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Removal of direct dyes by coagulation: The performance of preformed polymeric aluminum species

Baoyou Shi [a,*], Guohong Li [b], Dongsheng Wang [a], Chenghong Feng [a], Hongxiao Tang [a]

[a] *State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China*

[b] *School of Water Resources and Environment, China University of Geosciences, Beijing 100083, China*

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Abstract

Removal of three direct dyes (Direct Black 19, Direct Red 28, and Direct Blue 86) by coagulation with three different Al based coagulants was investigated. The main purpose of this paper is to examine the coagulation features of polymeric aluminum coagulants in treatment of dye-polluted waters and the emphasis was placed on the roles of preformed Al species, particularly Al_{13}. The performance of Al_{13} in coagulation of dyes was observed through jar tests by comparing traditional Al salt, polyaluminum chloride (PACl), and purified Al_{13}. The results showed that under most cases Al_{13} had significantly higher efficiency in removal of direct dyes than traditional Al salt and commercial PACl with the exception of Direct Red 28 removal under high pH range. The coagulation of direct dyes could be greatly affected by pH. Reducing pH was favorable for preformed Al species in a broad pH range. For traditional Al coagulant, efficient dye removal only occurred in a relatively narrow pH range of near 6.0. The outstanding coagulation behavior of Al_{13} could be ascribed to its high charge neutralization ability, relative stability and potential self-assembly tendency.

Keywords: Direct dye; Coagulation; Al speciation; Polyaluminum chloride; Al_{13}

1. Introduction

The release of dye compounds from industries of textile dyeing, printing, as well as food and papermaking can cause severe water pollution problems. It has been estimated that more than 700,000 tonnes of dyestuff are produced annually, and about 10–15% of these dyes are left in effluents during dyeing processes [1,2]. The presence of dyes in water is aesthetically undesirable, even very low concentration of dyes is highly visible. On the other hand, dye polluted natural waters can result in serious disturbance to aquatic biosphere due to the reduction of sunlight penetration and depletion of dissolved oxygen. Additionally, the majority of synthetic dyes are highly water-soluble azo dyes, which are toxic to some aquatic organisms and may pose serious health threat to human beings. It has been found that some azo dyes are able to produce carcinogenic aromatic amines in the process of reductive degradation [3,4]. In the recent years, regulations on dye pollutants are becoming more and more stringent world widely. Thus, dyes in wastewater have to be removed completely before discharged into receiving waters.

However, since synthetic dye compounds usually have very complex structure and are intentionally designed to be recalcitrant with poor biodegradability, they are difficult to decolorize by conventional aerobic biological treatments, such as activated sludge process. The widely used methods for dyeing wastewater treatment involve many physical–chemical techniques, such as coagulation, adsorption, membrane filtration, and advanced oxidation, etc. [5–8]. Each treatment method has its advantages and disadvantages. Generally, advanced oxidation processes are effective for removal of most dyes, but a common problem with such operations is their relatively high cost in large-scale utilization [1,9]. In addition, chemical oxidation usually attacks only the chromophore groups of dyes instead of mineralizing organic dyes completely. Moreover, the possible occurrence of some more toxic intermediate products could be of concern. Adsorption techniques have much potential in the treatment of

* Corresponding author. Tel.: +86 10 62849138; fax: +86 10 62923541.
E-mail address: byshi@rcees.ac.cn (B. Shi).

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dye-containing waters if high performance and cheap adsorbents are available [10]. Membrane filtration has some special features unrivalled by other methods, but the high capital cost and clogging problems associated with this method may limit its application.

Coagulation/flocculation is one of the most popular unit operations in water and wastewater treatment trains. Dye removal by coagulation is not based on the partial decomposition of dye compounds, thus no potentially harmful and toxic intermediates are produced. Furthermore, this process can be used in large-scale operation with relatively high operability and cost effectiveness [2,11,12]. A limitation of this technique is that some high-soluble, low molecular and cationic dyes might not be effectively removed. The disposal of sludge produced by coagulation could be another restriction associated with this technique.

Although the application of coagulation in water and wastewater treatment has a long history, the mechanisms involved in this process are still not fully understood. Coagulation is a very complicated process involving a series of physical–chemical interactions. The type of coagulant applied can play important roles in the removal of target pollutants. Aluminum and ferric-based salts, such as alum, aluminum chloride, ferric chloride, ferric sulfate, are commonly used traditional coagulants. After dosing, aluminum and ferric ions will experience continuous self-hydrolysis and evolve into hydroxide solids finally. The *in situ* formed hydrolysis products and hydroxide solids can neutralize, and/or adsorb particulate and dissolved matters to achieve removal of pollutants. The hydrolyzing process of aluminum and ferric salts are subject to water quality conditions. Alkalinity, pH, temperature and co-existing ions can significantly affect the treatment effectiveness of such traditional coagulants. During the last decades, inorganic polymer flocculants (IPFs) are receiving more and more attention as a new generation of flocculants. Polyaluminum chloride (PACl) is one of the most important IPFs and being more and more widely used in the world. PACl contains polymeric Al species formed by partially neutralization. The preformed Al species in PACl are relatively stable after dosing, and thus their effectiveness can be less influenced by the specific water quality conditions [13–17]. Al_{13} ($[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$) is considered as the most important species in PACl and has long been research interest.

The removal of reactive and disperse dyes by regular coagulation and electro-coagulation has been studied by some researchers [9,18–22]. The coagulants used in most of the studies are traditional aluminum, ferric-based salts or synthesized organic coagulants. Although PACl has ever been applied in color removal [9,22], the comparative study on coagulation of dye by PACl and traditional Al salts has not been extensively and systematically carried out to date. Furthermore, the potential roles of Al_{13} in dye removal need to be elucidated.

In this work, the coagulation behaviors of direct dye removal by different Al based coagulants were investigated in detail using jar tests. Emphasis was placed on the distinct roles of Al_{13} species in coagulation of direct dyes. Three commonly used direct dyes were chosen as model dye pollutants. $AlCl_3$ and commercially available PACl were applied as typical traditional coagulant and inorganic polymer flocculant. Since PACl contains multiple Al species including both Al_{13} and colloidal species, it is difficult to distinguish the roles of Al_{13} from other species. In this study, laboratory purified Al_{13} as a novel material was utilized to identify the exclusive functions of Al_{13}. The effect of pH on coagulation was examined to give better insights into the possible mechanisms involved in direct dye removal by different Al species.

2. Experimental

2.1. Dye compounds and test waters

Three direct dyes—Direct Black 19, Direct Red 28, and Direct Blue 86 (Tianjin Chemical Material Co., China) were used to simulate dye-polluted waters. These dyes were selected because they are currently among the widely used commercial dyes, especially in some Asian countries. In addition, the chemical structures of these dyes are different so that the treatability of dyes with different molecular characteristics could be compared. The molecular structures of these dye compounds are presented in Fig. 1. Stock dye solutions of $1000\,mg\,l^{-1}$ were prepared and then diluted using tap water to obtain final concentration of $50\,mg\,l^{-1}$. The pH of the simulated test water was controlled within 7.80 ± 0.05; the alkalinity was $155\,mg\,l^{-1}$ as $CaCO_3$. The wavelengths of maximum absorbance (λ_{max}) of these dyes with the background of tap water were determined according to scanning patterns performed on an UV–vis 8500 Spectrophotometer (Shanghai, China). The λ_{max} values of Direct Black 19, Direct Red 28 and Direct Blue 86 in the visible light range are shown in Table 1.

2.2. Coagulants and speciation characterization

Analytical grade of $AlCl_3{\cdot}6H_2O$ was used as traditional Al salt. Solid PACl product was obtained from Wanshui® Water Purifying Chemicals Co. (Beijing, China). Purified Al_{13} material was prepared in laboratory following the method described in [23]. The coagulants were dissolved in deionized water, and the total Al concentrations were measured using ICP-OES (1100-1155V, Jarrell-Ash, USA). The species distribution of these coagulants was characterized by both ferron assay [24] and ^{27}Al NMR (Avance 500, Bruker, USA). Ferron assay can differentiate Al species into three categories: Al_a, the monomeric species; Al_b, the polymeric species; Al_c, the colloidal species. ^{27}Al NMR technique can identify both monomeric and Al_{13} species. The ^{27}Al NMR patterns of the three coagulants are demonstrated in Fig. 2. The signal at 0 ppm corresponds to monomeric species

Table 1
The relationship between dye concentration (C, $mg\,l^{-1}$) and absorbance (A)

Dye name	λ_{max} (nm)	Equation	R^2
Direct Black 19	630	$C = 144.9A - 0.1$	0.999
Direct Red 28	490	$C = 117.6A - 0.4$	0.999
Direct Blue 86	610	$C = 147.0A + 0.0$	0.998