Effects of raw diatomite on coagulation performance and residual aluminum during the micropolluted raw water treatment with polyaluminum chloride
W. C. Hu, C. D. Wu and L. G. Liu

ABSTRACT
The effects of raw diatomite on coagulation performance (CP) and the contents of residual aluminum (RAI) during the Pearl River water treatment with polyaluminum chloride (PAC) were investigated. Results demonstrated that the addition of raw diatomite could significantly improve the CP. The removal efficiencies (REs) of turbidity, dissolved organic carbon and UV254 could achieve 97.63%, 44.31% and 52.31%, respectively, at PAC dose of 20 mg/L and diatomite dose of 40 mg/L. Furthermore, adding appropriate dose of diatomite (less than 40 mg/L) could greatly reduce the RAI contents. The residual total aluminum and residual total dissolved aluminum both reached the lowest concentrations (0.185 mg/L and 0.06 mg/L, respectively) when the PAC dose was 15 mg/L and diatomite dose was 40 mg/L.

Key words | coagulation performance, PAC, raw diatomite, residual aluminum

INTRODUCTION
Coagulation is a common process in water and wastewater treatment, which destabilizes the suspended and dissolved materials, followed by aggregation into large flocs that are easily separated from the water by subsequent sedimentation/flotation and filtration processes (Chen et al. 2006). There is no doubt that coagulant plays a very important role in the process of coagulation. Polyaluminum chloride (PAC) has been widely used at water treatment plants to remove turbidity and dissolved substances from water since the 1980s throughout the world (Yu et al. 2007; Kimura et al. 2013). The advantages of PAC are obvious due to their stable preformed polymeric species, less pH dependence, higher efficiency and relatively lower costs compared with the traditional coagulants (Yu et al. 2007). In addition, PAC is more effective at lower dosages than other Al preparations for the coagulation of high turbidity (more than 100 NTU) waters, particularly at low temperature or acidic pH, and also PAC is an effective filter aid for low turbidity waters, providing for destabilization and subsequent filtration of particles at acidic and neutral pH values (O’Melia et al. 1989). It has been proven to be an effective coagulant for the removal of certain contaminants (such as organic matter, algae, heavy metal and so on), turbidity and color (Shen & Dempsey 1998).

However, concerns have been raised that the use of PAC may increase Al concentrations in treated waters (Ohno et al. 2009), because it is made by partial hydrolysis of acid Al chloride solution using a specific reactor (Gao et al. 2005). To be precise, it is produced by adding base to Al chloride until an empirical formula of Al(OH)nCl3-n (with n from 1.0 to 2.5) is achieved. Although its use is effective for removing turbidity and dissolved organic materials, PAC may result in elevated concentrations of Al in treated waters. High Al concentrations in treated water are associated with several problems, including increased turbidity due to the formation of Al precipitates and have potential risks to public health (Flaten 2001; World Health Organization 2004; Gupta et al. 2005). The
previous studies have pointed out serious drawbacks of PAC. For example, Alzheimer’s disease and similar health-related problems have been associated with residual aluminum (RAI) in treated waters (Flaten 2001), the neurotoxic effects of Al are beyond any doubt both in experimental animals and in humans (Gupta et al. 2005). Therefore, the concentration of RAI should be controlled in water treatment plants, especially in plants which use Al coagulants (Kimura et al. 2013). Most countries have established guidelines/standards for the control of Al in drinking water (Schintu et al. 2000). In China, the drinking water quality guideline for Al is 0.2 mg/L, but the practices have proved that the concentration of RAI in the treated water is often more than the guideline value with PAC only.

Most studies on the RAI in a coagulation process rarely involve how to reduce the content of RAI by the use of a coagulant aid. Diatomite is highly porous with its structure containing up to 80–90% voids and density 1.9–2.5 g/cm³, and is a siliceous rock available in large deposits around the world (Khraisheh et al. 2004). It has a unique combination of physical and chemical properties, large surface area, strong adsorption capacity, and is chemically stable, which make it applicable as adsorbent and coagulant aid for pollutants encountered in water (Erdem et al. 2005). Additionally, diatomite used for the sorption of heavy metals has been discussed in the literature (Bello et al. 2014). However, the functions of diatomite, such as a coagulant aid and reducing the RAI in a coagulation process, are rarely studied and reported.

The overall goal of this paper was to investigate the effects of raw diatomite on coagulation performance (CP) and RAI in the treatment of the Pearl River water with PAC.

MATERIALS AND METHODS

Test water

The raw water samples were collected from the Guangzhou section of the Pearl River, which is one of China’s seven major rivers and the most important river in south China. Test water quality parameters: T, 22 ± 3 °C, pH, 7.56–7.80, turbidity, 11.2–34.2 NTU, dissolved organic carbon (DOC), 2.83–4.10 mg/L, UV254, 0.045–0.055 cm⁻¹, Total Al, 0.127–0.211 mg/L, Total dissolved Al, 0.124–0.188 mg/L. None of them was too extraordinary compared with the water examined in other studies (Yan et al. 2008).

Reagents

The raw diatomite was obtained from the Tianjin Damao Chemical Reagent Factory, Tianjin, China. PAC product was provided by a local factory containing 29 weight percent as Al₂O₃; stock alum solutions were prepared at a concentration of 1,200 mg/L as Al₂O₃.

Analytical methods

Samples were analyzed for turbidity, DOC, UV254, residual total aluminum (RTAl) (an unfiltered sample was acidified with nitric acid and was then analyzed) and residual total dissolved aluminum (RTDAl) (particulate and dissolved Al forms were operationally isolated by filtering the water samples with a 0.45 μm membrane filter, acidified and analyzed) (Yang et al. 2010b). Turbidity was measured using a 2100 Q turbidimeter (HACH Company, USA). DOC was measured by a Liqui TOC analyzer (Elementar, Germany). The samples were filtered through a 0.45 μm filter to remove undissolved impurities. UV254 absorbance was measured using a UV-5800 spectrophotometer (METTASH, China) at a wavelength of 254 nm with a 1 cm quartz cell. The samples were first filtered through a pre-washed 0.45 μm filter to remove turbidity, which can interfere with this measurement, and a blank with distilled ultra-filtered water was run prior to sample analysis (Wu et al. 2011).

The concentrations of the RTAl and RTDAl were measured by spectrophotometer. They were analyzed by chrome azurol S colorimetric analysis. The Al fractionation method was carried out under a modification of previously developed procedures (Van Benschoten & Edzwald 1990). Nucleopore polycarbonate 0.45 μm filters were used for the separation of the RTAl and RTDAl, which were measured with a UV-5800 spectrophotometer at a wavelength of 620 nm (METTASH, China). The detection limit was 0.008 mg/L.

The X-ray fluorescence (XRF) analysis was performed on a PANalytical Axios (PW4400) XRF spectrometer. The scanning electron microscopy (SEM) was performed using...
a Carl Zeiss EVO LSIO scanning electron microscope (LEO, Germany). The X-ray diffraction (XRD) analysis to investigate crystalline structures was conducted by use of a D8ADVANCE X-ray diffraction system (Bruker, Germany) equipped with Cu Kα radiation (λ = 0.15418 nm).

**Jar test**

Jar tests were performed in the Six-paddle stirrer (ZR4-6, China) at normal temperature (~25 °C) unless otherwise noted, taking the same batch of test water into six 1-L glass beakers, and adding a diatomite dose of 0 mg/L, 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, and 50 mg/L, respectively, to each glass. For the mixing beaker experiment diatomite was put into a beaker, then PAC added at 10 mg/L, 15 mg/L, and 20 mg/L, respectively, to each glass. Each sample was rapidly mixed for 2 min at 200 rpm (G = 99.7 s⁻¹), and then mixed for 10 min at 50 rpm. After a quiet settling of 30 min, each sample was measured for turbidity, DOC, UV254, RTAl, and RTDAI of the supernatant. Except for changing the doses of PAC and/or diatomite, the other conditions remained the same.

**RESULTS AND DISCUSSION**

**Characterization of raw diatomite**

Chemical composition of raw diatomite was obtained by the XRF spectrometer (Table 1). The raw diatomite was mainly composed of 87.894% SiO₂, 2.581% Al₂O₃, 1.625% Fe₂O₃, 0.329% MgO, 0.035% MnO and 0.235% CaO. This suggests that the chemical composition of diatomite used in this experiment was similar to sources found in other countries (Danil de Namor et al. 2012; Knoerr et al. 2013). The SEM images showed that the surface morphology of the raw diatomite was a frustules honeycomb structure, and many pores can be seen on its surface (Figure 1(a)). Two diffraction bands were centered at 21.9° and 36.1° (2θ degree) of the XRD patterns, which is the characteristic peak for amorphous SiO₂ (JCPDS 29-0085) (Figure 1(b)).

**Effects of raw diatomite on CP**

The effects of raw diatomite on CP were investigated. PAC dose was set to 10 mg/L, 15 mg/L and 20 mg/L, respectively, and the dose of diatomite was from 0 to 50 mg/L. The removal efficiency (RE) of turbidity increased with increasing diatomite dose under the same dose of PAC (Figure 2(a)). When the doses of PAC increased from 10 to 20 mg/L and the diatomite doses from 0 to 40 mg/L, the REs increased from 90.8%, 93.52% and 96.7% to 95.73%, 97.28% and 97.63%, respectively. All the three situations have improved the RE of turbidity compared with the situations without diatomite. In addition, it is important to note that the RE of turbidity slightly decreased at excess of diatomite dose (such as 50 mg/L). The addition of diatomite greatly improved the REs of DOC and UV₂₅₄, with enhancement slightly higher (13.15–16.03% and 14.86–20.09%, respectively) than that for the coagulation by PAC alone (Figure 2(b) and 2(c)). At PAC 10, 15 and 20 mg/L, and at the diatomite dose of 0–50 mg/L, the RE of DOC increased from 23.41%, 26.65% and 31.44% to 38.19%, 42.68% and 44.59%, respectively. At the same time, the RE of UV₂₅₄ increased from 29.09%, 32.74% and 38.18% to 45.28%, 52.83% and 53.04%, respectively. Figure 2(b) and 2(c) also show that the REs of DOC and UV₂₅₄ increased sharply when the diatomite dose was less than 40 mg/L, but they increased slowly with continuously increasing diatomite dose.

The mechanisms to explain the coagulation of particle and organic substances include charge neutralization, precipitation, bridge-aggregation, adsorption, and sweep-flocculation (Cheng et al. 2008). The four mechanisms could be used to explain coagulation/flocculation phenomena in this study, but adsorption and precipitation may be the main mechanisms. The use of diatomite improves the physical and chemical properties of the flocs,

<table>
<thead>
<tr>
<th>Compound</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>K₂O</th>
<th>CaO</th>
<th>MnO</th>
<th>TiO₂</th>
<th>Na₂O</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (%)</td>
<td>87.894</td>
<td>2.581</td>
<td>1.625</td>
<td>0.329</td>
<td>0.273</td>
<td>0.235</td>
<td>0.035</td>
<td>0.097</td>
<td>2.468</td>
<td>4.463</td>
</tr>
</tbody>
</table>
such as antiparticle bridging and settling velocity, thus incorporating the cells into flocs more efficiently, producing settleable flocs of greater density, size and strength (Wu et al. 2014); therefore the RE of turbidity was improved. Furthermore, as diatomite enhances the coagulation and adsorption of organic impurities and extracellular organic matters, a higher proportion of DOC and UV$_{254}$ reduction can be obtained. Adsorption, precipitation and sweep-flocculation are the main mechanisms to explain the removals of DOC and UV$_{254}$. The unique characteristics of high porosity, great specific surface area and high chemical stability make diatomite applicable for adsorption of organic pollutants. And the crystal structure of diatomite contains some ion-exchangeable cations which can be exchanged with organic and inorganic cations (Erdem et al. 2005). It has been reported that diatomite addition into an anaerobic/oxic membrane bioreactor (A/O MBR) is proven to be very effective in improving dissolved organic matter removal (Yang et al. 2010a).

**Effects of raw diatomite on RAI**

In order to investigate the effects of raw diatomite on the RTAI and RTDAI, PAC dose was adjusted to 10 mg/L, 15 mg/L, and 20 mg/L, respectively. The concentrations of the two Al forms represented a similar tendency, expressed as going down at the beginning and then going up later.
When the doses of PAC were changed from 10 to 20 mg/L and the diatomite doses increased from 0 to 40 mg/L, the RTAl decreased from 0.22 mg/L, 0.206 mg/L, and 0.284 mg/L to 0.193 mg/L, 0.185 mg/L, and 0.222 mg/L, respectively (Figure 3(a)), and the RTDAl decreased from 0.15 mg/L, 0.144 mg/L, and 0.138 mg/L to 0.105 mg/L, 0.06 mg/L, and 0.098 mg/L, respectively (Figure 3(b)). 0.193 mg/L and 0.185 mg/L of the RTAl are both below the Chinese drinking water quality guideline for Al (0.2 mg/L). The two kinds of Al began to increase when the diatomite dose was in excess (such as 50 mg/L). It is worth noting that the RTAl and RTDAl were both the lowest at PAC 15 mg/L and diatomite 40 mg/L.

It has been evidenced that the surfaces of diatomite are negatively charged in the wide pH range of 2–12 (Sheng et al. 2009). When the initial pH range was between 6.0 and 8.0, there were some high polymeric positive hydrolyzates and Al(OH)₃ formed in solution (Panyue et al. 2008). The charge neutralization was enhanced after adding diatomite, which was conducive to some positive forms of Al to take off the stability. This may be because of the electrostatic interactions between the hydroxy-Al cations in solution and the negatively charged surface of the diatomite. What’s more, diatomite has a large surface area and strong adsorption capacity; it is likely to adsorb Al(OH)₃ precipitation. The active silica surface with large specific surface area is of great importance in adsorption and ion exchange applications (Bello et al. 2014). There was a small amount of Al₂O₃ in the diatomite (Table 1), and it may be the main reason for the rise of RAl concentration when the diatomite dose was in excess.

**CONCLUSIONS**

Adding moderate amounts of raw diatomite into water could not only significantly enhance the CP but also reduce the contents of RAl in the process of PAC coagulation. The RES of turbidity, DOC, and UV₂₅₄ all improved. The concentrations of RTAl and RTDAl both reduced after adding some diatomite (less than 40 mg/L). The CP and reduction of RAl both increased with the increase of diatomite dose (less than 40 mg/L). The optimum PAC and raw diatomite dosage was 15 mg/L and 40 mg/L, respectively.

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