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.
- CN^- oxidation and 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 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 (CN^-) by active chlorine and the subsequent coagulation of cadmium ion (Cd^{2+}) by Al_{13} polymer. Two stages were carried out for complete CN^- oxidation and effective Cd^{2+} coagulation. The first stage involves the conversion of CN^- to cyanate (CNO^-), and the second stage involves the conversion of CNO^- to nitrogen and the coagulation of the liberated 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 CN^- decomposition. Under the optimal conditions for $[\text{Cd}(\text{CN})_4]^{2-}$ treatment, the stoichiometric weight ratio of Cl_2/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 (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 Cd^{2+} by CN^- is quite 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 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 ($\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_7^{12+}$) 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 $[\text{Cd}(\text{CN})_4]^{2-}$ 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 $[\text{Cd}(\text{CN})_4]^{2-}$ 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 $[\text{Cd}(\text{CN})_4]^{2-}$ 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 $[\text{Cd}(\text{CN})_4]^{2-}$ stock solution. Water sample was synthesized by spiking a certain volume of stock solution into deionized water containing 5×10^{-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 $[\text{Cd}(\text{CN})_4]^{2-}$ 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

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_n [i.e. larger polymer species and/or solid phase $\text{Al}(\text{OH})_3$] 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 $[\text{Cd}(\text{CN})_4]^{2-}$ 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 μm 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 $[\text{Cd}(\text{CN})_4]^{2-}$ 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

Table 1
Characteristics of PACC.

Coagulant	B	Al_T (g/L)	Active chloride (g Cl_2/L)	Weight ratio (Cl_2/Al)	Al_m	Al_{13} (%)	Al_n
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

stage is the conversion of CN^- to CNO^- at strong alkaline environment and the second stage involves the transformation of CNO^- to nitrogen and carbonates at mild alkaline condition. The stoichiometries of CN^- and CNO^- oxidation by PACC were determined at pH 11 and pH 8.5, respectively. When the initial active chlorine in PACC increased from 0 to 0.34 mmol/L, CNO^- linearly increased with a slope of 0.96 (Fig. 1). When the initial active chlorine concentration was greater than 0.34 mmol/L, the formed CNO^- was constant at 0.34 mmol/L, which was equal to the initial concentration of CN^- . These results indicated that the conversion of CN^- to CNO^- by the oxidation of active chlorine followed a stoichiometric rate (SR) of 1.04 mol Cl_2 /mol CN^- , which was very close to the theoretical SR [1 mol Cl_2 /mol CN^-] according to the reaction of CN^- with hypochlorite (Eq. (1)).

An increase of PACC dosage resulted in a decrease of residual CNO^- that followed linear relationship (Fig. 2). The slope of the linear line presented stoichiometries for the reaction of CNO^- with active chlorine as -0.64 , which is approximately consistent to the theoretical SR [1.5 mol Cl_2 /mol CNO^-] according to the reaction of CNO^- with hypochlorite (Eq. (2)).

The final product of CN^- is nitrogen and bicarbonate. Considering the two stage the proposed net reaction of $[\text{Cd}(\text{CN})_4]^{2-}$ with active chlorine in PACC is as Eq. (3), which indicates that the SR is 2.5 mol Cl_2 /mol CN^- for complete oxidation of CN^- by PACC.

3.2. Determination of optimum working conditions

3.2.1. pH

The reaction rates of CN^- and CNO^- with active chlorine were determined using a stopped-flow spectrophotometer at different pH conditions. The rate expression for the reactions can be written as

$$\frac{d[\text{OCL}^-]}{dt} = -k_{\text{obs}}[\text{OCL}^-] \quad (4)$$

where k_{obs} (determined by model fitting of experimental kinetic data) represents apparent first-order rate constant at a particular pH value. Fig. 3, which shows the magnitude of k_{obs} at various pH values, illustrates that the reaction rate of PACC with CN^- and CNO^- decrease with the increase of pH value.

Fig. 1. Concentration plot for CNO^- generated after the reaction of 0.085 mmol/L $[\text{Cd}(\text{CN})_4]^{2-}$ with various concentrations of PACC at initial pH 11.

Fig. 2. Concentration plot for residual CNO^- after the reaction of 0.48 mmol/L CNO^- with various concentrations of PACC at initial pH 8.5.

Fig. 3. Observed pseudo-first-order rate constant for CN^- oxidation by PACC at different pH value (a, experiments conducted at $[\text{CN}^-] = 2.8$ mmol/L and $[\text{Cl}_2] = 0.28$ mmol/L). Observed pseudo-first-order rate constant for CNO^- oxidation by PACC at different pH value (b, experiments conducted at $[\text{CNO}^-] = 11.30$ mmol/L and $[\text{Cl}_2] = 1.13$ mmol/L).

In fact, the initial oxidation product of the reaction between CN^- and hypochlorite is volatile cyanogens chloride (Eq. (5)) [2,16].

At alkaline pH environment, the formed CNCl formed undergoes rapid hydrolysis according to the following reaction (Eq. (6)).

The k_{obs} values in Fig. 3 at different pH actually reflects the reaction rates of the conversion of CN^- to CNCl , and shows that PACC reacts very rapidly with CN^- . For example, k_{obs} is 300.42 s^{-1} at pH 11, corresponding to a $t_{1/2}$, CN^- of 2.31 ms. A previous kinetics study [16] indicated that the half-lives of CNCl at pH 11 and 9 were estimated to be 1.31 and 131 min, respectively. Therefore, the decisive process for the reaction (Eq. (1)) rate is the hydrolysis of

formed CNCl (Eq. (6)). The rate of CNCl hydrolysis is positively correlated with pH value. The time for 99.9% conversion takes about 13 min at pH 11 [14,16]. Considering the facilitation of CN^- destruction and the cost of pH adjustment, pH 11 was selected as the optimum pH condition for the first stage of $[\text{Cd}(\text{CN})_4]^{2-}$ treatment by PACC.

The effect of pH on Cd^{2+} removal by PACC coagulation has been examined under mildly alkaline (Fig. 4). The result indicates that high pH facilitates Cd^{2+} removal. It may be attributed to the lower solubility of Cd^{2+} at high pH, which favors the generation of $\text{Cd}(\text{OH})_2(\text{s})$ that has a stronger affinity to the surface of hydrolyzed aluminum flocs. It has been demonstrated that Al_{13} species is very stable and is the predominant Al species during the coagulation process of Al_{13} -rich polyaluminum chloride (PACl) even at alkaline condition [17,18]. In addition, Al_{13} -aggregate is the main composition in the hydroxide flocs of Al_{13} -rich PACl [19]. Thereby Al_{13} polymer is the most active species responsible for the liberated Cd^{2+} removal by PACC coagulation. On the other hand, from Fig. 3, lowering pH in the alkaline region increased the reaction rate of active chlorine in PACC with CNO^- , which is mainly due to the increase in the concentration of hypochlorous that is a more powerful oxidant comparing with hypochlorite [15]. Considering the facilitation of CNO^- decomposition and Cd^{2+} removal together, pH 8.5 was selected as the optimum pH condition for the second stage $[\text{Cd}(\text{CN})_4]^{2-}$ treatment by PACC, because it could not only meet the required pH environment for CNO^- oxidation by active chlorine but also provide a suitable pH condition for Cd^{2+} coagulation by Al_{13} polymer.

3.2.2. Reaction time and dosage

The effect of reaction time on the complete CN^- oxidation by PACC was investigated under one time dosage strategy at the start of the first stage. The conversion of CN^- to CNO^- with time is not presented here, since the reaction (Eq. (6)) of CNCl hydrolysis cannot be terminated. CNO^- decomposition as a function of reaction time was monitored (Fig. 5). According to the last section and in prior studies, 13 min was used as the reaction time for the first stage, after which 2 min was used to regulate an appropriate pH for the second stage. The amount of PACC dosage was determined according to the SR (Eq. (3)), i.e. complete oxidation of CN^- by active chlorine. Fig. 5 shows that the rate of CNO^- decomposition increases with increasing active chlorine concentration, which was consistent with the previous results [14]. Complete CNO^- decomposition needed about 150 min when active chlorine dosage of theoretical requirement was used, while with an active chlorine dosage 130% of theoretical requirement a retention time of about 30 min was enough for complete oxidation. It was reported that overdosing of active chlorine could increase the conversion of

Fig. 4. Effect of pH on Cd^{2+} removal by PACC coagulation. Initial Cd^{2+} concentration was 5 mg/L.

Fig. 5. CNO^- concentration as a function of reaction time with various PACC dosages. The active chlorine 100%, 110%, 120% and 130% of the theoretical requirement for complete CN^- oxidation were used. The initial concentration of CN^- was 8.85 mg/L. The reaction was terminated through adding Na_2SO_3 to ensure reaction time exactly.

CNO^- to nitrate [20]. The active chlorine dosage 130% of the theoretical requirement and 30 min reaction time for CNO^- decomposition are to be optimum.

The effect of PACC dose on Cd^{2+} removal by coagulation was studied at pH 8.5. As shown in Fig. 6, with PACC doses greater than 20 mg Al/L, Cd^{2+} removal maintained about 93% that is the maximal efficiency. As PACC doses increased from 0 to 20 mg Al/L, Cd^{2+} was linearly removed with a gradient of approximate 0.25. These results suggests that for the treatment of 1 mg/L Cd^{2+} , the required minimal dosage to remove Cd^{2+} to the maximal efficiency by PACC was approximately 4 mg Al/L at pH 8.5. In view of the treatment of $[\text{Cd}(\text{CN})_4]^{2-}$ by PACC under the optimal working conditions, the stoichiometric weight ratio of Cl_2/Al in PACC was approximately 2, which is the optimal Cl_2/Al weight ratio of PACC for $[\text{Cd}(\text{CN})_4]^{2-}$ removal. We prepared PACC2 with a Cl_2/Al weight ratio of 2, which was used to further investigate the performance on $[\text{Cd}(\text{CN})_4]^{2-}$ removal.

3.3. Process and performance of $[\text{Cd}(\text{CN})_4]^{2-}$ removal

The performance of $[\text{Cd}(\text{CN})_4]^{2-}$ removal by PACC is closely related with dosage, pH and reaction time. According to above results, the process of $[\text{Cd}(\text{CN})_4]^{2-}$ removal by PACC is proposed in Fig. 7. Treatment process involved the two stages, whose pH values are 11 and 8.5, respectively. Reaction time included 13 min of the first stage and 30 min of the second stage. After the two stages

Fig. 6. Concentration plot of Cd^{2+} removal with PACC dosage at pH 8.5. Initial Cd^{2+} concentration was 4.6 mg/L.

Fig. 7. Schematic diagram of the process of $[\text{Cd}(\text{CN})_4]^{2-}$ removal by PACC.

treatment and solid-liquid separation, effluent may meet the requirement of water treatment for CN^- and Cd^{2+} .

Special experiment was conducted to evaluate the performance of $[\text{Cd}(\text{CN})_4]^{2-}$ removal by PACC2 at the optimal working conditions. NaClO was used to make a comparison with PACC2. As shown in Fig. 8, CNO^- was produced and accumulated continuously before the dosage of 12.8 mg Cl_2/L , which is the SR value of active chlorine to oxidize CN^- to CNO^- . The maximal concentration of formed CNO^- was about 7.6 mg/L. Whereafter, CNO^- concentration decreased with the increase of active chlorine dosage, because the formed CNO^- was further oxidized into nitrogen and bicarbonate. When active chlorine dosage was greater than 40 mg Cl_2/L , CNO^- concentration was near zero. It indicated that CN^- was completely oxidized by active chlorine. The trend of CNO^- concentration with addition of PACC2 was very similar to that of NaClO . However, there was a significant difference in removing Cd^{2+} between PACC and NaClO . PACC showed a much higher ability to remove Cd^{2+} due to the function of Al_{13} coagulation. Cd^{2+} concentration decreased with increase of PACC2 dosage. After CN^- destruction by active chlorine in PACC2, Cd^{2+} was released from $[\text{Cd}(\text{CN})_4]^{2-}$ complex and subsequently removed by Al_{13} coagulation.

Fig. 8. CN^- and Cd^{2+} removal by NaClO (a) and PACC2 (b). Initial $[\text{Cd}(\text{CN})_4]^{2-}$ concentration was 0.045 mmol/L.

4. Conclusions

With high content of active chlorine and Al_{13} polymer, PACC is very effective for the treatment of $[\text{Cd}(\text{CN})_4]^{2-}$. CN^- and Cd^{2+} can be simultaneously removed due to the combined function of oxidation and coagulation. The SR is 2.5 mol $\text{Cl}_2/\text{mol CN}^-$ for the complete CN^- oxidation by PACC. Two stages should be carried out for complete CN^- oxidation and effective Cd^{2+} coagulation. The first stage involves the conversion of CN^- to CNO^- at pH 11 and the second stage from CNO^- to final product and the coagulation of the liberated Cd^{2+} at pH 8.5. The active chlorine dosage 130% of the theoretical requirement for CN^- decomposition appears to be optimum. Under the optimal pH and dosage conditions, the reaction time for the first stage and the second stage should be 13 min and 30 min, respectively. Under the optimal working conditions, the stoichiometric weight ratio of Cl_2/Al in PACC is 2 for the treatment of $[\text{Cd}(\text{CN})_4]^{2-}$.

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