Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.977959

57 (2016) 1733–1748
January

Taylor & Francis
Taylor & Francis Group

Chemical coagulation process for the removal of heavy metals from water: a review

Xiaomin Tang[a,b], Huaili Zheng[a,b,*], Houkai Teng[c], Yongjun Sun[a,b], Jinsong Guo[d], Wanying Xie[a,b], Qingqing Yang[a,b], Wei Chen[a,b]

[a] *Key Laboratory of the Three Gorges Reservoir Region's Eco-Environment, State Ministry of Education, Chongqing University, Chongqing 400045, P.R. China, Tel./Fax: +86 023 65120827; email: zhl@cqu.edu.cn (H. Zheng)*
[b] *National Centre for International Research of Low-carbon and Green Buildings, Chongqing University, Chongqing 400045, P.R. China*
[c] *Tianjin Chemical Research and Design Institute, Tianjin 300131, P.R. China*
[d] *Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, P.R. China*

Received 23 March 2014; Accepted 9 October 2014

ABSTRACT

Heavy metal pollution has become one of the most urgent environmental issues, which also poses a potential threat to the human health. This article is suggested to review the advance on the performance of chemical coagulation process in removing heavy metal from water. Chemical coagulation process is considered to be a valid method which is determined by the hydrolyzed species of the inorganic coagulants under different raw water and coagulation conditions. And the main mechanisms of the removal of heavy metals are adsorption, complexation, and coprecipitation. Compared with the aluminum-based coagulants, the iron-based coagulants have better performance due to the use of wide pH range and large surface area of the resulting flocs. During the chemical coagulation process, the valence state of arsenic and antimony could affect the removal efficiency. Thus, the oxidants and reductants are often combined with inorganic coagulants used in this process. It is found that pH is an important factor greatly influencing the performance directly or indirectly. The complex resulting from the interaction between the inorganic/organic pollutant and inorganic coagulant may contribute to the removal of heavy metals. Overall, chemical coagulation is an effective way to control heavy metal pollution with/without other water treatment technologies.

Keywords: Heavy metal; Coagulation; Adsorption; Inorganic coagulant; Organic substance; Water treatment technology

1. Introduction

The industrialization and urbanization, even the growth of population as well as other drivers of human activities, make the heavy metal pollution become a serious worldwide problem, especially in developing countries [1,2]. Although the concentration of heavy metal is low in water, they can reach to a higher level with the biological accumulation and biological magnification. More attention has been paid to it over the past several years, because of this potential threat to human beings [3,4].

Some technologies are available to purify water/wastewater containing heavy metals, such as

---

*Corresponding author.

coagulation/flocculation [5], ion-exchange [6,7], membrane filtration [8,9], sand filtration [10,11], advanced oxidation [12], activated carbon adsorption [13,14], etc. The activated sludge is rarely applicable to treat the high concentration of heavy metals for the biotoxicity [15]. These water treatment technologies have their own advantages and disadvantages. And their range of application should be considered before they are used in different types of water/wastewater treatment [16]. Coagulation is the traditional water treatment technology which is widely applied in the drinking water treatment [17]. It is interesting to study the feasibility of coagulation/flocculation technology to treat the heavy metal in water for the pollution control. In the coagulation/flocculation process, the chemicals, namely coagulants or flocculants, are added into water to play a major role in the removal of heavy metals[5]. These chemicals could be roughly classified into three categories, inorganic-based coagulant, and organic-based flocculant and hybrid materials, according to their chemical composition [18]. Among them, the inorganic coagulant owning the cost-efficiency has aroused extensive concern [19].

The present review article attempts to provide an overview of recent information concerning the research advance about the removal of heavy metals in the coagulation process. Before that, the feature of heavy metal and inorganic coagulants are considered. And, a particular emphasis is given on the removal mechanism of coagulation process under different conditions, and the factors governing removal efficiency are discussed in terms of different inorganic coagulants with different hydrolysis species, coagulation condition and other inorganic/organic pollutants. Furthermore, the hybrid water treatment technology and the control of residual melt salt are also represented.

2. Sources and feature of heavy metals in water

Heavy metals are often found in agriculture as components of pesticides, herbicides, and raticides as well as applied in industrial manufacture as raw materials or auxiliary materials [20,21]. Heavy metal is introduced into the natural water system through rock weathering, mining, fossil-fuel consumptions, metal electroplating, and other industrial activities [22]. The pollution level is determined by the rainfall capacity, run-off, permeability, level of industrialization, and water treatment capacity [16,22,23]. Heavy metal ions are almost positively charged in the aqueous solution. They could react with hydroxide, sulfide, and other anions to yield the precipitation or complex, which may contribute to the removal of heavy metals from water [16].

Besides, heavy metals are harmful to mammal on account of the biological toxicity, genotoxicity, carcinogenicity, and accumulative toxicity [24–26]. The toxicity of heavy metals is extensively linked to the generation of reactive oxygen species, the inhibitory effect on electron transport, and the reduction of enzyme activity for binding with biotic ligands [27,28]. The concentrations of heavy metals might be far beyond the acceptable level in aquatic animal, even though the actual concentration of them in natural water is low (shown in Table 1). And, it has been detected that the concentrations of zinc, copper, lead, cadmium, mercury, chromium, and arsenic in the eriocheir sinensis can reach to 18.76, 50.8, 0.142, 0.262, 0.054, 0.06, and 0.024 mg/kg, respectively, with heavy metals existing in water and sediment [29]. When people take these aquatic animals as food, they are exposed to the risk of heavy metals. Consequently, the concentration of heavy metals in food products is a very important factor which should be considered in the assessment of the health risk [30]. Moreover, geoaccumulation index recommended by US Environmental Protection Agency is used as a reference to estimate the extent of heavy metals pollution in aquatic system and to assess the potential risk rank of heavy metals to human [31].

Since heavy metals with other pollutants influence the physic-chemical characteristic of the aqueous solution, and determine the choice of inorganic coagulants, dosage, and coagulation condition. It is, therefore, important to investigate the characteristics of raw water before the coagulation process is carried out. Many methods, including chemical titration, atomic absorption spectroscopy, inductively coupled plasma mass spectrometry, ultraviolet-visible spectrophotometry, are being used to detect heavy metal ions in the aqueous solution [32,33]. Nowadays, some online detection technologies are also applied to monitor the concentration of heavy metals in effluent from wastewater plant. And, other water quality parameters which can be easily detected should also be used to indirectly present the pollution level of heavy metals in water [34].

3. Heavy metal removal in coagulation process

There are some factors that have been found to seriously influence heavy metals removal from water in coagulation process. And the removal efficiency of heavy metals is often different in diverse raw water and coagulation condition [35–40]. A few such examples and mechanisms are given below.

Table 1
The adverse effects and actual concentration of heavy metals in natural water

Heavy metal	Adverse effect (From WHO)	MCL (From WHO)	Actual concentration (mg/L)	Reference
Arsenic	Carcinogenicity	0.01 mg/L (Provisional)	0.098 (Manchar Lake)	[114]
	Toxicity		0.0069 (Gombak)	[115]
			0.0024 (Kralkızı Dam)	[116]
			0.002 (Tap water, Mexico)	[90]
Mercury	Tubular necrosis/proteinuria	0.006 mg/L	0.0003 (Gombak)	[115]
	Genotoxicity		0.44×10^{-3} (Marano Lagoon)	[117]
			8.97 pmol/L(Twitchell)	[118]
Antimony	Genotoxicity	0.03 mg/L	Not detected (Pearl River)	[38]
	Carcinogenicity		163 ng/L (Bulgaria)	[119]
			50 ng/L (Skellefte River)	[120]
Lead	Toxicity	0.01 mg/L	0.0101 (Gombak)	[115]
	Interfering calcium metabolism/nervous system		0.0026 (Kralkızı Dam)	[116]
			0.001–0.004 (India)	[121]
Cadmium	Carcinogenicity	0.003 mg/L	0.0012 (Gombak)	[115]
	Genotoxicity		0.15 (Bara River)	[122]
			0.024 (Hindon River)	[31]
			0.0014 (Tigris River)	[123]
Chromium	Carcinogenicity	0.05 mg/L (Provisional)	0.0027 (Gombak)	[115]
	Genotoxicity		0.022 (Kralkızı Dam)	[116]
			0.332 (Hindon River)	[31]
Manganese	Neurological effects	0.4 mg/L	0.388 (Tigris River)	[123]
			0.858 (Hindon River)	[31]
			0.235 (Malgara groundwater)	[124]

Note: MCL = maximum contamination level.

3.1. Characterization of conventional coagulants

Metal salts, such as alum, aluminum chloride, ferric sulfate, and ferric chloride, are traditional coagulants. Adding these metal salts into the aqueous solution, will set off a series of complex chemical reactions which are known as dissolution, hydrolysis and polymerization [41]. And polymerized species that are generally acknowledged the active ingredients for the removal of turbidity and contaminants are gradually formed during these processes [42]. Along with the development of the research, prehydrolyzed coagulants, such as polyaluminum chloride and polymeric ferric sulfate, produced by the forced hydrolysis are believed to have an excellent performance in water treatment [17,43]. The prehydrolysis degree of them could be represented as basicity, namely, the OH/Al ratio or OH/Fe ratio. And the polynuclear species are different with various basicities [44,45]. For instance, the main aluminum species are Al^{3+} and monomeric species $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_3{}^0(aq)$ at low basicity. The small/middle polymeric Al and higher polymeric Al are formed following the increase in basicity. And in this process, the transient polymeric Al species form the stable Al_{13} ($AlO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}$) and Al_{30} ($Al_{30}O_8(OH)_{56}(H_2O)_{2,4}{}^{18+}$) which are believed to be the key part to achieve outstanding performance [46,47]. Although these polynuclear species are also generated in the hydrolysis of traditional coagulants, the monomeric and middle polymeric species are dominant. And the character of polymeric species is not always the same between traditional coagulants and prehydrolyzed coagulants, which will be described later [48]. Additionally, when the basicity is near 3.0, the amorphous sol/gel $Al(OH)_3$ is observable [46]. The adsorption property of polymeric species may relate to the removal of heavy metals.

3.2. Removal efficiency of heavy metals

The efficiency of coagulation in removing heavy metals from water solution has been studied in a number of different forms ranging from batch experiment to field trial. The performance of inorganic coagulant is represented under different conditions (shown in the Table 2). The removal rate of heavy metals mostly depends on the hydrolyzed species of these inorganic coagulants in raw water [35]. It is not like the way of removing colloid particles in which the

Table 2
The removal of heavy metals in coagulation process

Type	Source	Initial concentration (mg/L)	Coagulant	Dosage (mg/L)	pH	Removal efficiency	Reference
Arsenic	Simulated groundwater	0.28 mg/L	Aluminium chloride	6 mg/L	4.0–9.0	Below 0.01 mg/L	[35]
Arsenic	–	0.3 mg/L	Alum	30 mg/L	<6.5	20%	[65,125]
Arsenic	Tap water with adding As(V)	0.1 mg/L	Alum	30 mg/L	6.0–8.0	65%	[106]
Arsenic	Tap water with adding of As(V)	10(500) μg/L	Ferric sulfate	60 mg/L	9.0	63%(91%)	[36]
Arsenic	Simulated water	0.125–6.25 mmol/L	Fe-based WTR[a]	100 mg	6.0	122.6 mmol/kg	[55]
Methylmercury	Drainage canal(Twitchell)	1.20 pmol/L	Ferric chloride	1.05 mmol/L	3.5	75%	[70]
Methylmercury	Drainage canal(Twitchell)	1.20 pmol/L	Polyaluminum chloride	1.61 mmol/L	7.2	70.83%	[70]
Manganese	Simulated water	1 mg/L	Amorphous $Al(OH)_3$[b]	0.2 g/240 mL	6.5	To 0.08 mg/L	[39]
Lead	Simulated water	5–100 mg/L	Iron (hydr)oxides[c]	4 g/L	5.5	0.579 mmol/g	[54]
Lead	Tap water	17 mg/L	Alum	100 mg/L	6.5–7.0	To 1.3 mg/L	[57]
Lead	Simulated wastewater	0.002 M	Ferric sulfate	0.1;0.14;0.2 mol/L	9.0–10.0	To 0.25 mg/L[c]	[126]
Cadmium	Simulated water	5–100 mg/L	Iron (hydr)oxides[c]	4 g/L	5.5	0.187 mmol/g	[54]
Cadmium	River water	0.3 mg/L	Ferric sulfate	–	7.2(8.0)	20%(90%)	[127]
Cadmium	Simulated wastewater	0.002 M	Ferric sulfate	0.1;0.14;0.2 mol/L	9.0–10.0	Below 0.03 mg/L[c]	[126]
Chromium	Simulated water	10 mg/L	Ferric chloride	0.7 g/L	7.0	90%	[50]
Chromium	Tap water	15 mg/L	Alum	100 mg/L	6.5–7.0	To 0.2 mg/L	[57]
Chromium	Simulated wastewater	0.002 M	Ferric sulfate	0.1;0.14;0.2 mol/L	9.0–10.0	To 0.569 mg/L[c]	[126]
Copper	Tap water	15 mg/L	Alum	100 mg/L	6.5–7.0	Tp 1.7 mg/L	[57]
Zinc	Simulated water	5–100 mg/L	Iron (hydr)oxides[d]	4 g/L	5.5	0.612 mmol/g	[54]
Zinc	Tap water	17 mg/L	Alum	100 mg/L	6.5–7.0	To 11 mg/L	[57]
Antimony	Reservoir water with adding Sb(III)	6 μg/L	Polyaluminum chloride	5.4 mg/L	5–10	About 10%	[56]
Antimony	Reservoir water with adding Sb(III)	6 μg/L	Ferric chloride	20 mg/L	5.0	About 90%	[56]
Nickel	Tap water	16 mg/L	Alum	100 mg/L	6.5–7.0	Null	[57]
Nickel	Simulated wastewater	0.002 M	Ferric sulfate	0.1;0.14;0.2 mol/L	9.0–10.0	To 0.389 mg/L[c]	[126]
Cobalt	Tap water	12 mg/L	Alum	100 mg/L	6.5–7.0	Null	[57]

[a] The Fe-based WTR was obtained from the drinking water treatment plant where iron sulfate is used as the coagulant.

[b] The amorphous $Al(OH)_3$ made from the hydrolysis of Alum. Its surface area was about 160 m^2/g.

[c] In this reference, the heavy metals from the sludge would be below the toxicity characteristic leaching procedure (TCLP) limits. And the TCLP limits of lead, cadmium, chromium, nickel were 0.05 mg/L (limit: 5.0 mg/L), 0.821 mg/L (limit: 1.0 mg/L), 0.419 mg/L (limit: 5.0 mg/L), and 0.496 mg/L (limit: –) respectively.

[d] The iron (hydr)oxides, as the main composition, were water treatment residuals which were collected from a drinking water treatment plant. And their removal efficiencies were substituted by sorption capacities. Its surface area was about 170.7 m^2/g.

charge neutralization plays an important role in the process, whereas the complexation, adsorption, and coprecipitation are dominant in the removal of heavy metals[49]. For instance, chromium ions can react with the hydrolyzed products of ferric chloride, and insoluble complex of ferric chromate [$Fe_2(CrO_4)_3$] and/or ferric dichromate [$Fe_2(Cr_2O_7)_3$] are formed [50]. And, based on the EXAFS spectrum analyses, two O atoms from an AsO_4 unit individually bond to two Al atoms through As–O–Al, which helps in the removal of heavy metals [51]. Additionally, the higher polynuclear species have larger surface areas which contribute to the adsorption of heavy metals. So when these species are dominant in the treatment process, better results are often obtained [35]. It also can partly explain the controversy about whether the performance of prehydrolyzed coagulant is better than the traditional coagulant. It was reported that the prehydrolyzed coagulants had better removal efficiencies than the conventional monomeric Al coagulants, since more stable Al_{13} was produced [43,52]. But there are opposite views. The aluminum chloride produced the *in situ* Al_{13} is not stable, and it further hydrolyzed into the larger polymer contributing to the removal of heavy metals. While, the polyaluminum chloride produced the crystal hydroxide which was quite stable throughout the coagulation-flocculation process even in flocs. And the surface area of amorphous hydroxide in aluminum chloride was larger than that of crystal hydroxide in polyaluminum chloride. The larger surface area was always related to the stronger adsorption ability [35,53]. Thus, the essential factor of hydrolysis, raw water, and coagulation condition, which affect the species of hydrolysis product should be made clear before comparing the removal efficiency of prehydrolyzed coagulants and traditional coagulants.

Aluminum-based coagulants and iron-based coagulants, as the inorganic coagulants, share a lot in common during the processes the removal of heavy metals. However, the performance of them is not always identical. And iron-based coagulants often perform slightly better than aluminum-based coagulants for the wider pH range and the larger surface area of resulting flocs [39,54,55]. The flocs formed by iron-based coagulants are always open and loose, which ensure three-dimensional lattice size and a large available surface area for complexing and adsorbing heavy metals [56]. Furthermore, the performance varies with different heavy metals under the same coagulation condition [57]. It may be ascribed to different adsorption capacities by coagulants, which can be represented as the adsorption enthalpy of heavy metal ions for metal hydroxide [56]. Adsorption enthalpy describes the bonding energy between the adsorbed ion and the metal hydroxide [58] as represented in the following equation:

$$H = f\left(\frac{z^2}{R_H}\right) \tag{1}$$

where H is the adsorption enthalpy, z is the valance charge of the adsorbed ion, and R_H is hydrated radius. The removal rate of heavy metals by coagulants is partly determined by the adsorption enthalpy.

Enhanced coagulation, increasing the dosage of inorganic coagulant and optimizing the coagulation condition, makes a better performance in the coagulation process [59]. An advantage of the increase in the dosage is to enhance the amount of aluminum/iron hydroxide flocs which provide more available surface area to adsorb heavy metals [60]. And, it promotes the capacity of charge neutralization that contributes to the coprecipitation of heavy metals with colloidal particles and natural organic matter (NOM) [40]. However, the advantage is balanced by the corrosivity, residual metal salt, cost, and large amounts of waste sludge [61]. Beside, pH of the solution drops apparently when the superfluous inorganic coagulants are added. And, the decrease in pH will affect the removal of heavy metals, which needs further study.

3.3. Factors governing the removal efficiency of heavy metals

The performance is determined to a great extent by the raw water and coagulation condition. In this part, we will focus on the effect of initial concentration and valence state of heavy metals and the effect of pH and temperature in the solution. Moreover, the interaction between heavy metals and other inorganic/organic substances is also discussed.

3.3.1. Effect of initial concentration and valence state of heavy metals

Lower pollutant loading always causes lower removal efficiency, since the formed flocs are few, large size, and low density. For instance, compared with high initial arsenate concentration (500 μg/L), the high coagulant dose is required to achieve good performance in the low initial arsenate concentrations (10 μg/L) because of the difficulty in inducing collision between the colloids [36].

The valence state of heavy metals, such as As(III) and As(V), has considerable influence on its removal. It has been described that As(III) is less favorably adsorbed on inorganic coagulants than the As(V). And, coagulant alone is not available to reduce the concentration of As(III) below 10 μg/L [37,62]. It is, therefore, advisable to pre-oxidize As(III) to As(V) by $KMnO_4$, MnO_2, NaClO, and O_3 before the coagulation process to minimize the chemical consumption [62–65]. The coagulants, Fe(VI) and PACC, which have oxidation capacity can be also used in the removal of As (III). Fe (VI) whose redox potential reaches to 2.20 V in the acidic environment oxidizes As(III) to As(V), and it is transformed to Fe(III). Then, arsenic is removed via coprecipitation with the hydrolysis product of iron salt [66]. PACC which contains the active chlorine and high Al_{13} polymer has similar mechanism to remove arsenic. The residual concentration of arsenic is below the maximum contamination level after the oxidization and coagulation [64]. However, the higher valence state of heavy metals does not always perform better than the lower one. The removal efficiency of antimony decreases, while Sb(III) is oxidized by NaClO because of the conversion of the less water soluble Sb(III) to the more water soluble Sb(V). And, the removal mechanism of Sb(III) and Sb(V) has some difference. Although they are both removed by coagulants via coprecipitation and adsorption, Sb(III) is mainly through hydrophobic bonding, and Sb(V) is mainly through ionic bonding [56]. It will be interesting to further study the removal efficiency of other heavy metals with different valence states in the coagulation process.

3.3.2. Effect of pH and temperature

The effect of pH on the removal of heavy metals is complex. The precipitation of heavy metals is formed under alkaline condition, which contributes to their removal through enmeshment and adsorption by resulting flocs [67]. But it does not mean that higher pH results in the removal of higher heavy metals, since the hydrolyzed species of inorganic coagulant are different when it is beyond the optimal pH range [68]. In the range, the dependence of removal rates on pH is insignificant. But the removal rate decreases sharply when pH is out of the range [38,69,70]. The hydrolyzed species of conventional inorganic coagulants are negatively charged at high pH values (pH 9–10). Electrostatic repulsions between the negative heavy metal species and negatively charged hydrolyzed species would hinder the diffusion and sorption processes. And, the competition of OH^- with heavy metals at high pH would be also responsible for the poor sorption of heavy metals by inorganic coagulants [19]. Besides, pH has an effect on the oxidation-reduction reaction. The reaction rate of oxidant always decreases with an increase in pH, and it also increases the oxidant dose and reaction time. For that reason, the conversion efficiency of heavy metals is low, which influences the performance of inorganic coagulants [71]. The effect of pH is not limited in the range of heavy metals and inorganic coagulants, and it also affects the reaction of other inorganic substances and organic substances to heavy metals which will be represented in the following.

Only a handful of studies have specifically focused on the effect of temperature in the case of the removal of heavy metals in the coagulation process. And, less attention has been given to the low temperature. Generally, low temperature deteriorates the coagulation efficiency, because of inhibiting the hydrolysis of metal salts, increasing the viscosity of water, decelerating the Brownian movement, and reducing the collision probability [72–74] and further study should be made.

3.3.3. Effect of other inorganic substances

The other inorganic substances always coexist with heavy metals in the solution. The reaction among them influences the removal of heavy metals in coagulation process. Some ions, such as S^{2-}, can react with heavy metal to generate the precipitation, which contributes to high performance [16]. And, considering the Ca^{2+} ion commonly existing in water, it always enhances the removal efficiency of heavy metals. The reasons are represented as following: (a) the Ca^{2+} ion can compress the double layer thickness from 9 nm to about 1.5 nm, which reduces the charge exclusion and makes internal pores more accessible; (b) it can also reduce the negative charge on flocs; (c) it increases the amount of precipitation; (d) under the alkaline condition, the formed $CaCO_3$ improves the removal ratio of heavy metals due to the effects of coprecipitation, enmeshment, and adsorption [75,76]. And a study indicated that the promoting capacity of Mg^{2+} on Mn^{2+} removal is stronger than the Ca^{2+} [39].

Some inorganic substances could form the specific inner-sphere complexes with conventional inorganic coagulants, and they competed with heavy metals for the adsorption sites. In this situation, the removal rate of heavy metals is often lower than expected [77,78]. The research confirms that the silica competes with arsenate for the adsorption sites. And, the effect of silica is greater at pH 8.5 than at pH 6.5 for the increase in the amount of negatively charged $H_3SiO_4^-$. Phosphate has drawn the similar conclusion. The chemical behavior of monovalent state ($H_2PO_4^-$) and divalent state (HPO_4^{2-}) is close to $H_2AsO_4^-$ and $HAsO_4^{2-}$. All of them can have ligand exchange with hydrolyzed species of inorganic coagulants, which causes the competition between phosphate and arsenate [49]. But the level of competition is determined by the concentration of phosphate, pH, and other conditions. Consequently, more studies should be conducted to deeply analyze the interaction between heavy metals and inorganic substances under different raw water.

3.3.4. Effect of organic substances

The heavy metals and organic substances can react with each other to generate the soluble complex, colloidal or insoluble substance in the solution. The dominant form is determined by the characteristics of organic substances and inorganic coagulants. And the dominant form also affects the removal of heavy metals[79]. It is represented that humic acid (HA) conduces to gain the maximum removal of heavy metals when the optimum ratio of humic substance to metal ratio is discovered. And, with an increase in pH, the removal efficiency of heavy metals is improved in the presence of humic substances [80]. Similar conclusion is drawn that binding heavy metals to the HA at high concentration leads to the higher removal rate of heavy metals in coagulation process [40]. However, the removal rate of antimony dramatically reduces with the presence of HA since the HA supermolecules and HA-originated functional groups occupy the adsorption sites on the surface of iron oxy-hydroxide. And, part of antimony ions adsorb on the HA increases the solubility of complex in water [78]. Specifically, the competition is keen among the contaminants for the adsorption sites at low dose of coagulant, which causes the low removal rate of heavy metals. But it was negligible at high dose for the simultaneous removal of organic and inorganic contaminants [64].

The removal mechanism of heavy metals with organic substances by coagulation process is complicated. The colloidal particles in water absorb the heavy metals on the surface via charge attraction and ion exchange [81]. Then, the charge neutralization of aluminum/iron hydroxide complexes plays an important role in the aggregation of the colloidal particles. And during the precipitation process, the resulting flocs capture and adsorb some heavy metal ions, and coprecipitation also partly contributes their removal in this process [16,40]. However, when the heavy metal ions aggregate with colloids to form the soluble complex, it will increase the retention of heavy metals in water [82]. Moreover, the capacity of charge neutralization of inorganic coagulant could be indicated by the value of zeta potential which can also be used to determine the optimal dosage of coagulant in the treatment [83]. But it has disproved that zeta potential was only applied in predicting the optimal dosage of coagulant when charge neutralization works as the predominant coagulation mechanism. In other cases, the floc size and the fractal dimension could be taken as the substitute to determine the optimum dosage range [84,85]. Flocs take an effect on the removal of heavy metals during the coagulation process. The characteristic of flocs, such as size, strength, and surface area, influences the adsorption of heavy metals on the amorphous aluminum/iron hydroxides [54,86]. But few studies have specially drawn an attention to this effect. It has been indicated that there is an obvious increase of the floc strength when pH is adjusted from 5.2 to 6.0, and there is a corresponding increase in the removal efficiency of contaminants [87]. And flocs aggregation depends not only on the type and dose of coagulants, but also on the characteristic of solution and hydraulic condition [88]. The high shear forces results in the breakage of flocs. Although the regrowth of flocs takes place after the subsequent low shear phase, the flocs regain about 50% of the size compared with the initial coagulation process [89]. Thus, the effect of the character of flocs on the removal of heavy metals should be further studied.

4. Coagulation-based combined/hybrid processes

Coagulation coupled with other water treatment technologies, such as advanced oxidation, membrane filtration, adsorption, and flocculation (in Table 3), is an effective way to control the pollution caused by heavy metals [82,90].

In water, heavy metal ions are easy to bond with ethylenediaminetetraacetic acid (EDTA), iminodiacetic acid (IDA), and other organic matter, which usually decreases the removal rate of heavy metals. Thus, the oxidants, such as Fenton reagent, lead to the oxidation and mineralization of organic contaminant. And with these chemical reactions, heavy metal ions are released from the inorganic-organic compound, and the dissolved compound transforms to the colloid or precipitation, which facilitate the simultaneous removal of heavy metals and organic contaminants [91,92]. And the oxidants are also been used to transform the valence state of heavy metals, which has been mentioned before.

The membrane technology has also been applied in the treatment of heavy metals with coagulation [16]. Although excellent performance could be obtained by

Table 3
The removal of heavy metals in combined/hybrid processes

Type	Source	Initial Concentration	Coagulant	Dosage	pH	Combination Process/ Reagent	Removal Efficiency	Reference
Arsenic	Simulated groundwater	25 mg/L	Ferric salts	250 mg/L	5	Pre-oxidation; nanofiltration; calcium salt	98.4%	[128]
Arsenic	Simulated groundwater(East-Pannonian)	2 mmol/L	Polyaluminum granulate	0.5 g/50 mL	7.5	Calcium	85–99.8%	[61]
Arsenic	Synthetic wastewater	0.1–0.5 mg/L	Ferric chloride	25 mg/L	7.0–7.5	Potassium permanganate	About 0.005 mg/L	[62]
Arsenic	–	0.3 mg/L	Alum	30 mg/L	<6.5	Chlorine	90%	[65,125]
Arsenic	Cerrito Blanco channel	5.07 mg/L	Ferric sulfate	100 mg/L	6.0	Calcite	99%	[99]
Antimony	Pearl River with anitimony	0.03–0.158 mg/L	Ferric coagulant	0.4 mmol	7.1–7.9	Flocculation; ultrafiltration	To 1.0–2.0 μg/L	[38]
Antimony	Kim reservoir water with Sb(III)	6 μg/L	Ferric chloride	10.3 mg/L	5.0	Sodium hypochlorite	About 85%	[56]
Lead	Lake (China)	0.086 mg/L	Polyaluminum chloride	30 mg/L	7.5	Diatomite	83.7%	[98]
Copper	Electroplating wastewater	20 mg/L	Polyferric sulfate	25 mg/L	10.0–11.5	DDTC	99.6%	[129,130]
Manganese	Groundwater (Malgara)	0.235 mg/L	Iron chloride/sulfate-based caogulant	180 g/L	Natural pH	Aeration; biological oxidation; sand filtration; disinfection	To 0.05 mg/L	[124]
Manganese	Landfill leachate (Gaziantep)	0.20 mg/L	Alum	6 g/L	–	Anionic polyelectrolyte & lime	75%	[131]
Manganese	Landfill leachate (Guangdong)	0.77 mg/L	Polyferric sulfate	–	5.0	SBR; Fenton; BAF	98.7%	[132]
Cadmium	Lake (China)	0.086 mg/L	Polyaluminum chloride	30 mg/L	7.5.	Diatomite	22.2%	[98]
Chromium	Landfill leachate (Gaziantep)	0.72 mg/L	Ferric sulfate	4 g/L	–	Anionic polyelectrolyte & lime	To 0.22 mg/L	[131]
Nickel	Landfill leachate (Guangdong)	0.58 mg/L	Polyferric sulfate	–	5.0	SBR; Fenton; BAF	98.2%	[132]
Barium	Oil sands process affected water	0.35 mg/L	Alum	250 mg/L	8.5	Flocculation (PolyDADMAC)	42–63%	[133]
Vanadium	Oil sands process affected water	0.018 mg/L	Alum	250 mg/L	8.5	Flocculation (PolyDADMAC)	67–78%	[133]

Note: SBR = sequencing batch reactor; BAF = biological aerated filtering; DDTC = sodium diethyldithiocarbamate; PolyDADMAC = polydiallydimethylammonium chloride.

the membrane filtration, and the performance is insensitive to raw water, it has the disadvantage of membrane fouling which decreases membrane permeability, shortens membrane lifetime and increases the operating cost [93,94]. The problem with membrane fouling always puzzles people [95]. In the coagulation-membrane filtration hybrid technology, the inorganic coagulant has the functions of enlarging flocs and reducing the initial transmembrane pressure, which not only retard the membrane fouling, but also improve the removal efficiency of heavy metals through forming the colloid particles and precipitation [38,96].

The role of adsorption for the removal of heavy metals from water is beyond suspicion [97]. And the performance is always satisfied when the adsorbents are added in the coagulation process [98]. However, the cost should be considered in the practical application. The combined action mechanism of ferric sulfate and calcite has been discussed. The calcite surfaces are coated by small coagulants, which behave similar to the calcite in gravitational sedimentation and filtration, and thus heavy metals are easily removed from water. Whether it can be used in the other treatment with different adsorbents should be further investigated [99].

The capacities of bridging and adsorption of conventional inorganic coagulants are reinforced through synthesizing them with other inorganic coagulants or organic flocculants [18,100]. These novel inorganic-inorganic and inorganic-organic hybrid coagulants always have better performance in water treatment, and they are more stable than the traditional inorganic coagulants during storage [101,102]. Due to the high molecular weight of the organic flocculants which also possess active functional groups, flocs formed by inorganic-organic hybrid coagulants are provided with superior properties in the floc size and the floc strength. And the growth and regrowth of flocs is less affected by the mixing speed, shear force, and breakage time [103]. However, these novel inorganic-inorganic and inorganic-organic hybrid coagulants are rarely studied in the treatment of heavy metals. Thus, it is meaningful to research a new hybrid chemical which can remove heavy metals from water perfectly.

5. The control of residual metal salts

The residual metal salts are always detected in the treated water when the conventional inorganic coagulants are applied in water treatment [104]. The problems of the residual aluminum/iron salts are related to the resource waste and health risk [105]. It has been reported that residual aluminum in the drinking water may be a risk factor for Alzheimer’s disease [106,107]. And, the maximum concentration level of residual aluminum in drinking water guided by WHO is at

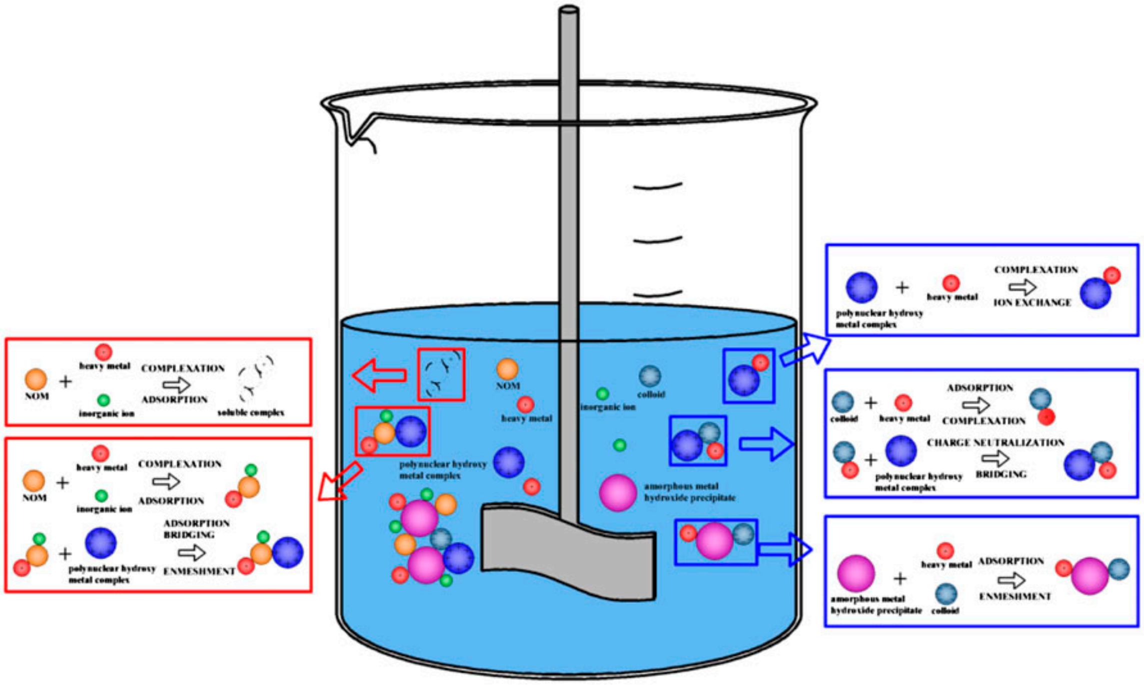

Fig. 1. The recommended mechanism of the removal of heavy metals in coagulation process.

Table 4
The feature of the novel inorganic coagulants

	Function & Composition	Positives[a]	Negatives	Toxicity	Reference
Fe(VI)	Supercharged iron molecule; dual function of oxidation and coagulation (ferric hydroxide); great redox potential	Low dosage; high removal efficiency of NOM, phosphate, organic contaminants, especially micropollutants	Unstable of the Fe(VI) solution; costly	Nontoxic	[134,135] [71,136]
Ti-based coagulant	Including titanium tetrachloride, polytitanium tetrachloride, titanium dioxide (photocatalytic coagulant)	Low dosage; higher removal efficiency of organic pollutants and turbidity; higher floc growth rate (450 μm/min); compact floc structure; strong recoverability at high B value (OH/Ti molar ratio) of polytitanium tetrachloride; potential for sludge recovery to produce valuable by-product	pH of the effluent after $TiCl_4$ coagulation was much lower; at the low B value, the flocs were weak recoverability	Nontoxic	[137,138] [139]
Zr-based coagulant	Containing 20% weight equivalent ZrO_2 consisting of cationic hydroxylated polynuclear zirconium species	Low dosage; better removal rates of DOC, NOM, turbidity; generate more positive zeta potentials; higher isoelectric point; large floc size (930 μm); moderate floc growth rates (220 μm/min); strong, robust flocs	Narrower optimum pH range (pH:5–6); low floc growth rate; longer time to reach the steady state size; require careful control dosage to avoid charge reversal and restabilization	Nontoxic	[140]

[a]The positives and negatives of the novel inorganic coagulants were compared with the aluminum/iron-based coagulants.

0.2 mg/L [108]. The speciation analysis demonstrates that monomeric aluminum is the dominant species in the residual total aluminum, while non-labile monomeric aluminum is the dominant species in residual monomeric aluminum [109]. Several control technologies have been introduced to reduce the residual concentration of aluminum/iron salts in the treated water. One method is maintaining the inorganic coagulant dosage in the optimal range. And it is indicated that the residual aluminum concentration was at a low level under the optimum coagulant dosage. Additionally, increasing the basicity of coagulants and optimizing the coagulation condition can achieve the same purpose [110]. It is represented that the solution pH is a key to minimize the residual aluminum concentration [111]. Apart from this, adding appropriate organic flocculants, such as polydiallyl dimethyl ammonium chloride (PDMDAAC), contribute to the low residual aluminum concentration in water [112]. A composite coagulant synthesized by PAC and a microbial flocculant confirmed this conclusion [109]. Combining coagulation with membrane filtration is an accepted way as well [113].

6. Concluding remarks and future directions

Chemical coagulation process is an important water treatment technology, and it has been widely used in water purification. The hazardous heavy metals which are widespread in natural water threat the human health and bring a new challenge to the application of coagulation. This review highlights the middle/high polymeric species formed in the raw water mainly contribute towards the removal of heavy metals. And, it should take full consideration of the factors which significantly influences the performance in the coagulation process, such as dosage, pH, temperature, valence state of heavy metals, etc. The effect of other inorganic and organic substances is different under varying condition. When the capacity of precipitation, coprecipitation, adsorption, and complexation is enhanced for the coexistence of inorganic/organic substances and heavy metals, the removal efficiency is always better than that when they are treated separately (shown in Fig. 1). However, if these coexisting matters compete with each other for the adsorption sites, it will result in worse performance. Moreover, the hybrid technology should be combined with coagulation for enhancing the treatment. And, the residual metal salt in the treated water requires more attention to prevent the potential health risk.

Additionally, it should emphasize more fundamental research on the mechanisms of interaction between inorganic/organic substanceand inorganic coagulant in different conditions, especially in low temperature or/and low turbidity water, so as to facilitate the removal of heavy metals. And, a special concern should be also paid to the novel and green inorganic coagulants (differing from the conventional aluminum/iron-based coagulants) which possess the advantages in performance and nontoxicity (shown in Table 4). They would be the potential chemical for the treatment of heavy metals.

Acknowledgments

We are grateful for the financial support provided by the National Science and Technology Support Program (Grant number 2012BAJ25B09), the National Natural Science Foundation of China (Project No. 51078366), and the National 111 Project (Project No. B13041).

References

[1] Z. Li, Z. Ma, T.J. van der Kuijp, Z. Yuan, L. Huang, A review of soil heavy metal pollution from mines in China: Pollution and health risk assessment, Sci. Total Environ. 468–469 (2014) 843–853.

[2] H.A. Naser, Assessment and management of heavy metal pollution in the marine environment of the Arabian Gulf: A review, Mar. Pollut. Bull. 72 (2013) 6–13.

[3] Z. Ben Salem, N. Capelli, X. Laffray, G. Elise, H. Ayadi, L. Aleya, Seasonal variation of heavy metals in water, sediment and roach tissues in a landfill draining system pond (Etueffont, France), Ecol. Eng. 69 (2014) 25–37.

[4] A. Azizullah, M.N.K. Khattak, P. Richter, D.-P. Häder, Water pollution in Pakistan and its impact on public health—A review, Environ. Int. 37 (2011) 479–497.

[5] F.M. Pang, P. Kumar, T.T. Teng, A.K. Mohd Omar, Wasewar, Removal of lead, zinc and iron by coagulation–flocculation, J. Taiwan Inst. Chem. Eng. 42 (2011) 809–815.

[6] A. Dąbrowski, Z. Hubicki, P. Podkościelny, E. Robens, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method, Chemosphere, 56 (2004) 91–106.

[7] N.H. Shaidan, U. Eldemerdash, S. Awad, Removal of Ni(II) ions from aqueous solutions using fixed-bed ion exchange column technique, J. Taiwan Inst. Chem. Eng. 43 (2012) 40–45.

[8] J. Gao, S.-P. Sun, W.-P. Zhu, T.-S. Chung, Chelating polymer modified P84 nanofiltration (NF) hollow fiber membranes for high efficient heavy metal removal, Water Res. 63 (2014) 252–261.

[9] W.P. Zhu, S.P. Sun, J. Gao, F.J. Fu, T.S. Chung, Dual-layer polybenzimidazole/polyethersulfone (PBI/PES) nanofiltration (NF) hollow fiber membranes for heavy metals removal from wastewater, J. Membr. Sci. 456 (2014) 117–127.

[10] C. Tizaoui, S.D. Rachmawati, N. Hilal, The removal of copper in water using manganese activated saturated and unsaturated sand filters, Chem. Eng. J. 209 (2012) 334–344.

[11] Z. Ding, X. Hu, V.L. Morales, B. Gao, Filtration and transport of heavy metals in graphene oxide enabled sand columns, Chem. Eng. J. 257 (2014) 248–252.

[12] K.P. Kowalski, Chapter 8—Advanced arsenic removal technologies review, in: E.G. Søgaard (Ed.), Chemistry of Advanced Environmental Purification Processes of Water, Elsevier, Amsterdam, 2014, pp. 285–337.

[13] S. Chaturvedi, P.N. Dave, Removal of iron for safe drinking water, Desalination 303 (2012) 1–11.

[14] P. Mondal, S. Bhowmick, D. Chatterjee, A. Figoli, B. Van der Bruggen, Remediation of inorganic arsenic in groundwater for safe water supply: A critical assessment of technological solutions, Chemosphere 92 (2013) 157–170.

[15] B. Feng, Z. Fang, J. Hou, X. Ma, Y. Huang, L. Huang, Effects of heavy metal wastewater on the anoxic/aerobic-membrane bioreactor bioprocess and membrane fouling, Bioresour. Technol. 142 (2013) 32–38.

[16] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, J. Environ. Manage. 92 (2011) 407–418.

[17] A. Matilainen, M. Vepsäläinen, M. Sillanpää, Natural organic matter removal by coagulation during drinking water treatment: A review, Adv. Colloid Interface Sci. 159 (2010) 189–197.

[18] K.E. Lee, N. Morad, T.T. Teng, B.T. Poh, Development, characterization and the application of hybrid materials in coagulation/flocculation of wastewater: A review, Chem. Eng. J. 203 (2012) 370–386.

[19] Y. Wang, J. Duan, S. Liu, W. Li, J. van Leeuwen, D. Mulcahy, Removal of As(III) and As(V) by ferric salts coagulation—Implications of particle size and zeta potential of precipitates, Sep. Purif. Technol. 135 (2014) 64–71.

[20] M. Vila, S. Sánchez-Salcedo, M. Vallet-Regí, Hydroxyapatite foams for the immobilization of heavy metals: From waters to the human body, Inorg. Chim. Acta 393 (2012) 24–35.

[21] Y. Xu, Q. Sun, L. Yi, X. Yin, A. Wang, Y. Li, J. Chen, The source of natural and anthropogenic heavy metals in the sediments of the Minjiang River Estuary (SE China): Implications for historical pollution, Sci. Total Environ. 493 (2014) 729–736.

[22] S.L. Wang, X.R. Xu, Y.X. Sun, J.L. Liu, H.B. Li, Heavy metal pollution in coastal areas of South China: A review, Mar. Pollut. Bull. 76 (2013) 7–15.

[23] M.I. Kabir, E. Daly, F. Maggi, A review of ion and metal pollutants in urban green water infrastructures, Sci. Total Environ. 470–471 (2014) 695–706.

[24] B. Nath, S.B. Basu Mallik, D. Stüben, D. Chatterjee, L. Charlet, Electrical resistivity investigation of the arsenic affected alluvial aquifers in West Bengal, India: Usefulness in identifying the areas of low and high groundwater arsenic, Environ. Earth Sci. 60 (2010) 873–884.

[25] K. Karlsson, M. Viklander, L. Scholes, M. Revitt, Heavy metal concentrations and toxicity in water and sediment from stormwater ponds and sedimentation tanks, J. Hazard. Mater. 178 (2010) 612–618.

[26] Z. Wang, L. Yao, G. Liu, W. Liu, Heavy metals in water, sediments and submerged macrophytes in ponds around the Dianchi Lake, China, Ecotoxicol. Environ. Saf. 107 (2014) 200–206.

[27] H. Xu, P. Song, W. Gu, Z. Yang, Effects of heavy metals on production of thiol compounds and antioxidant enzymes in Agaricus bisporus, Ecotoxicol. Environ. Saf. 74 (2011) 1685–1692.

[28] A. Hatano, R. Shoji, A new model for predicting time course toxicity of heavy metals based on Biotic Ligand Model (BLM), Comp. Biochem. Physiol. C: Toxicol. Pharmacol. 151 (2010) 25–32.

[29] Y. Yi, Z. Yang, S. Zhang, Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin, Environ. Pollut. 159 (2011) 2575–2585.

[30] P. Zhuang, B. Zou, N. Li, Z. Li, Heavy metal contamination in soils and food crops around Dabaoshan mine in Guangdong, China: Implication for human health, Environ. Geochem. Health 31 (2009) 707–715.

[31] S. Suthar, A.K. Nema, M. Chabukdhara, S.K. Gupta, Assessment of metals in water and sediments of Hindon River, India: Impact of industrial and urban discharges, J. Hazard. Mater. 171 (2009) 1088–1095.

[32] Y. Qin, Z. Zhang, L. Li, C. Chen, S. Shun, Y. Huang, Inductively coupled plasma orthogonal acceleration time-of-flight mass spectrometry (ICP-oa-TOF-MS) analysis of heavy metal content in Indocalamus tesselatus samples, Food Chem. 141 (2013) 2154–2157.

[33] J. Li, M. He, W. Han, Y. Gu, Analysis and assessment on heavy metal sources in the coastal soils developed from alluvial deposits using multivariate statistical methods, J. Hazard. Mater. 164 (2009) 976–981.

[34] S. Chakraborty, T. Bhattacharya, G. Singh, J.P. Maity, Benthic macroalgae as biological indicators of heavy metal pollution in the marine environments: A biomonitoring approach for pollution assessment, Ecotoxicol. Environ. Saf. 100 (2014) 61–68.

[35] C. Hu, H. Liu, G. Chen, J. Qu, Effect of aluminum speciation on arsenic removal during coagulation process, Sep. Purif. Technol. 86 (2012) 35–40.

[36] M.B. Baskan, A. Pala, Determination of arsenic removal efficiency by ferric ions using response surface methodology, J. Hazard. Mater. 166 (2009) 796–801.

[37] Y. Lee, I.-H. Um, J. Yoon, Arsenic (III) oxidation by iron (VI)(ferrate) and subsequent removal of arsenic (V) by iron (III) coagulation, Environ. Sci. Technol. 37 (2003) 5750–5756.

[38] X. Du, F. Qu, H. Liang, K. Li, H. Yu, L. Bai, G. Li, Removal of antimony (III) from polluted surface water using a hybrid coagulation–flocculation–ultrafiltration (CF–UF) process, Chem. Eng. J. 254 (2014) 293–301.

[39] W. Wang, X. Zhang, H. Wang, X. Wang, L. Zhou, R. Liu, Y. Liang, Laboratory study on the adsorption of Mn(2+) on suspended and deposited amorphous Al (OH)(3) in drinking water distribution systems, Water Res. 46 (2012) 4063–4070.

[40] N.P. Hankins, N. Lu, N. Hilal, Enhanced removal of heavy metal ions bound to humic acid by polyelectrolyte flocculation, Sep. Purif. Technol. 51 (2006) 48–56.

[41] A.C. Fournier, K.L. Shafran, C.C. Perry, Potentiometric determination of the “formal” hydrolysis ratio of aluminium species in aqueous solutions, Anal. Chim. Acta 607 (2008) 61–73.

[42] P.N. Johnson, A. Amirtharajah, Ferric chloride and alum as single and dual coagulants, J. Am. Water Works Assn. 75 (1983) 232–239.

[43] J. Duan, J. Gregory, Coagulation by hydrolysing metal salts, Adv. Colloid Interface Sci. 100–102 (2003) 475–502.

[44] N. Shirasaki, T. Matsushita, Y. Matsui, A. Oshiba, T. Marubayashi, S. Sato, Improved virus removal by high-basicity polyaluminum coagulants compared to commercially available aluminum-based coagulants, Water Res. 48 (2014) 375–386.

[45] H.-Z. Zhao, C. Liu, Y. Xu, J.-R. Ni, High-concentration polyaluminum chloride: Preparation and effects of the Al concentration on the distribution and transformation of Al species, Chem. Eng. J. 155 (2009) 528–533.

[46] S. Bi, Studies on the mechanism of hydrolysis and polymerization of aluminum salts in aqueous solution: Correlations between the “core-links” model and “cage-like” keggin-Al13 model, Coord. Chem. Rev. 248 (2004) 441–455.

[47] C. Feng, S. Zhao, Z. Bi, D. Wang, H. Tang, Speciation of prehydrolyzed Al salt coagulants with electrospray ionization time-of-flight mass spectrometry and 27Al NMR spectroscopy, Colloids Surf., A 392 (2011) 95–102.

[48] J.E. Van Benschoten, J.K. Edzwald, Chemical aspects of coagulation using aluminum salts—I, Hydrolytic reactions of alum and polyaluminum chloride, Water Res. 24 (1990) 1519–1526.

[49] D. Lakshmanan, D.A. Clifford, G. Samanta, Comparative study of arsenic removal by iron using electrocoagulation and chemical coagulation, Water Res. 44 (2010) 5641–5652.

[50] S. Golbaz, A.J. Jafari, M. Rafiee, R.R. Kalantary, Separate and simultaneous removal of phenol, chromium, and cyanide from aqueous solution by coagulation/precipitation: Mechanisms and theory, Chem. Eng. J. 253 (2014) 251–257.

[51] P. Kappen, J. Webb, An EXAFS study of arsenic bonding on amorphous aluminium hydroxide, Appl. Geochem. 31 (2013) 79–83.

[52] Z. Bi, C. Feng, D. Wang, X. Ge, H. Tang, Transformation of planar Mögel Al13 coagulant during the dilution and aging process, Colloids Surf., A 416 (2013) 73–79.

[53] W. Xu, B. Gao, Q. Yue, Q. Wang, Effect of preformed and non-preformed Al13 species on evolution of floc size, strength and fractal nature of humic acid flocs in coagulation process, Sep. Purif. Technol. 78 (2011) 83–90.

[54] Y.W. Chiang, K. Ghyselbrecht, R.M. Santos, J.A. Martens, R. Swennen, V. Cappuyns, B. Meesschaert, Adsorption of multi-heavy metals onto water treatment residuals: Sorption capacities and applications, Chem. Eng. J. 200–202 (2012) 405–415.

[55] A.G. Caporale, P. Punamiya, M. Pigna, A. Violante, D. Sarkar, Effect of particle size of drinking-water treatment residuals on the sorption of arsenic in the presence of competing ions, J. Hazard. Mater. 260 (2013) 644–651.

[56] M. Kang, T. Kamei, Y. Magara, Comparing polyaluminum chloride and ferric chloride for antimony removal, Water Res. 37 (2003) 4171–4179.

[57] R. Nilsson, Removal of metals by chemical treatment of municipal waste water, Water Res. 5 (1971) 51–60.

[58] G.C. Bond, Catalysis by Metals, Academic Press, New York, NY, 1962.

[59] D. Wang, Y. Zhao, J. Xie, C.W.K. Chow, J. van Leeuwen, Characterizing DOM and removal by enhanced coagulation: A survey with typical Chinese source waters, Sep. Purif. Technol. 110 (2013) 188–195.

[60] F. Xiao, M.F. Simcik, J.S. Gulliver, Mechanisms for removal of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from drinking water by conventional and enhanced coagulation, Water Res. 47 (2013) 49–56.

[61] J. Mertens, J.r.m. Rose, R. Kägi, P. Chaurand, M. Plötze, B. Wehrli, G. Furrer, Adsorption of arsenic on polyaluminum granulate, Environ. Sci. Technol. 46 (2012) 7310–7317.

[62] S. Bordoloi, S.K. Nath, S. Gogoi, R.K. Dutta, Arsenic and iron removal from groundwater by oxidation-coagulation at optimized pH: Laboratory and field studies, J. Hazard. Mater. 260 (2013) 618–626.

[63] M. Borho, P. Wilderer, Optimized removal of arsenate(III) by adaptation of oxidation and precipitation processes to the filtration step, Water Sci. Technol. 34 (1996) 25–31.

[64] C. Hu, H. Liu, G. Chen, W.A. Jefferson, J. Qu, As(III) Oxidation by active chlorine and subsequent removal of As(V) by Al13 polymer coagulation using a novel dual function reagent, Environ. Sci. Technol. 46 (2012) 6776–6782.

[65] T.S.Y. Choong, T.G. Chuah, Y. Robiah, F.L. Gregory Koay, I. Azni, Arsenic toxicity, health hazards and removal techniques from water: An overview, Desalination 217 (2007) 139–166.

[66] R. Prucek, J. Tuček, J. Kolařík, J. Filip, Z. Marušák, V.K. Sharma, R. Zbořil, Ferrate(VI)-induced arsenite and arsenate removal by *in situ* structural incorporation into magnetic iron(III) oxide nanoparticles, Environ. Sci. Technol. 47 (2013) 3283–3292.

[67] L. Charerntanyarak, Heavy metals removal by chemical coagulation and precipitation, Water Sci. Technol. 39 (1999) 135–138.

[68] H. Zhao, H. Liu, J. Qu, Effect of pH on the aluminum salts hydrolysis during coagulation process: Formation and decomposition of polymeric aluminum species, J. Colloid Interface Sci. 330 (2009) 105–112.

[69] N.J. Kabengi, S.H. Daroub, R.D. Rhue, Energetics of arsenate sorption on amorphous aluminum hydroxides studied using flow adsorption calorimetry, J. Colloid Interface Sci. 297 (2006) 86–94.

[70] Y.K. Henneberry, T.E. Kraus, J.A. Fleck, D.P. Krabbenhoft, P.M. Bachand, W.R. Horwath, Removal of inorganic mercury and methylmercury from surface waters following coagulation of dissolved organic matter with metal-based salts, Sci. Total Environ. 409 (2011) 631–637.

[71] E.M. Casbeer, V.K. Sharma, Z. Zajickova, D.D. Dionysiou, Kinetics and mechanism of oxidation of tryptophan by ferrate(VI), Environ. Sci. Technol. 47 (2013) 4572–4580.

[72] W.P. Cheng, F.H. Chi, C.C. Li, R.F. Yu, A study on the removal of organic substances from low-turbidity and low-alkalinity water with metal-polysilicate coagulants, Colloids Surf., A 312 (2008) 238–244.

[73] Z. Yang, B. Gao, B. Cao, W. Xu, Q. Yue, Effect of OH−/Al3+ ratio on the coagulation behavior and residual aluminum speciation of polyaluminum chloride (PAC) in surface water treatment, Sep. Purif. Technol. 80 (2011) 59–66.

[74] Z. Zhou, Y. Yang, X. Li, W. Gao, H. Liang, G. Li, Coagulation efficiency and flocs characteristics of recycling sludge during treatment of low temperature and micro-polluted water, J. Environ. Sci. 24 (2012) 1014–1020.

[75] X. Guan, J. Ma, H. Dong, L. Jiang, Removal of arsenic from water: Effect of calcium ions on As(III) removal in the KMnO(4)-Fe(II) process, Water Res. 43 (2009) 5119–5128.

[76] Y. Masue, R.H. Loeppert, T.A. Kramer, Arsenate and arsenite adsorption and desorption behavior on coprecipitated aluminum:Iron hydroxides, Environ. Sci. Technol. 41 (2006) 837–842.

[77] K.D. Kwon, J.D. Kubicki, Molecular orbital theory study on surface complex structures of phosphates to iron hydroxides: Calculation of vibrational frequencies and adsorption energies, Langmuir 20 (2004) 9249–9254.

[78] Z. Wu, M. He, X. Guo, R. Zhou, Removal of antimony (III) and antimony (V) from drinking water by ferric chloride coagulation: Competing ion effect and the mechanism analysis, Sep. Purif. Technol. 76 (2010) 184–190.

[79] R.A. Alvarez-Puebla, C. Valenzuela-Calahorro, J.J. Garrido, Retention of Co (II), Ni (II), and Cu (II) on a purified brown humic acid, Modeling and characterization of the sorption process, Langmuir 20 (2004) 3657–3664.

[80] A. Alpatova, S. Verbych, M. Bryk, R. Nigmatullin, N. Hilal, Ultrafiltration of water containing natural organic matter: Heavy metal removing in the hybrid complexation–ultrafiltration process, Sep. Purif. Technol. 40 (2004) 155–162.

[81] A. Escoda, M. Euvrard, S. Lakard, J. Husson, A.S. Mohamed, M. Knorr, Ultrafiltration-assisted retention of Cu(II) ions by adsorption on chitosan-functionalized colloidal silica particles, Sep. Purif. Technol. 118 (2013) 25–32.

[82] M. Al-Abri, A. Dakheel, C. Tizaoui, N. Hilal, Combined humic substance and heavy metals coagulation, and membrane filtration under saline conditions, Desalination 253 (2010) 46–50.
[83] B.-Y. Gao, Y. Wang, Q.-Y. Yue, J.-C. Wei, Q. Li, Color removal from simulated dye water and actual textile wastewater using a composite coagulant prepared by ployferric chloride and polydimethyldiallylammonium chloride, Sep. Purif. Technol. 54 (2007) 157–163.
[84] Z. Yang, B. Yuan, X. Huang, J. Zhou, J. Cai, H. Yang, A. Li, R. Cheng, Evaluation of the flocculation performance of carboxymethyl chitosan-graft-polyacrylamide, a novel amphoteric chemically bonded composite flocculant, Water Res. 46 (2012) 107–114.
[85] M.G. Rasteiro, F.A.P. Garcia, P. Ferreira, A. Blanco, C. Negro, E. Antunes, The use of LDS as a tool to evaluate flocculation mechanisms, Chem. Eng. Process. 47 (2008) 1323–1332.
[86] K.C. Makris, D. Sarkar, J.G. Parsons, R. Datta, J.L. Gardea-Torresdey, X-ray absorption spectroscopy as a tool investigating arsenic(III) and arsenic(V) sorption by an aluminum-based drinking-water treatment residual, J. Hazard. Mater. 171 (2009) 980–986.
[87] W.-Z. Yu, J. Gregory, H.-J. Liu, J.-H. Qu, Investigation of the property of kaolin–alum flocs at acidic pH, Colloids Surf., A 443 (2014) 177–181.
[88] C. Hu, H. Liu, J. Qu, D. Wang, J. Ru, Coagulation behavior of aluminum salts in eutrophic water: Significance of Al13 species and pH control, Environ. Sci. Technol. 40 (2005) 325–331.
[89] I. Slavik, S. Müller, R. Mokosch, J.A. Azongbilla, W. Uhl, Impact of shear stress and pH changes on floc size and removal of dissolved organic matter (DOM), Water Res. 46 (2012) 6543–6553.
[90] C.C. Mólgora, A.M. Domínguez, E.M. Avila, P. Drogui, G. Buelna, Removal of arsenic from drinking water: A comparative study between electrocoagulation–microfiltration and chemical coagulation–microfiltration processes, Sep. Purif. Technol. 118 (2013) 645–651.
[91] L. Pachuau, S.M. Lee, D. Tiwari, Ferrate(VI) in wastewater treatment contaminated with metal(II)-iminodiacetic acid complexed species, Chem. Eng. J. 230 (2013) 141–148.
[92] S. Lan, F. Ju, X. Wu, Treatment of wastewater containing EDTA-Cu(II) using the combined process of interior microelectrolysis and Fenton oxidation–coagulation, Sep. Purif. Technol. 89 (2012) 117–124.
[93] P. Xiao, F. Xiao, W. Zhang, B. Zhao, D. Wang, Insight into the combined colloidal-humic acid fouling on the hybrid coagulation microfiltration membrane process: The importance of aluminum, Colloids Surf., A 461 (2014) 98–104.
[94] H. Dong, B. Gao, Q. Yue, S. Sun, Y. Wang, Q. Li, Floc properties and membrane fouling of different monomer and polymer Fe coagulants in coagulation–ultrafiltration process: The role of Fe (III) species, Chem. Eng. J. 258 (2014) 442–449.
[95] B. Feng, Z. Fang, J. Hou, X. Ma, Y. Huang, L. Huang, Effects of heavy metal wastewater on the anoxic/aerobic-membrane bioreactor bioprocess and membrane fouling, Bioresour. Technol. 142 (2013) 32–38.
[96] M.T. Alarcon-Herrera, J. Bundschuh, B. Nath, H.B. Nicolli, M. Gutierrez, V.M. Reyes-Gomez, D. Nunez, I.R. Martin-Dominguez, O. Sracek, Co-occurrence of arsenic and fluoride in groundwater of semi-arid regions in Latin America: Genesis, mobility and remediation, J. Hazard. Mater. 262 (2013) 960–969.
[97] M.A. Martín-Lara, G. Blázquez, M.C. Trujillo, A. Pérez, M. Calero, New treatment of real electroplating wastewater containing heavy metal ions by adsorption onto olive stone, J. Clean. Prod. 81 (2014) 120–129.
[98] C.D. Wu, X.J. Xu, J.L. Liang, Q. Wang, Q. Dong, W.L. Liang, Enhanced coagulation for treating slightly polluted algae-containing surface water combining polyaluminum chloride (PAC) with diatomite, Desalination 279 (2011) 140–145.
[99] S. Song, A. Lopez-Valdivieso, D.J. Hernandez-Campos, C. Peng, M.G. Monroy-Fernandez, I. Razo-Soto, Arsenic removal from high-arsenic water by enhanced coagulation with ferric ions and coarse calcite, Water Res. 40 (2006) 364–372.
[100] M. Vedrenne, R. Vasquez-Medrano, D. Prato-Garcia, B.A. Frontana-Uribe, J.G. Ibanez, Characterization and detoxification of a mature landfill leachate using a combined coagulation–flocculation/photo Fenton treatment, J. Hazard. Mater. 205 (2012) 208–215.
[101] G. Zhu, H. Zheng, Z. Zhang, T. Tshukudu, P. Zhang, X. Xiang, Characterization and coagulation–flocculation behavior of polymeric aluminum ferric sulfate (PAFS), Chem. Eng. J. 178 (2011) 50–59.
[102] G. Zhu, H. Zheng, W. Chen, W. Fan, P. Zhang, T. Tshukudu, Preparation of a composite coagulant: Polymeric aluminum ferric sulfate (PAFS) for wastewater treatment, Desalination 285 (2012) 315–323.
[103] S. Zhao, B. Gao, Q. Yue, Y. Wang, Q. Li, F. Zhang, Effect of Enteromorpha extract on characteristics of flocs formed by aluminum sulfate in Yellow River water treatment under different hydraulic conditions, Chem. Eng. J. 215–216 (2013) 358–365.
[104] W. Xu, B. Gao, B. Du, Z. Xu, Y. Zhang, D. Wei, Influence of shear force on floc properties and residual aluminum in humic acid treatment by nano-Al13, J. Hazard. Mater. 271 (2014) 1–8.
[105] C.Y. Hu, S.L. Lo, C.L. Chang, F.L. Chen, Y.D. Wu, J.l. Ma, Treatment of highly turbid water using chitosan and aluminum salts, Sep. Purif. Technol. 104 (2013) 322–326.
[106] M. Bilici Baskan, A. Pala, A statistical experiment design approach for arsenic removal by coagulation process using aluminum sulfate, Desalination 254 (2010) 42–48.
[107] T.P. Flaten, Aluminium as a risk factor in Alzheimer's disease, with emphasis on drinking water, Brain Res. Bull. 55 (2001) 187–196.
[108] S.C. Bondy, Prolonged exposure to low levels of aluminum leads to changes associated with brain aging and neurodegeneration, Toxicology 315 (2014) 1–7.
[109] J. Huang, Z.H. Yang, G.M. Zeng, M. Ruan, H.Y. Xu, W.C. Gao, Y.L. Luo, H.M. Xie, Influence of composite flocculant of PAC and MBFGA1 on residual aluminum species distribution, Chem. Eng. J. 191 (2012) 269–277.

[110] M. Kimura, Y. Matsui, K. Kondo, T.B. Ishikawa, T. Matsushita, N. Shirasaki, Minimizing residual aluminum concentration in treated water by tailoring properties of polyaluminum coagulants, Water Res. 47 (2013) 2075–2084.

[111] Z. Yang, B. Gao, Y. Wang, Y. Zhao, Q. Yue, Fractionation of residual Al in natural water treatment from reservoir with poly-aluminum-silicate-chloride (PASiC): Effect of OH/Al, Si/Al molar ratios and initial pH, J. Environ. Sci. 24 (2012) 1908–1916.

[112] Z. Yang, B. Gao, Y. Wang, X. Zhang, Q. Yue, The effect of additional poly-diallyl dimethyl ammonium-chloride on the speciation distribution of residual aluminum (Al) in a low DOC and high alkalinity reservoir water treatment, Chem. Eng. J. 197 (2012) 56–66.

[113] D. Berube, C. Dorea, pH-Dependent retention changes during membrane filtration of aluminum-coagulated solutions and the effect of precentrifugation, Environ. Sci. Technol. 47 (2013) 2713–2720.

[114] M. Arain, T. Kazi, J. Baig, M. Jamali, H. Afridi, A. Shah, N. Jalbani, R. Sarfraz, Determination of arsenic levels in lake water, sediment, and foodstuff from selected area of Sindh, Pakistan: Estimation of daily dietary intake, Food Chem. Toxicol. 47 (2009) 242–248.

[115] Z. Ismail, K. Salim, S.Z. Othman, A.H. Ramli, S.M. Shirazi, R. Karim, S.Y. Khoo, Determining and comparing the levels of heavy metal concentrations in two selected urban river water, Measurement 46 (2013) 4135–4144.

[116] M. Varol, Dissolved heavy metal concentrations of the Kralkızı, Dicle and Batman dam reservoirs in the Tigris River basin, Turkey, Chemosphere 93 (2013) 954–962.

[117] A. Emili, A. Acquavita, N. Koron, S. Covelli, J. Faganeli, M. Horvat, S. Žižek, V. Fajon, Benthic flux measurements of Hg species in a northern Adriatic lagoon environment (Marano and Grado Lagoon, Italy), Estuarine Coastal Shelf Sci. 113 (2012) 71–84.

[118] Y.K. Henneberry, T.E.C. Kraus, J.A. Fleck, D.P. Krabbenhoft, P.M. Bachand, W.R. Horwath, Removal of inorganic mercury and methylmercury from surface waters following coagulation of dissolved organic matter with metal-based salts, Sci. Total Environ. 409 (2011) 631–637.

[119] J.M. Serafimovska, S. Arpadjan, T. Stafilov, Speciation of dissolved inorganic antimony in natural waters using liquid phase semi-microextraction combined with electrothermal atomic absorption spectrometry, Microchem. J. 99 (2011) 46–50.

[120] M. Filella, N. Belzile, Y.-W. Chen, Antimony in the environment: A review focused on natural waters: I. Occurrence, Earth Sci. Rev. 57 (2002) 125–176.

[121] L.K. Pandey, D. Kumar, A. Yadav, J. Rai, J.P. Gaur, Morphological abnormalities in periphytic diatoms as a tool for biomonitoring of heavy metal pollution in a river, Ecol. Indic. 36 (2014) 272–279.

[122] W. Nazif, S. Perveen, S.A. Shah, Evaluation of irrigation water for heavy metals of akbarpura area, J. Agric. Biol. Sci. 1 (2006) 25–29.

[123] M. Varol, B. Şen, Assessment of nutrient and heavy metal contamination in surface water and sediments of the upper Tigris River, Turkey, CATENA 92 (2012) 1–10.

[124] I.A. Katsoyiannis, A. Zikoudi, S.J. Hug, Arsenic removal from groundwaters containing iron, ammonium, manganese and phosphate: A case study from a treatment unit in northern Greece, Desalination 224 (2008) 330–339.

[125] E.O. Kartinen Jr., C.J. Martin, An overview of arsenic removal processes, Desalination 103 (1995) 79–88.

[126] Y.J. Tu, C.K. Chang, C.F. You, S.L. Wang, Treatment of complex heavy metal wastewater using a multi-staged ferrite process, J. Hazard. Mater. 209–210 (2012) 379–384.

[127] D. Purkayastha, U. Mishra, S. Biswas, A comprehensive review on Cd(II) removal from aqueous solution, J. Water Process Eng. 2 (2014) 105–128.

[128] P. Pal, S. Chakrabortty, L. Linnanen, A nanofiltration-coagulation integrated system for separation and stabilization of arsenic from groundwater, Sci. Total Environ. 476–477 (2014) 601–610.

[129] Y. Li, X. Zeng, Y. Liu, S. Yan, Z. Hu, Y. Ni, Study on the treatment of copper-electroplating wastewater by chemical trapping and flocculation, Sep. Purif. Technol. 31 (2003) 91–95.

[130] T.A. Kurniawan, G.Y.S. Chan, W.-H. Lo, S. Babel, Physico–chemical treatment techniques for wastewater laden with heavy metals, Chem. Eng. J. 118 (2006) 83–98.

[131] F. Cecen, G. Gursoy, Characterization of landfill leachates and studies on heavy metal removal, J. Environ. Monit. 2 (2000) 436–442.

[132] Y. Wu, S. Zhou, X. Ye, D. Chen, K. Zheng, F. Qin, Transformation of pollutants in landfill leachate treated by a combined sequence batch reactor, coagulation, Fenton oxidation and biological aerated filter technology, Process Saf. Environ. Prot. 89 (2011) 112–120.

[133] P. Pourrezaei, P. Drzewicz, Y. Wang, M. Gamal, El-Din, L.A. Perez-Estrada, J.W. Martin, J. Anderson, S. Wiseman, K. Liber, J.P. Giesy, The impact of metallic coagulants on the removal of organic compounds from oil sands process-affected water, Environ. Sci. Technol. 45 (2011) 8452–8459.

[134] B. Yang, G.G. Ying, J.L. Zhao, S. Liu, L.J. Zhou, F. Chen, Removal of selected endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) during ferrate(VI) treatment of secondary wastewater effluents, Water Res. 46 (2012) 2194–2204.

[135] J.-Q. Jiang, Z. Zhou, S. Patibandla, X. Shu, Pharmaceutical removal from wastewater by ferrate(VI) and preliminary effluent toxicity assessments by the zebrafish embryo model, Microchem. J. 110 (2013) 239–245.

[136] V.K. Sharma, Ferrate(VI) and ferrate(V) oxidation of organic compounds: Kinetics and mechanism, Coord. Chem. Rev. 257 (2013) 495–510.

[137] Y.X. Zhao, B.Y. Gao, Q.B. Qi, Y. Wang, S. Phuntsho, J.H. Kim, Q.Y. Yue, Q. Li, H.K. Shon, Cationic polyacrylamide as coagulant aid with titanium tetrachloride for low molecule organic matter removal, J. Hazard. Mater. 258–259 (2013) 84–92.

[138] Y.X. Zhao, S. Phuntsho, B.Y. Gao, X. Huang, Q.B. Qi, Q.Y. Yue, Y. Wang, J.H. Kim, H.K. Shon, Preparation and Characterization of Novel Polytitanium Tetrachloride Coagulant for Water Purification, Environ. Sci. Technol. 47 (2013) 12966–12975.

[139] I.H. Choi, S.m. Lee, I.C. Kim, B.-R. Min, K.H. Lee, Effect of new photocatalytic coagulant on NF membrane fouling, Ind. Eng. Chem. Res. 46 (2007) 2280–2285.

[140] P. Jarvis, E. Sharp, M. Pidou, R. Molinder, S.A. Parsons, B. Jefferson, Comparison of coagulation performance and floc properties using a novel zirconium coagulant against traditional ferric and alum coagulants, Water Res. 46 (2012) 4179–4187.