



Advantages of titanium xerogel over titanium tetrachloride and polytitanium tetrachloride in coagulation: A mechanism analysis

Xiaomeng Wang, Yonghai Gan, Shang Guo, Xueyan Ma, Mengshan Xu, Shujuan Zhang*

State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, 210023, PR China

ARTICLE INFO

Article history:

Received 30 October 2017

Received in revised form

26 December 2017

Accepted 30 December 2017

Available online 3 January 2018

Keywords:

Titanium-based coagulants

Mechanism

Turbidity

Organic matter

Acetylacetone

ABSTRACT

Titanium xerogel coagulant (TXC) worked better than titanium tetrachloride (TC) and polytitanium chloride (PTC) in a wider pH/dose range for the removal of turbidity. However, the underlying mechanisms were not comprehensively understood. In this work, the better coagulation performance of TXC than TC and PTC was systematically elucidated from the following aspects: the physicochemical properties of the three coagulants, the removal of turbidity and organic matter, and the complexation reactions in coagulation. The results demonstrate that the merits of TXC were attributable to the following characteristics: (1) the higher surface charge density/total surface site concentration/isoelectric point of TXC hydrolysates, (2) the formation of TXC hydrolysates with a net-work structure, and (3) the strong binding affinity of TXC hydrolysates to organic matter caused by the bonded acetylacetone in the TXC framework. In short, the hydrolysis behavior of TXC significantly differed from both its precursor, TC, and the prehydrolyzed PTC. The difference in the hydrolysis of TXC was derived from the gelation process, which led to the polymerization of Ti in a way different from prehydrolyzation. The elucidation of the hydrolysis mechanisms is useful for the better application of Ti-based coagulants and may shed light on the preparation of other metal salts.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

In water and wastewater treatment, coagulation is an important unit process (Gregor et al., 1997). Traditional coagulants, such as iron and aluminum salts, are widely employed for removal of suspended particles (Xiao et al., 2008), natural organic matter (Lee and Westerhoff, 2006), and inorganic ions, such as fluorine (Hu et al., 2005) and arsenite (Lee et al., 2003). Besides iron and aluminum salts, titanium (Ti) salts have also been investigated as coagulants for the several merits: (1) Ti has a larger charge than those of Al and Fe (Lakshmanan et al., 2008; Zhao et al., 2011), (2) the floc size formed by Ti salts was usually much larger than those formed by Al or Fe salts (Zhao et al., 2011; Chekli et al., 2017a), which is beneficial for a complete sedimentation in a short time, and (3) the final sludge could be calcined to valuable by-products, namely TiO₂ photocatalysts (Kagaya et al., 1999; Shon et al., 2007), which offers a novel solution to sludge disposal.

The effectiveness of Ti salts as coagulants has been proven in

removal of turbidity (Wu et al., 2011), organic matter (Zhao et al., 2013a), algae (Chekli et al., 2017a), nutrients (Wang et al., 2016), chroma (Wang et al., 2016), and heavy metals (Sun et al., 2013; Wang et al., 2016). Prehydrolysis is a useful strategy to improve the coagulation performance of metal salts (Huang et al., 2015; Zhao et al., 2013b). In a previous work (Wang et al., 2016), we demonstrated that gelation was a more effective strategy than prehydrolysis in modification of Ti-based coagulants. A series of titanium xerogel coagulants (TXC) was prepared by a sol-gel method with titanium tetrachloride (TC) as the precursor and acetylacetone (AcAc) as a modifying agent (Wang et al., 2016). Compared to TC and polytitanium tetrachloride (PTC), the resultant TXC possessed better removal capacity for nutrients/chromium and wider applicable coagulant dose/pH range in turbidity removal (Wang et al., 2016).

It is generally accepted that the solubility and the electrical property of metal hydrolysates determine the coagulation mechanism (Duan and Gregory, 2003; Wang et al., 2002). The more controllable hydrolysis of TXC than those of TC and PTC was proposed as one of the main reasons for its better performance (Wang et al., 2016). However, the detailed hydrolysis reactions of Ti salts were still unclear and the colloid chemistry in the related processes

* Corresponding author.

E-mail address: sjzhang@nju.edu.cn (S. Zhang).

needs further investigation. For example, in the coagulation tests for humic acid (HA)-kaolin simulated water, TXC presented a weaker ability for HA removal than TC and PTC. It is well known that solution pH has an apparent influence on the solubility of HA, which would affect the removal of HA in a coagulation process (Cheng and Chi, 2002). The effluent pH after TC/PTC coagulation decreased sharply, leading to a lowered solubility of HA and therefore a better removal of HA. On the contrary, the effluent pH from TXC coagulation was only mildly decreased. Therefore, the weaker ability of TXC for the removal of HA might be attributable to the effect of solution pH. If so, what would happen if the pH effect was isolated from the coagulation process? This needs to be clarified.

To address the above issues, the physicochemical properties, including surface charge, floc structure, and growth kinetics of the hydrolysates from the three coagulants, TC, PTC, and TXC, were systematically investigated. With these information, the coagulation performances of the three coagulants for the removal of turbidity and organic matter were fully interpreted.

2. Materials and methods

2.1. Materials

2.1.1. Reagents

All chemicals were of analytical grade and used as received without further purification. TC, NaOH, ethanol, AcAc, kaolin powder, HCl, NaClO₄, NaHCO₃, 1-hexadecylpyridinium chloride monohydrate (HPC), toluidine blue (TBO) were purchased from the Sinopharm Chemical Reagent Co., Ltd., China. Humic acid sodium salt (HA) was purchased from Sigma-Aldrich Co., USA. Silica microspheres (Si) with 3 μm average diameter (Fig. S1 in Supplementary Data-SD) (Wuhan Shuaier Company, China) were used as model particles. The chemical compositions of kaolin and Si microsphere are Al₂Si₂O₅(OH)₄ and SiO₂, respectively. Potassium salt of poly-2-acrylamide-2-methylpropane sulfonic acid (PAMPSK), as a standard polyanionic electrolyte in colloidal titration experiment, was obtained from Shanghai Hengli Company, China.

2.1.2. Coagulants

TXC and PTC were prepared as previously reported (Wang et al., 2016). In the preparation of TXC, the molar ratio of AcAc/Ti and H₂O/Ti was 1:4 and 4:1, respectively. After ageing at ambient conditions, the resultant xerogel was vacuum dried at 40 °C until a constant weight was obtained. PTC with a Ti/OH molar ratio of 1:1 was prepared with a slow alkaline titration method (Zhao et al., 2013b). A portion of 0.58 mL concentrated TC solution was dropwise added to 200 mL cold distilled water in an ice-water bath under a continuous stirring. Then, 25 mL NaOH solution (0.2 M) was dropwise added under an intensive agitation to yield a PTC solution (1 g Ti/L) with a basicity of 1.0. Stock solutions of TC and PTC of 1 g Ti/L were prepared freshly prior to use. Depending on the specific requirements of the analysis, hydrolysate products of the coagulants were prepared in advance and freeze-dried for nitrogen adsorption, Raman, X-ray diffractometer (XRD) analyses and in situ for zeta potential and atomic force microscope (AFM) analyses.

2.1.3. Simulated waters

Compared with kaolin powder, Si suspension was much more stable and chemical-inert (Pauling, 1930; Wu et al., 2007). Therefore, Si microspheres instead of kaolin powder were employed here to generate the needed turbidity. Three simulated waters of a high turbidity (500 ± 5 NTU), a medium turbidity (50 ± 1 NTU), and a low turbidity (5 ± 0.5 NTU) were prepared by dispersing certain

amounts of Si microspheres into 1 L tap water. The pH of the silica microsphere suspensions was adjusted with a 0.1 M HCl or a 0.1 M NaOH solution to 5.8 ± 0.1 or 9.8 ± 0.1 before jar test.

An HA stock solution was prepared by adding 1 g HA into 1 L deionized water and was then filtered with a 0.45 μm cellulose membrane in a vacuum suction device to remove any insoluble particles. The total dissolved organic carbon (DOC) concentration of the HA stock solution was 314.2 mg/L. Prior to coagulation experiments, the HA stock solution was diluted with deionized water to the designated concentrations. NaClO₄ was added to adjust the ionic strength to 10 mM. The pH of the HA solution was adjusted with a 0.1 M HCl or a 0.1 M NaOH solution to the desired value.

An HA-kaolin solution with an initial turbidity of 50 ± 1 NTU was prepared by adding 10 mg HA and 0.2 g kaolin powder into 1 L tap water. The pH of the HA-kaolin solution was adjusted with a HCl or NaOH solution to the range of 5–10.

2.2. Experimental section

2.2.1. Coagulation experiments

Coagulation tests were conducted with a program-controlled jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China) following the below procedure: 1 min rapid mixing (200 rpm), 15 min slow mixing (40 rpm), and 20 min sedimentation. After these procedures, the supernatants were collected for analysis from approximately 2 cm below the water surface using a syringe.

2.2.2. Adsorption experiments

Adsorption experiments were conducted to evaluate the uptakes of HA on the coagulated flocs. The ionic strength of the distilled water (1 L) was adjusted to 10 mM with NaClO₄. After the coagulants (12 mg Ti/L) was added, the reaction was adjusted to pH 6.0–7.0 with NaOH and stirred the same way as in the coagulation. After that the sample was distributed into several 250 mL flasks and adjusted to each designated pH, a certain amount of HA solution was added into each bottle. After shaken for 24 h at 150 rpm, the mixture was filtered through a 0.45 μm filter paper and the concentration of HA was measured.

2.3. Analytical approaches

2.3.1. Characterization of the hydrolysate products

The surface chemistry of the hydrolysate products was investigated with three methods: potentiometric acid-base titration, zeta potential determination, and colloid titration. Potentiometric acid-base titration of the 100 mg Ti/L coagulant solution was conducted with an automatic titration system (Text S1). The acid-base titration data were employed for the analysis of surface site concentration (Hs) with the Gran plot method (Gran, 1952). The newly prepared flocs after the rapid mixing in the jar test were measured with a Nano-Zetasizer (Malvern Co., UK) to estimate the isoelectric point of the hydrolysate products of the three coagulants. A back colloid titration method (Text S1) was used to quantitatively determine the surface charge densities of the hydrolysate products.

A continuous laser diffraction instrument (Mastersizer 3000, Malvern, UK) was employed in a modified jar test procedure to record the particle size of the flocs. A portion of 5 mg Ti/L coagulant was pipetted at the beginning of the rapid mixing to the beakers containing 800 mL HA-kaolin or Si suspensions with an initial turbidity of 50 ± 1 NTU. Raman, XRD, AFM, and nitrogen adsorption-desorption analyses were conducted to characterize the morphology and structure of the freeze-dried flocs and hydrolysate products (Text S1).

Download English Version:

<https://daneshyari.com/en/article/8874437>

Download Persian Version:

<https://daneshyari.com/article/8874437>

[Daneshyari.com](https://daneshyari.com)