

Photo induced dissociation of ferri and ferro cyanide in hydroponic solutions

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ABSTRACT: The potential for photo-induced dissociation of ferri- and ferro-cyanide was investigated. The overall reactions followed first order kinetics, judged by the free cyanide analyzed in aqueous solution. The dissociation rates for ferri- and ferro-cyanide were mathematically described by the equations: $C_{(CN,t)} = C_{(CN,0)}e^{-1.3t}$ and $C_{(CN,t)} = C_{(CN,0)}e^{-0.39t}$, respectively. In addition, photo-induced dissociation of both iron cyanides was enhanced under an alkaline environment than a neutral condition. Results from the temperature-dependent tests indicated that the dissociation rate of ferri-cyanide was significantly higher than that of ferro-cyanide at all treatment temperatures. The kinetic parameter, activation energy (E_a) was also experimentally determined to be 12.02 and 12.32 kJ/mol for ferri- and ferro-cyanide, respectively. The results obtained suggest that both iron cyanides are susceptible to photo-dissociation and the rates are positively correlated to the change of temperatures. The information collectively also has important implications for waste management of iron cyanides as well as for risk assessment in a field trial.

Keywords: Cyanide; Dissociation; Ferri-cyanide; Ferro-cyanide; Temperature

INTRODUCTION

The naturally occurring free cyanide (CN) associated with the hydrolysis of cyanogenic glycoside in plant cells is typically maintained at very low levels (Lechtenberg and Nahrstedt, 1999). The main input of cyanides in the environments is derived from industrial activities, e.g. former manufactured gas production, electroplating plants and precious metal mining operations (Zimmerman *et al.*, 2008). The substantial use of CN-containing chemicals results in significant release of cyanides into the environment on a continuous basis. It is estimated that more than 100,000 tons of anthropogenic cyanides enters the environment annually (Mudder and Botz, 2001). Therefore, the risks due to the unregulated disposal from industrial effluents have led to widespread concern.

The threat to human health and the environment greatly depends on the toxicity of cyanide and on its physicochemical behavior, both of which are strongly related to its chemical speciation (Meeussen *et al.*, 1992). Several chemical species of cyanides can be frequently detected in the environment, namely free

CN, weak-acid dissociable CN, stable complexes and thiocyanate (Ebbs *et al.*, 2008). Although free CN is the most widely used commercial commodity in the family of cyanides, the commonly found species in soils and groundwater is the stable complexes since free CN reacts quickly with available metal ions to form iron cyanides, e.g. ferro-cyanide $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, ferri-cyanide $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$, ferriferro-cyanide (Prussian blue) and ferroferricyanide (Turnbull's blue) (Theis and West, 1986; Meeussen *et al.*, 1992; Zimmerman *et al.*, 2008), which may be present at concentrations >1 % on Dry weight (DW) basis at contaminated sites (Samiotakis and Ebbs, 2004). It is evident that the speciation and fate of iron cyanides in the environment appears to be related to numerous biotic and abiotic factors, e.g. pH, redox potential, the availability and quality of solar radiation, biological activity and community and the presence of organisms as well (Meeussen *et al.*, 1995; Rennert and Mansfeldt, 2002; Ghosh *et al.*, 2004).

The dynamic interconversion between free CN and iron cyanides in soils and sediments is most likely and especially crucial (Theis *et al.*, 1994). Iron cyanides, though less toxic than free CN, are potentially hazardous

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due to the release of free CN dissociated for both compounds through photodecomposition (Meeussen *et al.*, 1992; Rader *et al.*, 1993). This might occur when iron-cyanides are transported into surface water via the ground water, or when groundwater contaminated with iron-cyanides is used for irrigation (Rennert and Mansfeldt, 2002). Therefore, efforts to cleanup cyanide contamination are necessary to protect the health of the environment. Indeed, various remediation technologies ranging from intensive engineering techniques to bioremediation and/or phytoremediation have been developed through either a destruction-based process or a recovery-based process (White *et al.*, 2000; Yngard *et al.*, 2007). Unfortunately, most of engineering approaches have not been tested as a good alternative to large scale application (Smith and Mudder, 1991; Meeussen *et al.*, 1992). Although free CN is biodegradable, iron cyanides are quite recalcitrant against microbial and fungal biodegradation (Meeussen *et al.*, 1992; Ghosh *et al.*, 1999). It is evident that phytoremediation exhibited much promise in the clean up of iron cyanides by different plants from three continents and climate zones (Larsen and Trapp, 2006; Ebbs *et al.*, 2008; Yu and Gu, 2008), but this process only functions in the plant growth reason (Salt *et al.*, 1998).

Photo-induced degradation has been shown to be a promising alternative for contaminant destruction, in which the usefulness of radiolysis technique for efficient degradation has been successfully confirmed for a variety of pollutants (Getoff, 2002). The decomposition of iron cyanides into free CN in soils in the absence of light was detected at pH of 3.8 and 4.2, while the half-life of iron cyanides was estimated to be approximately 100 years at pH of 6.5 using a decomposition model (Meeussen *et al.*, 1992). In the present work, ferri- and ferro-cyanide were chosen to investigate the potential for photo-induced dissociation of iron cyanide. The effects of the applied iron cyanides and temperatures on dissociation were also investigated. In addition, the kinetics involved was experimentally determined.

MATERIALS AND METHODS

Chemicals

Potassium ferri-cyanide [$K_3Fe(CN)_6$] and potassium ferro-cyanide [$K_4Fe(CN)_6$] were all analytical reagent grade with $\geq 95\%$ purity (Shanghai Chemical Reagent Co., Shanghai). Stock

solutions of ferro- and ferri-cyanide were prepared and stored in the dark at 4 °C. Potassium cyanide (Shanghai Chemical Reagent Co., Shanghai) was technical grade (92- 95 % purity); but the standard solution of KCN were calibrated with a standard solution of $AgNO_3$, which was also calibrated against a standard solution of NaCl (standard method of SEPA, P. R. China). It should be noted that 1 mg $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ equals to 0.474 and 0.424 mg CN, respectively.

Temperature dependent test

Sealed glass vessels (50 mL) containing either ferro- or ferri-cyanide solution were used. Two sets of the experiments were conducted for each testing chemical: one was the testing chemical dissolved in 0.1 % NaOH solution; the other was in the deionized water. The flasks were closed with glass stoppers and all placed in an incubator with a continuous artificial light (illumination intensity: 20,000 lux) for 27 h. The photo-dissociation of iron cyanides was tested at 10, 15, 20, 25 and 30 ± 0.5 °C. Two separate flasks were conducted for each temperature treatment. The control flasks wrapped with aluminum foil were also made for each testing group to quantify the loss of cyanides in the hydroponic solution in the absence of light. The concentration of free CN in the hydroponic solution was measured just prior to application and then in intervals of 3 h over 27 h, where the presence of total CN in the aqueous solution was also measured at the beginning and at the end of incubation.

Concentration-dependent test

The flasks containing either ferro- or ferri-cyanide solution were closed with glass stoppers and placed in an incubator with a continuous artificial light at a constant temperature of 20 ± 0.5 °C for 12 h. Five different treatment levels of iron cyanides were conducted in two replications. For each treatment level, two different treatments were made for each testing chemical: one dissolved in 0.1 % NaOH solution and the other dissolved in de-ionized water. The control flasks wrapped with aluminum foil were also made for each testing group. The concentration of free CN in the hydroponic solution was measured just prior to application and then in intervals of 3 h over 12 h.

Chemical analysis

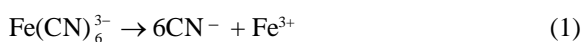
Free cyanide: One to five mL of aliquot solution

samples were pipetted into a 25 mL colorimetric cylinder (depending on the concentrations of cyanide in solution), and 0.1 % NaOH was added to the mark of 10 mL. Then 5.0 mL of a buffer solution with potassium dihydrogen phosphate and sodium phosphate were added. Quickly, 0.2 mL of 1 % (w/v) chloramine-T solution was introduced. The vessel was sealed with a stopper and left standing for 3 to 5 min. Five mL of the colour reagent consisting of isonicotinic acid and 3-methyl-1-phenyl-5-pyrazolone was then added. The content was diluted with deionized water to the mark (25 mL) and mixed thoroughly. Finally, the colorimetric cylinders were all kept in a water bath at a temperature of 32 °C for 40 min. The absorption of light at 638 nm was measured in a cuvette of optical path length of 10 mm against water as reference. The detection limit of this method was determined to be 0.004 mg CN/L, depending on the volume of the sample used. The sample preparation procedures used in this study were also checked against samples spiked with certified solution standards and the mean recovery was 98.46 %.

Total cyanide: Total CN is the sum of easy liberated cyanide (HCN and CN⁻) and complexed cyanide. The total cyanide in the solution was analyzed by a standard method (State Environmental Protection Administration of P. R. China, 1989, method number GB 7487-87). Ten milliliters of 1 % NaOH were added into the reservoir vessel of the distillation unit. Five mL of the spiked solution were placed in a 500 mL round bottom flask, and then 200 mL of distilled water was added. Then 10 mL of sodium ethylenediamine tetraacetate (EDTA) with concentration of 10 % (w/v) and 10 mL of phosphoric acid (≥ 85 % purity) were added before heating and mixing. Approximately 100 mL distilled solution containing cyanide from plant materials was collected, quantitatively transferred to a 100 mL volumetric flask and made up to the volume with deionized water. The solution was stored at below 6 °C until the concentration of cyanide was determined. All samples were analyzed within a maximum holding time of 4 h. The remaining procedure was identical to those described earlier.

Reaction Stoichiometry

The following reactions give the photocatalytic oxidation scheme of iron cyanides (Meeussen *et al.*, 1992):



RESULTS AND DISCUSSION

Effect of temperature on dissociation of ferri-cyanide

Fig. 1a and b show the concentrations of free CN in the hydroponic solution spiked with ferri-cyanide with time for a) in the 0.1 % NaOH solution and b) in the deionized water for the temperature range between 10 °C and 30 °C. Trace amounts of free CN was detected in the control solutions isolated from light (data not shown), probably due to the photodecomposition during handling. This suggests that the presence of free CN in the hydroponic solution can be accounted to the photo-dissociation of ferri-cyanide. Indeed, the amount of free CN in the sealed vessels significantly increased in all test flasks. Free CN in the NaOH solution was 170.38 μM at 10 °C after a 27-h period of exposure, and more detected at higher temperatures. In vessels with the deionized water spiked with ferri-cyanide, free CN was detected to be 123.46 μM after exposure at 10 °C. The dissociation rate was faster at higher treatment temperatures. Results also showed that more free CN was present in the NaOH solution than that in the deionized water at all treatment temperature, probably due to the fact that free CN liberated from ferri-cyanide was escaped from the deionized water to the headspace.

Table 1 gives the speciation of cyanides in the hydroponic solution after the exposures. Approximately 96.2 % (S.D: 0.913, n=5) of the applied ferri-cyanide was found in the NaOH solution after the 27h period of exposure, judged by the total CN analyzed. Presence of ferri-cyanide detected as total CN in the solution decreased from 60.78 % at 10 °C to 44.62 % at 30 °C, while free CN increased from 39.22 % at 10 °C to 55.38 % at 30 °C. In the deionized water, 85.35 % (S.D: 1.196, n=5) was recovered in the hydroponic solution and majority (54.72-71.1 %) was in the form of ferri-cyanide after the 27-h period of exposure. It is evident that cyanide anion is the dominant free cyanide species under alkaline condition (pH > 9.24) (Sehmel, 1989), while the presence of hydrogen cyanide appears to be inversely related to the pH of the ambient environment.

Dissociation of iron cyanides

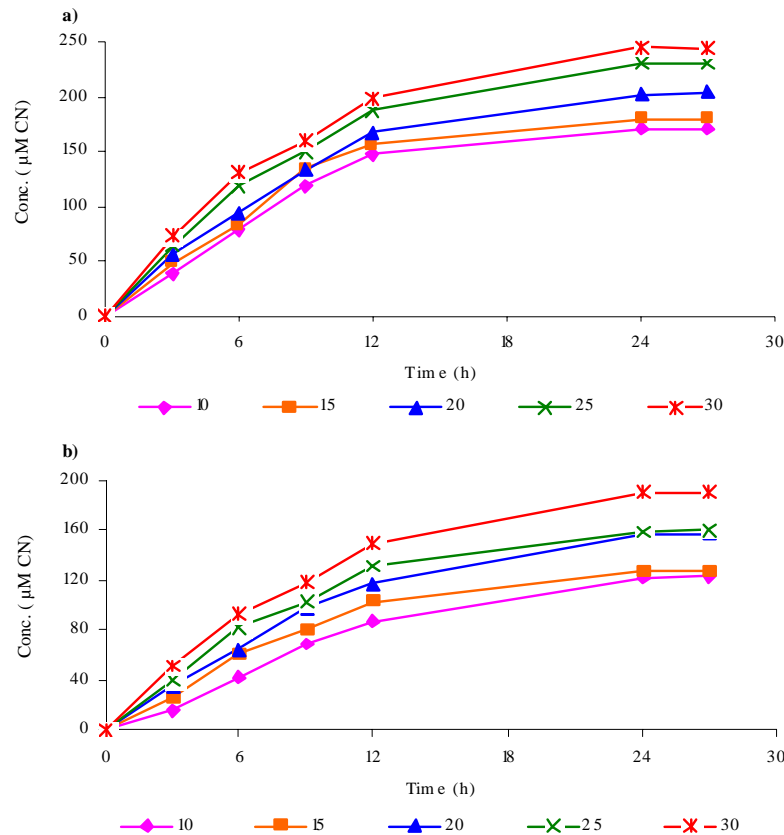


Fig. 1: Measured cyanide concentrations ($\mu\text{M CN}$) in aqueous solution at different temperatures, a) ferri-cyanide dissolved in the 0.1 % NaOH solution; b) ferri-cyanide dissolved in the deionized water. The values are the mean of two replicates for samples

Table 1: Speciation of ferri-cyanide in the hydroponic solution

Temp ($^{\circ}\text{C}$)	Treatment	Initial solution			Final solution			Recovery (%)
		Total CN ($\mu\text{M CN}$)	Free CN ($\mu\text{M CN}$)	pH	Total CN ($\mu\text{M CN}$)	Free CN ($\mu\text{M CN}$)	pH	
10	S-1	451.54	0.58	11.85	434.23	170.38	11.58	96.12
	S-2	480.77	0.69	6.26	427.31	123.46	6.67	86.45
15	S-1	451.54	0.58	11.85	431.54	178.46	11.60	95.52
	S-2	480.77	0.69	6.26	417.31	126.54	6.62	84.42
20	S-1	451.54	0.58	11.85	438.85	202.31	11.60	97.12
	S-2	480.77	0.69	6.26	428.08	156.92	6.91	86.58
25	S-1	451.54	0.58	11.85	430	230	11.59	95.12
	S-2	480.77	0.69	6.26	414.62	159.62	6.87	83.89
30	S-1	451.54	0.58	11.85	438.85	243.08	11.53	97.12
	S-2	480.77	0.69	6.26	422.31	191.15	6.73	85.42

* S-1: 0.1 % NaOH solution with ferri-cyanide; S-2: Deionized water with ferri-cyanide

In the observation, a pH of 11.53-11.60 was detected at different treatment temperatures at the termination of exposure, therefore there is a good reason to assume that all free CN dissociated from ferri-cyanide could be in the NaOH solution. Moreover, the volatilization of free CN from the deionized water can

be calculated from the free CN detected in the NaOH solution and that in the deionized water. It is of interest to find that the volatilization rate of free CN was independent of temperatures, in which the average rate was $243.46 \mu\text{M CN/h}$ (S.D: 0.566, n=5) at pH of 6.62-6.91.

Effect of temperature on dissociation of ferro-cyanide

The measured concentrations of free CN in hydroponic solution spiked with ferro-cyanide at different temperatures after 27 h of exposure in the presence of light are presented in Fig. 2. Negligible free CN was observed in the controls in the absence of light (data not shown). Compared to the treatment amended with ferri-cyanide, less free CN was detected in all flasks spiked with ferro-cyanide at all treatment temperatures after exposure. Free CN in the NaOH hydroponic solution was 77.31 μM at 10 °C after the 27 h period of exposure, while free CN was detected to be 68.08 μM in the vessel with the deionized water at the same treatment temperature. More free CN was found in the solutions at higher treatment temperatures. Results also showed that the presence of free CN in the NaOH solution was always higher than that in the deionized water at all treatment temperatures. speciation of cyanides in the hydroponic solution amended with ferro-cyanide after incubations is given in Table 2. More than 96 % (S.D: 0.456, n=5) of the

applied ferro-cyanide was recovered in the NaOH solution after the 27 h period of exposure, judged by the total CN analyzed. Between 16.6 % and 26.4 % of the applied ferro-cyanide detected as total CN was found to be able to dissociate into free CN, but majority (> 73 %) was still in the form of ferro-cyanide in the NaOH solution. On the contrary, slightly less applied ferro-cyanide (93.97 %, S.D: 1.018, n=5) was detected in the deionized water after 27 h exposure and more than 80 % was still in the complexed form. The average volatilization rate of free CN liberated from ferro-cyanide in the deionized water was obtained to be 50.0 $\mu\text{M CN/h}$ (S.D: 0.199, n=5) at a pH of 6.61-6.76.

Kinetics determination of photo-dissociation of iron cyanides

Like other chemical reactions, photo-dissociation of iron cyanide depends on either reduction of reactants or formation of products, when the illumination intensity is constant. In this study, the reactions followed first order kinetics as shown in Fig.1

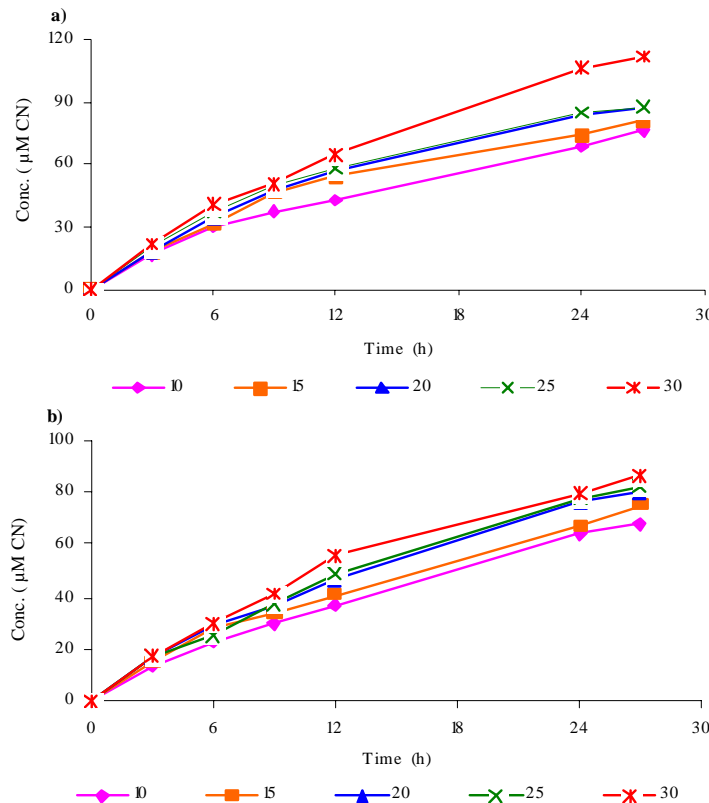


Fig. 2: Measured cyanide concentrations ($\mu\text{M CN}$) in aqueous solution at different temperatures, a) Ferro-cyanide dissolved in the 0.1 % NaOH solution; b) Ferro-cyanide dissolved in the deionized water. The values are the mean of two replicates for samples

Table 2: Speciation of ferro-cyanide in the hydroponic solution

Temp (°C)	Treatment	Initial solution			Final solution			Recovery (%)
		Total CN (μM CN)	Free CN (μM CN)	pH	Total CN (μM CN)	Free CN (μM CN)	pH	
10	S-1	485.77	0.58	11.84	466.92	77.31	11.55	96.11
	S-2	468.85	0.62	6.33	441.15	68.08	6.73	94.12
15	S-1	485.77	0.58	11.84	471.92	81.15	11.53	96.31
	S-2	468.85	0.62	6.33	439.62	75	6.61	93.78
20	S-1	485.77	0.58	11.84	471.92	86.54	11.57	97.12
	S-2	468.85	0.62	6.33	444.23	80.38	6.76	94.76
25	S-1	485.77	0.58	11.84	469.23	88.08	11.58	96.61
	S-2	468.85	0.62	6.33	444.62	82.31	6.75	94.86
30	S-1	485.77	0.58	11.84	471.92	124.62	11.63	97.12
	S-2	468.85	0.62	6.33	433.08	86.54	6.74	92.33

and 2. The overall reaction can be described mathematically by the following equation (Kim et al., 2001):

$$r = \frac{-d(C_{CN})}{dt} = kC_{CN}$$

or:

$$C_{(CN,t)} = C_{(CN,0)}e^{kt}$$

Where r is the reaction rate, k is the overall reaction constant, d is the differentiation function, t is the reaction time, $C_{(CN,t)}$ is the concentration of iron cyanide at time (t) and $C_{(CN,0)}$ is the initial concentration of iron cyanide.

The k value can be obtained by the analysis of initial velocities (r_i) at a series of applied iron cyanides concentrations. In this investigation, the reaction rate (r_i) at each treatment level of iron cyanide was determined from the presence of free CN in aqueous solution. Clearly, the plots of free cyanide (C) versus time (t) are linear at all treatments during the exposure period from 0 to 12 h (Fig. 3), judged by the regression coefficient R^2 (%). Therefore, the r_i values were obtained from the slopes of the lines.

In order to obtain the value of the overall reaction constant (k) from a straight line on graphs, the above equation can be rewritten as:

$$\log r = \log C_{CN} + \log k$$

When the log of the initial velocity ($\log r_i$) is plotted versus the log of the initial ferri-cyanide concentration (Fig. 4), the rate constant (k) can be obtained from the graph. That is, $\log k = 0.1126$, and $k = 1.30$. Therefore, the overall reaction of photo-dissociation of ferri-

cyanide in NaOH solution can be written mathematically as follow:

$$C_{(CN,t)} = C_{(CN,0)}e^{1.3t}$$

While for the treatment with ferri-cyanide dissolved in deionized water, the photodecomposition reaction can be described as follow:

$$C_{(CN,t)} = C_{(CN,0)}e^{0.97t}$$

Less free CN was detected in the hydroponic solutions amended with ferro-cyanide due to photodecomposition (Fig. 5).

A similar estimation was used for the treatment with ferro-cyanide (Fig. 6). Hence, the equation of photodecomposition of ferro-cyanide in NaOH solution can be obtained as:

$$C_{(CN,t)} = C_{(CN,0)}e^{0.39t}$$

For the treatment with ferro-cyanide dissolved in deionized water, the photodecomposition reaction can be expressed as:

$$C_{(CN,t)} = C_{(CN,0)}e^{0.27t}$$

From these estimations, it is clear that the photo-dissociation rate of ferri-cyanide was more than 3-fold higher than that of ferro-cyanide (if the reaction is zero order), indicating that ferri-cyanide is more susceptible to photodecomposition than ferro-cyanide. Additionally, the dissociation rates of both iron cyanides appeared to be related to the pH of the ambient environment.

Estimation of activation energy E_a

The temperature dependence of iron cyanides

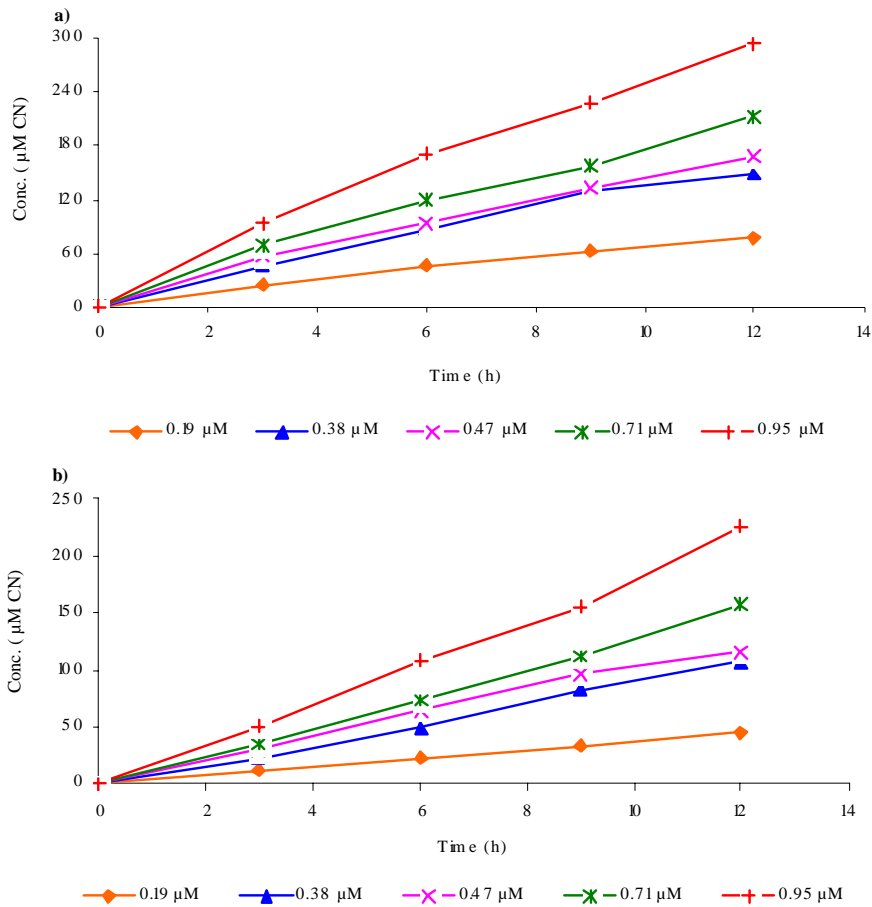


Fig. 3: Measured cyanide concentrations (µM CN) in aqueous solution at different initial concentrations, a) Ferri-cyanide dissolved in the 0.1 % NaOH solution; b) Ferri-cyanide dissolved in the deionized water. The values are the mean of two replicates for samples

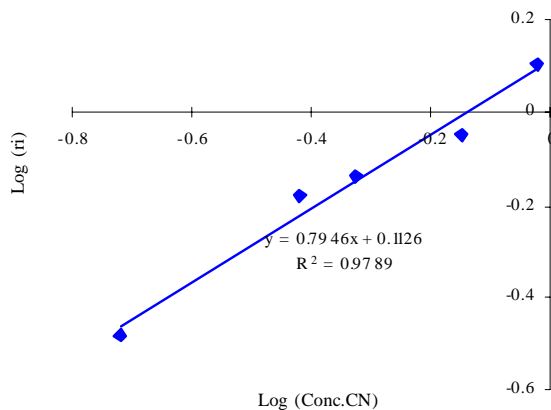


Fig. 4: Plot of $\text{log}(r_i)$ versus $\text{log}(\text{Conc.}_{CN})$ in the treatment with ferri-cyanide. Reaction was performed at 20 °C with constant illumination intensity

photodecomposition was studied in a range of 283 to 303 K (10 to 30 °C). Quantification of the temperature effect on the photo-dissociation rate (k) can be described by the Arrhenius equation (Meeussen *et al.*, 1992):

$$\ln k = -(E_a / RT) + \ln A$$

Where A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, and T is the temperature (K). Without discussing the physical meaning of E_a or A , it is evident that according to this equation $\ln(k)$ should be linear with $1/T$.

The k values at different treatment temperatures were obtained from the slopes of the lines of free cyanide (C_{CN}) versus time (t), judged by the regression coefficient R^2 (%). The Arrhenius plots of $\ln(k)$ against

Dissociation of iron cyanides

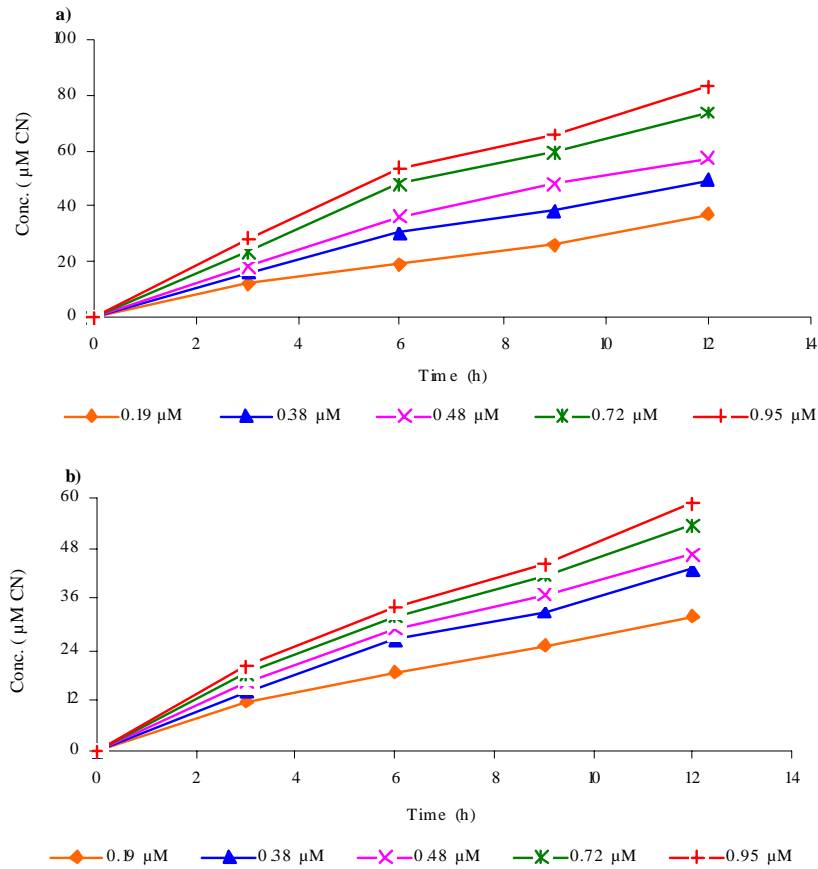


Fig. 5: Measured cyanide concentrations (µM CN) in aqueous solution at different initial concentrations, a) Ferro-cyanide dissolved in the 0.1 % NaOH solution; b) Ferro-cyanide dissolved in the deionized water. The values are the mean of two replicates for samples

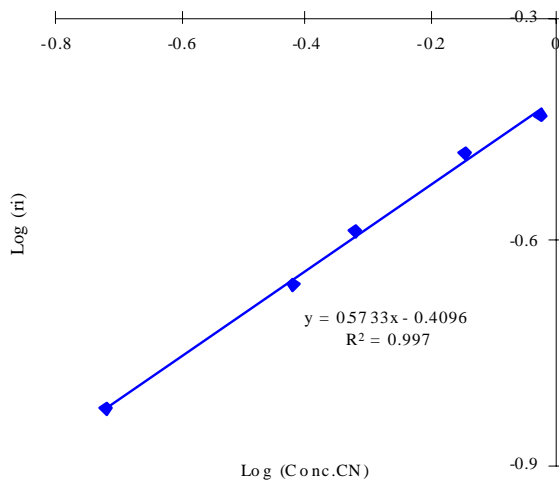


Fig. 6: Plot of $\log(r_i)$ versus $\log(\text{Conc. CN})$ in the treatment with ferro-cyanide. Reaction was performed at 20 °C with constant illumination intensity

the inverse temperature ($\times 10^3 K$) show a good linear relationship in both treatments (Fig. 7).

Treatments with ferri-cyanide dissolved in NaOH solution: $\ln r = -1445.7(1/T) + 4.65$

Treatments with ferro-cyanide dissolved in NaOH solution: $\ln r = -1481.6(1/T) + 3.67$

The E_a values can be calculated from the above equations as the gas constant R value is 8.314 J/k.mol. Therefore, the E_a values for ferri- and ferro-cyanide dissolved in NaOH solution are 12.02 and 12.32 kJ/mol, respectively. Higher E_a values were obtained for ferri- and ferro-cyanide dissolved in deionized water are 18.76 and 13.03 kJ/mol, respectively, indicating that photodecomposition of both iron cyanides in a neutral environment is more energy-consuming than that in an alkaline condition.

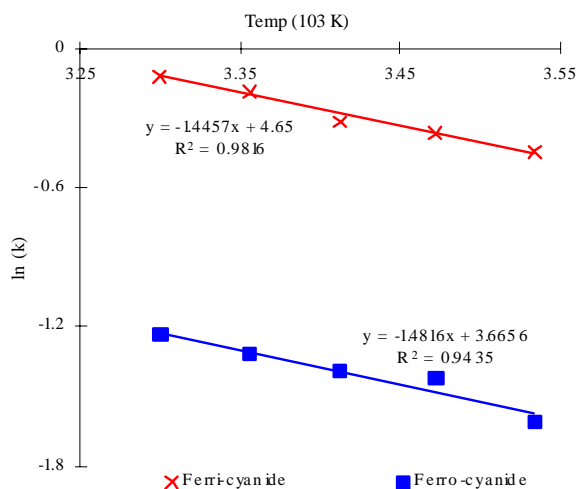


Fig. 7: Arrhenius plot of the photodecomposition of ferri- and ferro-cyanide

Difference in the degradation pathway between ferri- and ferro-cyanide

In this study, the photodecomposition rate of ferri-cyanide was always higher than that of ferro-cyanide. This suggests that ferro-cyanide was not the intermediate during the photodecomposition of ferri-cyanide, in which ferri-cyanide was quickly dissociated into free CN and Fe³⁺. It is of interest to note that the precipitation of Fe(OH)₃ was observed in the treatment spiked with ferro-cyanide in the presence of NaOH after 24 h period of exposure. Therefore, there is a good reason to propose a possible dissociation pathway involved in photodecomposition of ferro-cyanide: ferro-cyanide was dissociated into Fe²⁺ and CN⁻ first, and then Fe²⁺ was oxidized into Fe³⁺ by air.

It was also noted that more than 10 % of free CN detected in the deionized water amended with ferri-cyanide was volatilized, while only less than 3 % free cyanide was unable to detect in the solution spiked with ferro-cyanide. The volatilization rate of free CN was estimated to be 243.46 μM CN/h in the treatments spiked with ferri-cyanide, which is more than 4-fold higher than that of ferro-cyanide, suggesting that volatilization of free CN is highly dependant on the presence of free CN in water.

CONCLUSION

It was possible to experimentally estimate the dissociation of iron cyanides in hydroponic solution in

the presence of light, in which ferri-cyanide showed a higher potential than ferro-cyanide, particularly under an alkaline environment. The observed dissociation rate was positively correlated to the doses of the applied iron cyanides as well as the treatment temperatures. More cyanide detected as free CN was escaped from neutral solution than that from alkaline solution, but the volatilization rate of free CN was independent of the temperatures. These lead to the conclusion that both iron cyanides are susceptible to photodecomposition. For risk assessment, the dissociation of iron cyanides should be taken more cautiously and seriously. For waste management, especially for phytoremediation trials, the presence of free CN liberated from iron cyanides may cause toxic effects on plants and may even limit the effectiveness of remediation.

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