



# Effective treatment of cadmium–cyanide complex by a reagent with combined function of oxidation and coagulation



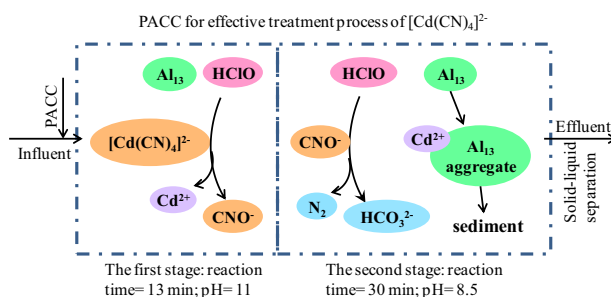
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## HIGHLIGHTS

- PACC is an efficient dual function reagent for  $[\text{Cd}(\text{CN})_4]^{2-}$  treatment.
- $\text{CN}^-$  oxidation and  $\text{Cd}^{2+}$  coagulation can be simultaneously achieved.
- Two stages need be carried out for complete removal of  $[\text{Cd}(\text{CN})_4]^{2-}$ .
- The optimum working conditions of PACC are presented.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The treatment of heavy metal–cyanide complex in industrial wastewater generally involves various processing units, such as chemical oxidation, hydrolysis precipitation and coagulation. A novel dual function reagent (PACC), which contains high content of active chlorine and  $\text{Al}_{13}$  polymer, shows a promising potential to shorten the process and heighten the treatment efficiency for cadmium–cyanide complex ( $[\text{Cd}(\text{CN})_4]^{2-}$ ). The results indicated that PACC is able to simultaneously achieve the complete oxidation of cyanide ( $\text{CN}^-$ ) by active chlorine and the subsequent coagulation of cadmium ion ( $\text{Cd}^{2+}$ ) by  $\text{Al}_{13}$  polymer. Two stages were carried out for complete  $\text{CN}^-$  oxidation and effective  $\text{Cd}^{2+}$  coagulation. The first stage involves the conversion of  $\text{CN}^-$  to cyanate ( $\text{CNO}^-$ ), and the second stage involves the conversion of  $\text{CNO}^-$  to nitrogen and the coagulation of the liberated  $\text{Cd}^{2+}$ . The optimum pH values for the first stage and the second stage are pH 11 and pH 8.5, respectively. The two stages for effective treatment of  $[\text{Cd}(\text{CN})_4]^{2-}$  at the optimal pH condition totally need about 43 min at active chlorine dosage 130% of the theoretical requirement for  $\text{CN}^-$  decomposition. Under the optimal conditions for  $[\text{Cd}(\text{CN})_4]^{2-}$  treatment, the stoichiometric weight ratio of  $\text{Cl}_2/\text{Al}$  in PACC is 2. This study presents a novel reagent and method to remove heavy metal–cyanide complexes from wastewater.

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## 1. Introduction

Cyanide and Cadmium (Cd) are very toxic to many life forms, and appear on international priority pollution lists. Cyanide ion ( $\text{CN}^-$ ) has a great tendency to act as a ligand, and associates with almost any metal ions to form complex [1]. Cadmium–cyanide

complex ( $[\text{Cd}(\text{CN})_4]^{2-}$ ) is widely found in electroplating and mining effluents. Since neutral and acidic conditions favor the conversion of cyanide to hydrogen cyanide that is exceedingly poisonous and readily evolves from water in gaseous phase [2], the treatment of cyanide must be conducted at alkaline condition. The bound  $\text{Cd}^{2+}$  by  $\text{CN}^-$  is quiet stable at alkaline condition [2]. Thus, it is difficult to be removed by conventional hydrolysis precipitation. The addition of oxidizing chemicals is the most popular method to destroy and remove cyanides [2], and then  $\text{Cd}^{2+}$  is liberated and

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available to be removed by hydrolysis precipitation and coagulation [3,4]. Fe(VI) has been reported to be effective for treating heavy metal–cyanide complex due to cyanide oxidation by Fe(VI) and subsequent removal of heavy metal by Fe(III) coagulation [5,6].

The alkaline chlorination method is the most widely applied for destruction of heavy metal cyanide complex and removal of cyanide from wastewater [2,7]. Coagulation using Al and Fe based salts followed by sedimentation and filtration is also employed to remove heavy metal from wastewater [4,8]. With high content of  $Al_{13}$  polymer ( $AlO_4Al_{12}(OH)_{24}(H_2O)_7^{12+}$ ) and active chlorine, a novel water treatment reagent (PACC) that can be synthesized by an electrochemical method [9,10] presents the dual function of coagulation and oxidation [9,11]. It is believed that  $Al_{13}$  polymer, with high positive charge and strong binding ability, is the most active species in Al based coagulants responsible for coagulation [12,13]. Active chlorine is the most widely used as a disinfectant and pre-oxidant in water treatment process. Therefore, PACC has the potential to simultaneously remove  $CN^-$  and  $Cd^{2+}$ , which may offer significant advantages in practice since the treatment process of  $[Cd(CN)_4]^{2-}$  can be shortened. Water treatment buildings are expected to be more compact and less management is required when using PACC, in comparison with the conventional two-unit system using alkaline chlorination and coagulation separately.

The present study was to evaluate the performance of PACC on  $[Cd(CN)_4]^{2-}$  removal through  $CN^-$  oxidation by active chlorine and subsequent removal of  $Cd^{2+}$  by  $Al_{13}$  species coagulation. The kinetics and stoichiometry of the complete oxidation of  $CN^-$  by active chlorine in PACC were investigated. The effect of pH, dosage and reaction time on the  $CN^-$  oxidation and  $Cd^{2+}$  coagulation were studied to illuminate the optimum work conditions for  $[Cd(CN)_4]^{2-}$  removal by PACC.

## 2. Materials and methods

### 2.1. Water samples

All reagents and chemicals used were of analytical grades. The stock solution of NaCN was prepared in NaOH solution, then it mixed with  $CdCl_2$  solution for 6 h to attain  $[Cd(CN)_4]^{2-}$  stock solution. Water sample was synthesized by spiking a certain volume of stock solution into deionized water containing  $5 \times 10^{-4}$  mol/L of  $NaHCO_3$  and  $NaNO_3$ .

### 2.2. The characteristics of PACC

PACC samples were prepared according to the method was described in our previous papers [9,10]. The properties of PACC used are summarized in Table 1. PACC1 was a general reagent for the most experiments, while PACC2 was specially prepared to evaluate the performance of  $[Cd(CN)_4]^{2-}$  removal. The  $Al_{13}$  species was the predominant Al speciation for PACC. Total Al concentrations ( $Al_T$ ) were determined using ICP-OES (PerkinElmer, Optima 2000, UK). Basicity values (B, OH/Al molar ratio) were determined by standard titrimetric methods (Standard method of the chemical industry of China). Active chlorine was determined by spectrophotometry using N,N-diethyl-1,4-phenylenediamine. The weight ratio of  $Cl_2/Al$  in PACC can be adjusted by regulating electrolyte

**Table 1**  
Characteristics of PACC.

Coagulant	B	$Al_T$ (g/L)	Active chlorine (g $Cl_2/L$ )	Weight ratio ( $Cl_2/Al$ )	$Al_m$	$Al_{13}$ (%)	$Al_u$
PACC1	2.5	1.6	6.0	3.8	8.50	79.02	12.48
PACC2	2.4	2.7	5.4	2.0	7.43	81.67	10.90

$Al_T$ , B value, and temperature during preparation. We used  $^{27}Al$  nuclear magnetic resonance (NMR) spectroscopy to characterize the Al species with  $^{27}Al$  NMR spectra obtained on a Varian UNITY INOVA (500 MHz) spectrometer. Each of  $Al_m$  (i.e. monomer + dimer),  $Al_{13}$ , and  $Al_u$  [i.e. larger polymer species and/or solid phase  $Al(OH)_3$ ] can be quantitatively analyzed according to the intensities of  $^{27}Al$  signals. Details of the quantitative analysis of the Al species can be found in literature [9,10].

### 2.3. Performance of $[Cd(CN)_4]^{2-}$ removal

The experiments of  $CN^-$  and  $Cd^{2+}$  removal by PACC or NaClO were conducted using jar test, which was performed using a six-paddle stirrer. The concentration of  $CN^-$  assessed in this study was 0.18–2.8 mmol/L, which simulated the practical water quality of industry effluent [2]. The concentration of  $Cd^{2+}$  in this study was determined according to the concentration of  $CN^-$ , since  $CN^-$  is the ligand of  $Cd^{2+}$ . The procedure of jar test consisted of a rapid mix of 250 rpm, slow mix of 40 rpm, and a 30 min settling period. After settling for 30 min, supernatants were sampled and filtered by 0.45  $\mu m$  pore size membrane filter. PACC or NaClO were added into water samples at the beginning of rapid mix period. The filtrates were tested for cyanate ( $CNO^-$ ) concentration using ion chromatograph (Dionex, ICS-2000, USA) and  $Cd^{2+}$  concentration using ICP-OES (PerkinElmer, Optima 2000, UK). Before PACC dosing a predetermined amount of 0.2 mol/L NaOH or 0.05 mol/L HCl solution was added into water samples to approximatively get an expected pH value. After dosing, water pH was accurately regulated to the expected value during rapid mix period by adding HCl or NaOH solution, after which water pH was constant during subsequent oxidation and coagulation process.

### 2.4. Stoichiometry

The stoichiometry of  $CN^-$  and  $CNO^-$  oxidation by PACC were examined by analysis of the formed and residual  $CNO^-$ , respectively. The reactions were conducted using a magnetic stirrer. The reaction time of  $CN^-$  and  $CNO^-$  oxidation by PACC were 30 min and 1 h, respectively. A certain amount of water was sampled at the end of reactions for  $CNO^-$  analysis. Before reaction, water pH values were regulated at either 11 or 8.5 by adding 0.2 mol/L of NaOH or 0.05 mol/L of HCl solution. Water pH was not adjusted during the reaction process. The PACC dosages gradually increased, while the  $CN^-$  and  $CNO^-$  concentration was fixed at 0.34 mmol/L and 0.48 mmol/L, respectively.

### 2.5. Stopped-flow kinetic

Apparent rate constants at various pH values for the reaction of  $CN^-$  and  $CNO^-$  oxidation by PACC were determined using an Applied Photophysics SX20 stopped-flow spectrophotometer. Kinetic studies were carried out under pseudo-first-order conditions at 25 °C. The concentrations of  $CN^-$  or  $CNO^-$  were kept in excess of active chlorine by at least 1 order of magnitude. Active chlorine absorbance at 292 nm was followed as a function of time to determine rate constants. In all experiments, PACC and  $[Cd(CN)_4]^{2-}$  solutions were buffered by 0.1 M phosphate to attain the desired pH.

## 3. Results and discussions

### 3.1. Stoichiometric study

A complete  $CN^-$  treatment by alkaline-chlorination-oxidation method should be carried out into two stages [14,15]. The first

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