucial, and should be ahead of or at least in parallel with development of analytical strategies. Although plenty of analytical techniques are available for nanoparticle characterization, a few of them can be applied directly for *in situ* detection and measurement. Reliable and robust analytical methods are the basis for other aspects of studies related to nanotechnology, such as toxicity and ecotoxicity, fate, transport, transformation, as well as bioaccumulation. Much more research work need to be done to tailor the available techniques to be particularly suitable for monitoring ENPs in environmental and biological samples, upon which analytical methods can be developed and standardized. On the other hand, there is limited available information with regard to protecting the consumer from exposure to nanoparticle in conventional water treatment. Thus, research efforts should be developed to create an integrated water treatment process, which should mitigate the potential risk of nanoparticles to humans. Despite hybrid coagulation-UF process has more attraction for ENPs removal in water treatment, a significant lack of knowledge and information concerning the effect of coagulation conditions, solution environment (solution pH, ionic strength and turbidity), properties (hydrophobicity, charge density, molecular weight) of NOM and characteristics of the membrane (membrane charge, hydrophobicity, and surface morphology) on the removal of ENPs. Therefore, much more efforts need to be done to fill the knowledge gap, which are significant for future integrated coagulation-UF technology to be implemented more widely for removing nanopaticles in complexity aquatic environment.

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