*Asian Journal of Chemistry; Vol. 27, No. 5 (2015), 1574-1580*

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17971

***REVIEW***

# Preparation of Some Inorganic Coagulants in Green, Hybrid and Novel Route

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*Received*: 9 May 2014; *Accepted*: 11 July 2014; *Published online*: 20 February 2015; AJC-16846

The inorganics and modified coagulants have significantly influenced water and wastewater treatment for centuries. With rapid economic growth, high efficient, better performance, environmental-friendly have been the key ingredients for water and wastewater treatment in recent years. Therefore, more attention has been directed at synthesis preparation routes of inorganic coagulants which are characterized as green, sustainable and energy-saving. Because the hybrid materials and industrial wastes have been promising for preparation of these chemicals, and thus their applications have received wide attention. The present review is of much significance, especially in three research directions including industrial wastes reusing, diverse organic polymers introducing and the application of relative novel metal salts. In this review, their current states as well as their potential utilization in future were reviewed and suggested, respectively, which are particularly important for those water workers to improve their working efficiency in water treatment.

**Keywords: Synthesis, Preparation, Inorganic coagulant, Inorganic-organic coagulant, Wastewater.**

## INTRODUCTION

The rational utilization of water, as an important resource for human consumption, is necessary. With economic development and industrialization, the demand of reliable water has become more and more crucial. And the serious pollution of water resources put pressure on solving environmental protection problem. Many researchers concentrated their efforts on the sustainable utilization of water and recycling water wastes due to the limitation on the amount of clean water resource. Wastewater treatment, which consists of typical process such as pretreatment, coagulation and flocculation, precipitation, separation and sludge disposal, is one common approach to purify and recycle this precious resource. Coagulation-flocculation plays an important role in the purification process *via* removing suspended solids and organic matter[1-4], as well as sludge dewatering from different industries such as textile dyes[5-8], oily water[9,10], food processing[11], metal smelting, mineral processing[12], cosmetics producing and treating environmental hormones[13], disinfection byproducts[14,15] and some other industries[16].

Coagulation and flocculation using different coagulants is an essential operational unit in the treatment process with the purpose of precipitation and separation between wastes and water through forming the flocs[17]. The definitions of coagulant differ and is mainly divided into two categories of inorganic and organic coagulants based on the mechanism of destabilization of colloidal particles in water[18]. Coagulants which make the solutes, colloidal or suspended particles destabilization by the compression of electrical double layer and surface charge neutralization are usually defined to inorganic coagulants while coagulants which make the same effect by the adsorption bridging or adsorption-charge neutralization are classified as organic coagulants. The aim of coagulation-flocculation is to remove the colloids and suspended solids which contain organic or/and inorganic pollutants from water. Inorganic and organic coagulants[19] have their own advantages and disadvantages and often could be utilized separately or in conjunction.

Aluminum and ferric salts are the most commonly used inorganic coagulants in the coagulation processing. However, it is vital to boost the treatment efficiency of inorganic coagulants because of some major drawbacks like the rapid formation of the coagulant species during dilution, the difficulty in controlling the formation of hydrolysis species and worsening performance with changing water temperature and in the natural raw water[4]. The emergency of inorganic polymer flocculants/coagulants (IPFSs/IPCSs)[20-22] and their composites is an alternative avenue to address the drawbacks mentioned above. The

IPFs/IPCs possess the merits of strong adaptability, more efficient and less costs, leading to potentially and worthy utilized in treating process.

In recent years, diverse and significant IPFs/IPCs have been developed rapidly, as well as inorganic-based coagulants, organic-based coagulants and some hybrid composite materials. Therefore, there is much necessity to follow the continuously increasing market demands even though many materials have been successfully used in removing pollutants. Three major directions of the inorganic development were proposed in this paper. Firstly, the industrial wastes reusing for the cost-efficient purpose was depicted. Secondly, the introductions of some hybrid composite coagulants[23,24] to enhance the superior aggregating ability due to the synergetic effect, were exhibited. Finally, diverse relative novel metal salts were applied corresponding for the pluralism direction of inorganic coagulants.

**Brief classification of hybrid coagulants:** Many papers and researchers have focused on classification and terminologies of coagulants based on the different preparation materials, such as composite coagulants, composite polymer coagulant, hybrid coagulant, hybrid polymer coagulant and so forth. However, structurally-hybridized materials, chemically-bound-hybridized materials, functionally-hybridized materials were proposed to avoid the confusion of coagulants through some previous study[25].

(1) Structurally-hybridized materials mean the physical mixtures with the absence of new chemical species and follow the regular rule of mixtures which combine the properties of the raw substrates at macroscopic gradation (*i.e.*, PAFS-CPAM hybrid) and as well as composites[2]. The major effect mechanism of this material is synergy effect.

(2) Chemically-bound-hybridized materials are distinguished from the structurally-hybridized due to the mixture combination of chemical species from the atoms and molecules degree. The conclusion is that some new chemical groups and bonds introduced into the molecular chain of raw regents by chemical modification. The preparation of those materials are commonly used methods *e.g.*, hydroxylation pre-polymerization, copolymerization and chemical grafting or cross linking. For instance, poly-silicic acid added into the molecular chain of poly-ferric sulfate(PFS)[26] to increase the molecular weight for the achievement of better aggregating capacity. Preparation of poly-aluminum silicate chloride (PASiC)[21] using poly-aluminum chloride (PACl) is similar to the production mechanism for PFSiS using PFS.

(3) Moreover, the detail concept of functionally-hybridized materials is still can't be proposed clearly. Some researchers[16,25] attempted to define it as the materials who have harmonizing function and utilization of interface function led to some new functions or super functions.

According to Morad *et al.*[16], the classification of those hybrid materials could be divided into four groups, such as inorganic, organic, natural polymer and biopolymer regardless of the macroscopic and microscopic properties of the preparation materials[27,28]. The preparation of hybrid coagulants utilizes two or more materials. An inorganic or inorganic-polymeric coagulants are often hybridized or modified with organic polymeric[29] or some natural materials[30,31], which showed a better and potential tendency and higher aggregating capacity.

**Novel preparation routes of some inorganic coagulants:** The methods modification and raw materials addition are both included of novel preparation routes to change the reaction procedures resulting in attaining the energy-saving or cost-saving goal through reusing of industries wastes or byproducts. Some inorganic components, such as silicate group[32], magnesium[33,34], zinc[35], were added to improve coagulation capacity with the advantages of higher molecular weight, bigger aggregating capacity and more adaptable to pH changes. Some organic polymers like polyacrylamide (PAM)[36,37], polydimethyl diallylammonium chloride (PDADMAC)[38], poly-epichlorohydrin-dimethylamine (PECH-DAM) and other cationic polyelectrolytes[29,39] could also be introduced into inorganic coagulants to obtain inorganic-organic hybrid coagulants[40,41].

**Green synthesis of inorganic coagulant**

**Polyaluminum chloride (PAC) prepared through energy-saving route:** Conventional preparation methods of PAC comprise two different ways. That PAC prepared through the mixing of an aluminum containing raw material (*e.g.* $Al_2O_3$ or other minerals contained Al) with concentrated acid (*e.g.* HCl, or an appropriate mixture of HCl and $H_3PO_4$) is the first method. Another route is PAC produced by the dissolution of aluminum raw material in strong alkaline solution.

Previous research[42] proposed an alternative cost-effective method to prepare PAC through the energy-saving approach for the cost-effective. Granular Al was introduced slowly into a preheated acid solution to obtain the aluminum solution. As the reaction is exothermic, further heating was not necessary. On the side, sodium aluminate solution was produced using granular Al and sodium hydroxide solution. Then, an appropriate amounts of sodium aluminum solution was added into the aluminum solution at appropriate temperatures. There is no need for continuously heating except for the aluminum solution preparation. Preparation through this route saves energy as the composition is attained at room temperature and in mild conditions.

**Poly-ferric aluminum chloride (PFAC) prepared by hydrochloric pickle liquor:** Pickling, as one important route[43], was used to remove the oxides and scale from the metal surface[44] increasing industrial profits at the same time resulting in the production of pickling liquors. Pickling, which contains some residual acids or salts, leads to high amounts of wastes in many countries[45]. With the purpose of cost-saving and waste-recycling, hydrochloric acid or industrial hydrochloric acid with hydrochloric pickle liquor could be used to prepare inorganic coagulant from the pickling liquors.

Some researchers[46] indicated that the poly-ferric aluminum chloride (PFAC) could be synthesized by hydrochloric pickle liquor and calcium aluminate. The hydrochloric pickling liquor which contains both HCl and $FeCl_2$, was put into the flask and placed in an electric heat constant temperature water bath, sodium chlorate was slowly introduced to oxidize Fe(II). Calcium aluminate was added into the pickling liquor mixture to produce a product with different weight/volume ratio. Lastly, stabilizing agents were added to make the solution stable after filtration. The COD and turbidity removal efficiency of the products showed better performance than some traditional ferric salts. This synthesis method provides one feasible way to recycle waste, making less environmental pollutions while at the same time yielding higher economic benefits.

**Poly-silicate ferro-aluminum chloride prepared by red mud:** Red mud is one solid waste residue formed during the digestion of bauxite ores using caustic during production in the aluminum industry[47]. Large amounts of those wastes should be utilized effectively for better environmental conservation. Red mud could be applied in various ways, such as sorbent agent[48], conducting filler with polyaniline[49], new geo-polymer formulation[50] and so on. In recent years, treating wastewater using red mud has gained attention. Recent studies[51] attempted to study transformation process of red mud into liquid or solid, which indicates it contains high amounts of Al and Fe for coagulants preparation. One feasible method[52] revealed production cost-saving purpose *via* the utilization of red mud, which contains highly alkaline due to the existence of metal oxides such as $SiO_2$, $Fe_2O_3$, $Al_2O_3$, CaO, $Na_2O$ and so forth. Hydrochloric pickle liquor of bauxite, which contains $Al_2O_3$, was put into flask and heated constantly before the red mud was introduced to reaction mixture. As the reaction temperatures increased, the mixture reacted producing the coagulants. Lastly, the coagulants mixture was cooled to room temperature. The metal oxides reacted with the hydrochloric acid in the pickling liquor leading to the hydrolyzation of Al (III) and Fe(III). The coagulant mixture is classified as poly-silicate ferro-aluminum chloride due to the polymerization of hydroxyl and the hydrolysis complexes. For application in the removal of phosphate, the new coagulant exhibited superb performance compared to some commercial products.

**Poly-silicic-cation coagulant prepared by fly ash and pyrite slag:** Fly ash was produced largely[53] for many countries[54] from coal-fired thermal power plants. However, the majority of pyrite slag could not be piled up very well[55], which as one by-product produced by sulfuric acid manufacturing industry and which contains silicon, aluminum, iron, calcium and some other compounds[56]. Some previous studies[58,59] pointed that the wastes streams could be utilized to produce inorganic polymeric coagulant. Some researchers[57] used the synchronous-polymerization method[58] to prepare poly-silicic-cation coagulant. In this study, the same method was used to prepare the poly-silicic-cationic coagulant[60] by waste stream mentioned above. Certain amounts of fly ash and sodium hydroxide were added to a heated reaction vessel with stirring for a certain amount of time. In addition, some insoluble ash particles and water were added. Then, an appropriate amounts of pyrite slag, alkali-leached fly ash and wasted sulfuric acid were added to the reaction vessel under stirring with continuous heating. After a few hours, the mixture was filtered. The polymerization process occurred after various amounts of water glass solution was added to the metal salt solution at low rate stirring. The PSiC was prepared after aging for few days at normal temperature. This new complex compounds prepared by industrial wastes contribute to environmental conservation and cost-saving.

**Poly-Al-Zn-Fe (PAZF) prepared by galvanized aluminum slag:** Galvanized aluminum slag is one solid waste generated from hot dip galvanizing process in which iron or steel are mixed with molten zinc to form zinc coating. However, it is difficult to dispose this waste due to some characteristics, high melting point, high mounts of zinc and multi-alloy substance consisting of many metal elements which includes zinc, aluminum and iron, for instance[61-63].

Galvanized aluminum slag, as raw material, was used to prepare inorganic coagulant[35] *via* the two steps methodology, leaching with a mixed acid and polymerizing with alkali. The major procedures of the preparation are as follows: Firstly, galvanized aluminum slag was reduced to smaller molecular through the addition of acidic solution; secondly, the reacting mixture was leached with heating to obtain the leaching solution; lastly, NaOH solution was slowly introduced into the filtrate solution to obtain liquid PAZF through polymerization for few hours under stirring and heating condition. Compared with PAC, PAZF showed better efficiency for the simultaneous removal of nitrogen and organic matters due to the net-work structure and lager surface area. This is not only an appropriate route to dispose this industrial waste, but also save the cost of raw materials.

**Polymeric aluminum ferric sulfate (PAFS) prepared by titanium pigment:** The ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), one major content of industrial byproduct named titanium pigment[64], was utilized to prepare one inorganic composite coagulant by Zheng *et al.*[65]. Firstly, $FeSO_4{\cdot}7H_2O$ was mixed with distilled water to form a thin uniform paste. Secondly, the mixture was acidulated using industrial aluminum oxide and $H_2SO_4$ as acidulent. Thirdly, $HNO_3$ was added to oxidize the new mixture with slow stirring in a thermostatic water bath for few minutes. Lastly, $H_3PO_4$ was added to improve the hydrolysis and polymerization effect during the synthesis process while NaOH solution was used to adjust the alkalinity. The liquid coagulant was produced after aging for sometimes. In the end, bonds such as Fe-O-Fe, Al-O-Al, *etc*. were introduced into the PFS. This novel coagulant showed better performance than some traditional coagulants for the removal of turbidity and chlorophyll.

The nitric acid could also be the oxidant during the preparation of PAFS except for $H_2SO_4$. In addition, Zheng *et al.*[66,67] suggested different preparation methods for the same efficient coagulant. Firstly, the $HNO_3$ and $FeSO_4{\cdot}7H_2O$ were mixed at room temperature until a homogeneous liquid mixture formed. Secondly, $Al_2(SO_4)_3$ solution was added with slow stirring at a pre-determined temperature to form a new mixture. Thirdly, $H_3PO_4$ which acts as a stabilizer to improve the hydrolysis and polymerization effect was added to the reaction mixture. $Na_2CO_3$ powder was added to the reaction mixture to acquire the desired OH/Fe ratio. Lastly, PAFS was prepared after storage and aging for a few hours. Phase structures like $Fe^{2+}$ $Al_2O_4$ were formed as new chemical bonds were introduced into PFS.

Different procedure using the same raw materials leads to different structures and morphology. However, it showed better treatment performance than conventional coagulants.

**Polymeric phosphate-aluminum chloride (PPAC) prepared in advanced route:** To promote coagulation capability of conventional inorganic polymer coagulant like PAC is becoming more and more significant. Previous research work has improved the polymerization of the product by adding diverse substances like silicic acid or silica[21,68].

In the study by Zheng *et al.*[69], phosphate ion was introduced into the inorganic coagulant. Firstly, aluminum hydroxide, hydrochloric acid and de-ionized water were mixed at high temperature with reflux condensation to prepare polyaluminum chloride. $H_3PO_4$ was gradually added to the reaction system. Lastly, polymeric phosphate-aluminum chloride (PPAC) was prepared after aging for a few days. The phosphate ions introduced into PAC played an important role to increase the polymerization degree. Experiments on the treatment of wastewater using the coagulant showed an increase in the COD and turbidity removal efficiency in alkaline conditions. However, there is very little research work analyzing the structure of polymeric phosphate-aluminium chloride.

**Synthesis of inorganic-organic polymer composite/hybrid coagulants:** The aggregation capacity of inorganic polymer coagulants/flocculants is limited due to lower molecular weight and size, leading to a worse coagulation-flocculation performance compared to organic polymeric coagulants[58,61]. As such, the combination of organic and inorganic monomers result in better performance for water treatment and thus, have attracted a lot of attention as an alternative to using the coagulant individually[70,71]. Compared to the combination of different inorganic coagulants, inorganic-organic coagulants have high charge density and water solubility in addition to high aggregation capacity as an advantage[72-74]. Therefore, there is a rapid development in research work where various organic polymers such as poly-acrylamide (PAM)[33,34], poly-dimethyl-diallyl-ammonium chloride (PDMDAAC)[75-85], cationic poly-acrylamide (CPAM)[86], epichlorohydrin-dimethylamine polyamine (EPI-DMA-PM)[77,87] could be introduced into coagulants based on inorganic slats, such as $Al(OH)_3$[88-91], $FeCl_3$[92], PAC[93], PFS[2].

**Cationic polyelectrolyte (CP) hybrided with inorganic coagulants:** Organic polymers additives are classified based on their charge as cationic, anionic or non-anionic monomers. Poly-dimethyl-diallyl-ammonium chloride (PDMDAAC) is a cationic monomer which is non-toxic at room temperature and is commonly utilized in synthesizing organic-inorganic coagulants for the vast majority of wastewater treatment processes.

Zouboulis *et al.*[29] used PDMDAAC and the pre-polymerized inorganic coagulant PFS to prepare a composite coagulant using two preparatory methods, composite polymerization and co-polymerization. For composite polymerization, pre-polymerized polyferric sulfate was initially prepared at the optimum OH/Fe ratio. And then, the PDMDAAC solution was added into the PFS solution at constant temperature. However, the product of composite-polymerization was the mixture of PFS and PDMDAAC. For co-polymerization, ferrous sulfate was pre-oxidized in an acidic environment to make the iron trivalent with heating before the organic basic solution was added. The analysis of iron species distribution and morphological analysis of the composite coagulant didn't indicate the formation of new chemical bonds, which could be recognized as belonging to structurally-hybridized materials. The coagulation experiments demonstrated a superior coagulation performance for the turbid kaolin-humic acid suspension due to the enhancement of both the destabilization and bridge formation capacity.

Even the PDMDAAC[94-96] could be used as a primary coagulant for natural organic matters removal due to its high charge density, however it's costly and at the same time produces small flocs. Some researchers[38] attempted to prepare one composite coagulant through premixing PDMDAAC and polymeric ferric aluminum chloride (PFACl) for the purpose of better performance and lower cost. This composite coagulant had some dissimilar characteristics to the PFS-PDMDAAC which mentioned before. The difference is that $Na_2HPO_4$ was introduced into the PFACl solution before adding the PDMDAAC solution to promote the polymerization degree. This composite coagulant could considered as a blending mixture of structurally-hybridized materials.

Nevertheless, recent studies have concentrated on modifying the structure of the inorganic coagulants by taking advantage of the synergy effect between the organic and inorganic components[97]. Ying *et al.*[98] made the modification of the polysilicic-ferric (PSiF) by using DMDAAC which as an additive. The PFSi prepared with the same method proposed from some previous studies[99]. The preparation steps for PSiF-DMDAAC were as follow. Firstly, $FeSO_4$ solution was prepared using $FeSO_4 \cdot 7H_2O$ and $H_2SO_4$; secondly, a certain amount of DMDAAC was mixed with the $FeSO_4$ solution; the polysilicic acid solution was obtained after 2 h of polymerization between water glass and $H_2SO_4$ solution. The mixture was stirred before adding sodium chlorate ($NaClO_3$); the stabilizer M, prepared using $C_2H_4O_6Na_2 \cdot 2H_2O$ and NaClO in a ratio of 1:6.5 was diluted to the appropriate Fe concentration. The characterization studies of PSiF-DMDAAC indicated silicate cross-linking was generated. The Fe-OH-Fe bonds was replaced by Fe-OH-M bonds, which could be recognized as belonging to chemically-bound-hybridized materials with the ability for higher color removal, larger floc growth and sedimentation rate than inorganic salt.

**Anionic polyelectrolyte (AP) hybrided with inorganic coagulants:** The most aforementioned preparation methods are the combination of inorganic coagulants and cationic polyelectrolyte (like DMDAAC)[38], but not the anionic polyelectrolyte. However, some anionic polyelectrolyte could be introduced into inorganic metal salts[97,100] to obtain a higher molecular weight than with the non-ionic polymers, which has a better coagulation property.

Some other researchers[93] attempted to introduce an anionic polyelectrolyte, one commercial product with common name Magnafloc LT-25® which actually is a copolymer of acrylamide and acrylic acid, into the polyaluminum chloride (PAC) by the co-polymerization avenue, which differs from the composite physical mixing method. Firstly, a pre-determined amount of the anionic solution was added into $AlCl_3$ solution under magnetic stirring with heating. Afterwards, an appropriate amount of NaOH solution was introduced to obtain the desired [OH]/[Al] molar ratio. Additional, composite polymerization technique was utilized to compare the different preparation methods. The latter preparation procedures differ from the formers. Firstly, PAC solution was prepared and added to the anionic solution. The characterization of this hybrid coagulant revealed that incorporation of the anionic polyelectrolyte into PAC's structure affects its initial properties and the interactions took place between Al species and anionic polyelectrolyte molecules. In addition, new composite species were formed, which may be classified as an amino (or amidic) groups of polyelectrolyte and the -O- or the -OH- groups of Al species are involved. This coagulant could be categorized as belonging to chemically-bound-hybridized materials with the characteristics of higher efficiency and cost-effectiveness.

**Polyferric chloride-poly-epichlorohydrin-dimethylamine (PFC-ECH-DAM):** The effluent from textile dyeing processing causes many environmental problems, such as aesthetical problem, upsetting biological processes by impeding the light penetration and being toxic to aquatic organisms[101,102]. Poly-epichlorohydrin-dimethylamine (ECH-DAM), is a positively charges copolymer with the advantage of less affected by the external environmental[103,104] and less corrosive compared to $FeCl_3$[105], was selected to synthesize a composite coagulant with polyferric chloride for treating the reactive red dyes and exhibited better treatment performance. The ECH-DAM was previously used as an anti-swelling agent in petroleum industry[106]. However, ECH-DAM could be combined with some inorganic compounds to act as one coagulant in wastewater treatment, especially in the dye wastewater[90].

Some scholars[107] combined ECH-DAM with polyferric chloride (PFC) to synthesize a composite coagulant. The PFC was prepared by using $FeCl_3 \cdot 6H_2O$, $Na_2CO_3$ and $Na_2HPO_4 \cdot 12H_2O$. The ECH-DAM copolymer[108] was prepared by polycondensation reaction of peichlorohydrin and dimethylamine with diverse cross-linkers, ethylenediamine (EDM), diethylenetriamine (DTM) and triethylenetetramine (TTM)[105] through the micellar free radical copolymerization technique[109]. Poly-ECH-DAM was synthesized by following steps. Firstly, predetermined amount of epichlorohydrin (AR) was cooled to 10 ºC from ambient temperature. Then, the dimethylamine was added into the reactor under constant stirring. A viscous polymer solution was produced after the mixture was kept at a certain temperature with stirring for few hours. The hybrid coagulant was prepared after introducing a certain amount of P(ECH-DAM) into PFC solution with the cross-linker under magnetic stirring for few hours. The efficiency of composite coagulant was significantly improved by the synergic effect and was more suitable for removing reactive red dye when compared with PFC or ECH-DAM used individually.

**PAFS-CPAM prepared by poly-aluminum ferric sulfate and cationic polyacrylamide:** The cationic polyacrylamide (CPAM) have been proved could improve the aggregating capacity of coagulant due to the enhancement of adsorption-bridging mechanism[110] besides the DMDAAC.

Zheng *et al.*[111] put forward a relative novel route to prepare a composite coagulant using a cationic polyacrylamide (CPAM) and polymeric aluminum ferric sulfate(PAFS). The synthesis method of PAFS was discussed by Zheng *et al.*[66,67] while CPAM was a commercial product. A measured amount of CPAM was mixed with the stock solution of PAFS under vigorous stirring at a certain high temperature. The FTIR analysis indicated the coagulant was only a physical mixture with a complex formation of two raw materials, which could be regarded as one structurally-hybridized materials, whereas the synergy effect increase the (Fe-Al)b species. Coagulation experiments indicate a better turbidity and COD removal efficiency by the composite coagulants with low sludge volume which led to cost savings for sludge handling.

**Synthesis or application of some relative novel inorganic coagulants:** There are many other materials that could be used as coagulants apart from the aluminum salts, ferric salts, or the modification of those traditional inorganic salts. The applications of polytitanium salt, zirconium salt and the ferrate ($Fe^{6+}$) in wastewater treatment have attracted more attention in an attempt to obtain better treatment performance.

**Polytitanium tetrachloride (PTC):** The Ti-based coagulants could achieve greater efficiency of NOM removal compared to the traditional coagulants[112,113], however, there have been few studies utilizing poly-titanium salts as coagulants in water treatment due to the charge neutralization that occurs during its hydrolysis process.

Some researchers[114] have proposed a synthesis route for polytitanium tetrachloride (PTC) coagulant. Firstly, distilled water is added to a certain amount of $TiCl_4$ to achieve the desired concentration of titanium tetrachloride ($TiCl_4$) in the mixture. Secondly, a pre-determined amount of NaOH is added to the reaction mixture through titration under intensive agitation. The electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) technique was utilized to determine the Ti hydrolysis species of the coagulant. The PTC coagulant showed higher removal of turbidity and organic matters in comparison to $TiCl_4$. In addition, the PTC flocculated sludge could be recycle to produce the $TiO_2$ photo-catalyst.

**Zirconium coagulant:** The zirconium salts, which have been investigated for the treatment of NOM[115] and arsenic[116], could be proposed as one potential route to solve the problem of reduced floc strength and inadequate NOM removal.

Some researchers[127] utilized a zirconium oxy-chloride based coagulant for DOC and NOM removal and compared its performance with iron and aluminum salts. The zirconium coagulant contained $ZrO_2$ which consists of cationic hydroxylated polynuclear zirconium species. Coagulation experiments indicated an improvement in NOM removal compared to the ferric and aluminum salts. However, during jar testing, particle re-destabilization was observed which could be attributed to enhancement due to high positive charge and narrow pH range compared to alternative coagulants. Therefore, careful control of the coagulation conditions before charge reversal and re-destabilization is necessary.

**Ferrate (VI) salts:** There are some studies which have shown the addition of iron to water achieves improvement on the treated wastewater and sludge quality[118]. Truthfully, ferrate(VI) is a strong oxidants used in wastewater treatment to remove both organic and inorganic compounds[119].

Some research[120] focused on the reproducibility and treating performance of ferrate(VI) salt for domestic wastewater treatment. Ferrate(VI) was generated from the electrochemical reactor with steels as anode and cathode and was produced using sodium hydroxide electrolyte after a certain synthesis duration. The Fe(VI) salts, ferric chloride and ferric sulphate, were chosen for comparison between different species of diverse ferric salts. The experimental results indicated ferrate(VI) salt, at very low doses, could achieve similar performance to ferric salts at high doses. In addition, the high phosphorus removal efficiency by the ferrate(VI) salt was attributed to the reduced form of ferrate(VI).

In addition, ferrate(VI) salt, as an aid agent of photocatalytic oxidation, can be used together with $TiO_2$ to enhance treatment performance. It's well known that $TiO_2$ is an efficient and environmentally benign photocatalyst and has been widely used for many areas[121-125]. Some researches[126] indicated enhancement in the oxidation process for some specific compounds (ammonia, cyanate, formic acid and bisphenol-A *etc.*) in wastewater by utilizing $TiO_2$ and the protonated Fe(VI) species, $HFeO_4^-$/ $FeO_4^{2-}$. The photocatalytic oxidation was significant in the presence of ferrate which has the inhibition recombination on the surface of $TiO_2$ due to the synergistic effect.

## Conclusion

In recent years, the inorganic coagulants had been utilized widely in wastewater treatment. In addition, the preparation methods of those inorganic coagulants were inclined to be sustainable, energy-saving and cost-saving direction under the premise of guaranteed treatment effect. Furthermore, diverse valuable materials such as organic polymer monomers or other inorganic metal salts could be introduced into inorganic coagulant. The performance of the modified novel coagulants greatly assisted in the removal of different pollutants. However, it's necessary to study the coagulation mechanism of those relative novel inorganic coagulants from the theory aspect in detail. Therefore, more attention should be directed to studies on the toxicity problems for various organic-inorganic coagulants.

## ACKNOWLEDGEMENTS

The authors thank the financial support provided by the National Key Technologies R & D Program of China (2012-BAJ25B09), the National Natural Science Foundation of China (No. NSFC, 21177164) and the National 111 Project (Project No. B13041).

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