



## Treatment of a synthetic solution of galvanization effluent via the conversion of sodium cyanide into an insoluble safe complex

Ibrahim Ismail, Nabil Abdel-Monem, Seif-Eddeen Fateen\*, Waleed Abdelazeem

Department of Chemical Engineering, Cairo University, Giza, Egypt

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### ABSTRACT

Wastewater discharged from metal-finishing processes usually contains cyanide, a hazardous substance that is used extensively in the surface finishing industry. In the present study, a synthetic solution resembling the contaminated wastewater was chemically treated using ferrous sulfate. This simple one-step process was applied successfully to remove cyanide from metal finishing wastewater. The experiments were carried out on a synthetic solution containing ions of cyanide and zinc. The effects of mixing velocity, ratio of ferrous ions to cyanide ions, ferrous ions concentration, initial cyanide concentration, pH of solution, temperature, mixing time and zinc ions concentration were studied. The results showed that the removal efficiency of cyanide increased as the mixing velocity increased, ferrous ion molar ratio to cyanide ions increased, temperature increased and time of mixing increased at an optimum of pH 8. The reduction of cyanide concentration reached the allowable limit for wastewater discharge according to the Egyptian Environmental Law decree 44/2000, which is 0.2 mg/l. The formed complexes were analyzed and the stability of each complex was studied under different pH value solutions after 7 days of contact. A typical example of electroplating wastewater from a local company in the field of metal finishing, which contains 18 mg/l  $\text{CN}^-$  and 12 mg/l  $\text{Zn}^{2+}$ , was treated according to the determined optimum conditions for the treatment process and the concentration of  $\text{CN}^-$  was reduced to 0.095 mg/l after 15 min of agitation.

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### 1. Introduction

Cyanide, a poisonous substance dangerous to humans, animals, plants and aquatic organisms, can be found in the effluent of several industries such as paint and ink formulation, petroleum refining, explosives, case hardening, automobile industry, chemicals industry, pesticides industries, synthetic fiber production, electroplating, thermoelectric power stations, mining, electronics, and coke [1–18]. Its effects on the human and the environment have been well reviewed by Mudder and Botz [14]. Due to its toxic nature, cyanide must be recovered, removed or destroyed. There are many reported processes for treating cyanide-containing effluents [1–30]. These processes can be categorized as biodegradation [1,24,26]; adsorption on activated carbon [6,18]; oxidation via chemical, electrochemical or photochemical processes [7,9,10,12,15,19,23]; chemical precipitation [11]; hollow fiber gas membranes [13]; ultrasonic waves [15]; ion exchange [17]; extraction [20]; photocatalytic using Ti catalyst [22,25]; and volatilization then absorption by NaOH [21]. The suitability of any

of the above-mentioned processes to a specific cyanide-containing effluent depends on the effluent flow rate, cyanide concentration, associate chemical species, permissible level of cyanide in the effluent after treatment, technical level of the entity's employees and the economy and finances of the process.

In Egypt, electroplating workshops are major sources for cyanide-contaminated wastewater. They are geographically distributed all over the country. Most of them are small size entities operated by a few low technical level labors. Due to these uncomfortable circumstances, it is not possible to individually treat the effluent of every workshop using an advanced technique or to collect the effluent of these small entities to be treated in a centralized treatment unit. Currently, most of these workshops do not treat their waste by any means. They discharge the effluents as is to the nearest sewage line creating a severe environmental problem. A real case study of a medium-size Egyptian electroplating workshop producing effluent of 31 m<sup>3</sup>/day was presented by Abou-Ellela et al. [8]. They treated the cyanide-containing effluent using alkaline chlorination, which does not destroy the pollutants completely [27]. In caustic chlorine treatment, cyanide is converted to cyanate which is also toxic. Complete destruction of cyanate is difficult. The chlorination process also produces secondary by-products such as trihalo-methanes, which are highly toxic and carcinogenic [28]. The treated water contains huge amount of dissolved chlorine. Considering the nature of the cyanide effluents of the Egyptian

\* Corresponding author. Tel.: +20 011 400 888.

E-mail addresses: [dr.ismail@instruchem.org](mailto:dr.ismail@instruchem.org) (I. Ismail), [nabil.a.monem@hotmail.com](mailto:nabil.a.monem@hotmail.com) (N. Abdel-Monem), [sfateen@alum.mit.edu](mailto:sfateen@alum.mit.edu) (S.-E. Fateen).

electroplating industry, there is a need for another treatment method, which can completely remove cyanides. Besides, the process to be adopted must have two other criteria: (1) economic for small-scale operation and (2) easy to handle by unskillful labor.

In this work, we recommend ferrous sulfate addition to the cyanide-containing wastewater as a simple and efficient treatment process. The use of an iron salt is appropriate for all cyanide concentrations, slurry application and solution application. Ferrous sulfate also has the advantage of low cost and wide availability, as it is generated from the steel pickling in the metal surface finishing industry. The effects of mixing velocity, time of stirring, pH, concentration of ferrous ions and its molar ratio to cyanide ions, and the temperature of reaction on the removal process were investigated. The elemental analysis of the precipitated complex and its stability in solutions with varying pH value has been also studied.

## 2. Experimental work

### 2.1. Materials

The chemicals used during this work were pure grade. Sodium cyanide, ferrous sulfate and zinc oxide were supplied by United Co., while sodium hydroxide and sulfuric acid were supplied by ADWIC Co. Distilled water was used to prepare the solution and to wash the glassware in each experimental run.

### 2.2. Instrumentation

All samples and chemicals used in the preparation of solutions were weighed using an analytical balance of “Sartorius” type with a sensitivity of  $10^{-4}$  g.

Mixing was performed using J. P. Selecta magnetic stirrer whose speed can be varied from 100 to 1600 rpm. The pH of solutions was measured by using Inolab pH meter. The cyanide is the key parameter selected for determining the treatment efficiency. It was measured using 975-MP Spectrophotometer, which is obtained from ORBECO Analytical Systems, Inc. Kits 975 MP/32 were used during measurements. Elemental analyses of Zn and Fe were performed using GBC 902 Atomic Absorption, while the analyses of C and N were done using PerkinElmer CHNS/O elemental analysis.

### 2.3. Preparation of cyanide solutions

In this study, the cyanide solution was prepared by dissolving 0.2 g of sodium cyanide 96% purity and 0.16 g of zinc oxide 90% purity in a small amount of distilled water. Then the solution was transferred to a measuring flask and distilled water was added to make up a total volume of 1000 ml.

### 2.4. Preparation of ferrous sulfate solution

The ferrous sulfate solution was prepared by dissolving 2 g of ferrous sulfate 90% purity in a small amount of distilled water. Then the solution was transferred to a measuring flask and distilled water was added to make up a total volume of 1000 ml.

### 2.5. Experimental procedure

A known volume of ferrous sulfate is added to a known volume of cyanide solution in a glass flask. The solution was mixed at a certain RPM for a certain time. The solution was then filtrated using a quantitative filter paper. The filtrate was then analyzed for cyanide concentration, while the precipitated complex was elementally analyzed using atomic absorption and CHNS/O analyzer. This procedure was used to obtain the optimum mixing intensity,

$\text{Fe}^{2+}/\text{CN}^-$  molar ratio, pH,  $\text{Fe}^{2+}$  concentration, time, temperature and  $\text{Zn}^{2+}/\text{CN}^-$  molar ratio.

### 2.6. Cyanide determination

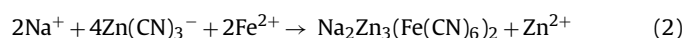
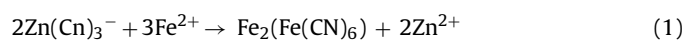
The analysis of cyanide is not an easy task as it is subjected to various types of interferences. Different analysis techniques have been reported such as colorimetric techniques using a spectrophotometer after cyanides distillation [6,11,19], potentiometric techniques using silver electrode [18], titration method using silver nitrate and 4-dimethylaminobenzylidinerhodanine indicator [19,21], ion pair/ion interaction chromatography (IIC) [29,30], the EPA Standard Method 335.4 [31] and the EPA Standard Method OIA-1677 [32].

Although, the above-mentioned techniques give reliable results, we preferred to use the simple colorimetric method using ORBECO spectrophotometer with a pretested chemical kit as it is a straightforward method. The aim is to reach a simple procedure suitable for being adopted by the local electroplating workshops labor. Any analysis method that involves the liberation of HCN was discarded for safety reasons.

## 3. Results and discussions

### 3.1. Analysis of the formed complex

Elemental analyses for the formed complex have been done using the instruments described above. Table 1 shows the weight percentage of every element. The results of these analysis showed that the atomic ratios of Na, Zn, Fe, C and N are 2, 3, 5.4, 14.5 and 14.5, respectively. Although it is not easy to determine the structure of the formed precipitate based on the elemental analysis only, we can only suggest that the precipitate that forms in the reaction between  $\text{Fe}^{2+}$  and  $\text{CN}^-$  in case of presence of  $\text{Zn}^{2+}$  and  $\text{Na}^+$  ions is comprising mainly insoluble sodium–zinc hexacyanoferrate  $\text{Na}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$  and iron ferrocyanide  $\text{Fe}_2[\text{Fe}(\text{CN})_6]$  according to the reactions below:



### 3.2. Effect of mixing velocity

In this set of experiments, the mixing velocity was varied between 100 and 1600 rpm. The concentration of the cyanide in the solution was measured as a function of mixing intensity, as shown in Fig. 1, which shows the effect of mixing velocity on cyanide removal at different mixing times. The increase in the cyanide removal is due to the increase in the rate of collisions between reactant species, which finally leads to the increase of the rate of reaction. An appreciable increase in the rate of reaction occurs as mixing velocity and time increase, which is due to the increase in contact time between species of reactants, which finally leads to the increase the rate of reaction. Mixing velocity of 1600 rpm with 30 min of mixing gave the highest efficiency for cyanide removal process.

**Table 1**  
The elemental analysis (%) for the formed complex.

Na	4.17
Fe	30.44
Zn	19.72
C	17.4
N	20.29

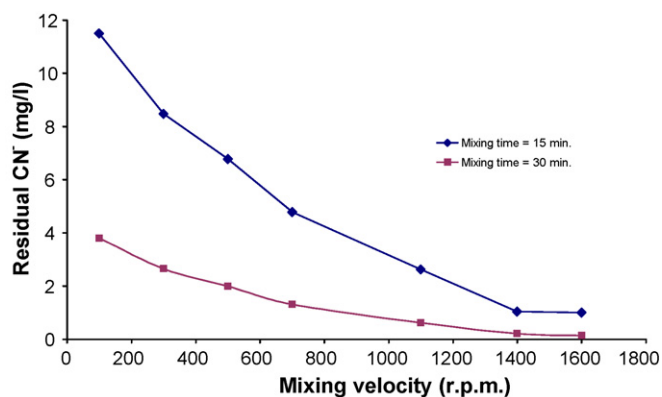


Fig. 1. Effect of mixing velocity on the residual cyanide after 15 and 30 min of mixing ( $C_i(\text{CN}^-) = 102 \text{ mg/l}$ ,  $\text{Fe}^{2+}/\text{CN}^-$  molar ratio = 1.6).

### 3.3. Effect of $\text{Fe}^{2+}:\text{CN}^-$ ratio

In this set of experiments, the  $\text{Fe}^{2+}/\text{CN}^-$  ratio was varied between 0.32 and 3.2. The cyanide concentration in the solution was measured as a function of  $\text{Fe}^{2+}/\text{CN}^-$  molar ratio. As shown in Fig. 2, at  $\text{Fe}^{2+}/\text{CN}^-$  of 0.32, 0.5 and 0.64 there is insufficient  $\text{Fe}^{2+}$  to complex with all  $\text{CN}^-$ . At  $\text{Fe}^{2+}/\text{CN}^-$  ratios of 1 and higher, a very low, allowable, cyanide concentration was remaining in solution after 30 min of agitation. This means that the optimum ratio is more than three times the stoichiometry ratio, which is 0.28 according to Eqs. (1) and (2). This excess amount of  $\text{Fe}^{2+}$  ions shifts the reaction towards the product side and helps minimizing the concentration of the remaining cyanide ions in solution.

### 3.4. Effect of $\text{Fe}^{2+}$ concentration

In this set of experiments, the  $\text{Fe}^{2+}$  concentration was varied between 0.6 and 72 mg/l, and the concentration of the cyanide in the solution was measured as a function of  $\text{Fe}^{2+}$  concentration, as illustrated in Fig. 3. Increasing the  $\text{Fe}^{2+}$  concentration gradually increased the efficiency of cyanide removal process till it reached a value of 0.193 mg/l at a concentration of 60 g/l of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .

It is well understood that an increase in concentration of  $\text{Fe}^{2+}$  has the effect of increasing reaction rate, because an increase in concentration produces a proportional increase in the frequency of collisions between reactants.

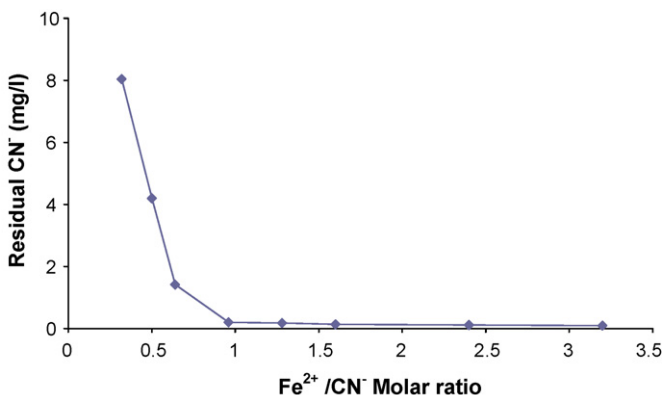


Fig. 2. Effect of  $\text{Fe}^{2+}/\text{CN}^-$  molar ratio on the residual cyanide ( $C_i(\text{CN}^-) = 102 \text{ mg/l}$ , mixing velocity = 1600 rpm, mixing time = 30 min).

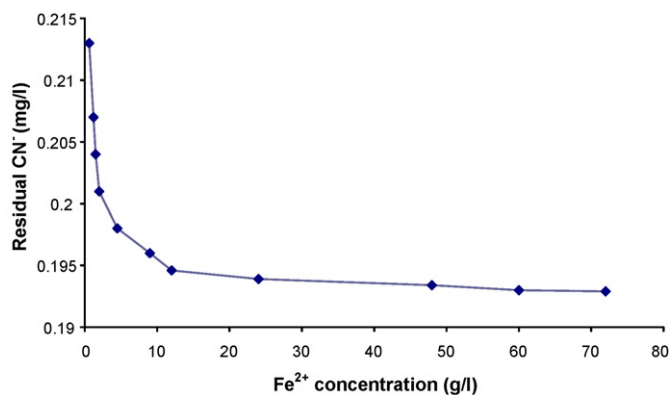


Fig. 3. Effect of  $\text{Fe}^{2+}$  concentration on the residual cyanide ( $C_i(\text{CN}^-) = 102 \text{ mg/l}$ ,  $\text{Fe}^{2+}/\text{CN}^-$  molar ratio = 0.96, mixing time = 30 min, mixing velocity = 1600 rpm).

### 3.5. Effect of pH

In this set of experiments, the pH of the Zn-cyanide solution in presence of iron ions was adjusted between 4 and 13, using 1N NaOH or 20%  $\text{H}_2\text{SO}_4$ . The concentration of cyanide in the solution was measured as a function of equilibrium pH, as shown in Fig. 4. The cyanide concentration in solution decreased with pH increasing up to 8 and then it started to increase slightly with increasing the pH above 8. In liquid solution, zinc forms different complexes with cyanide. The structure of these complexes varies with the hydrogen ion concentration as was shown by Yngard et al. [33], who determined the different Zn species in  $\text{Zn(II)}/\text{CN}^-/\text{OH}^-$  system based on the different formation constants available in literature. It was found that by increasing the pH up to 8, the main Zn-cyanide species are  $\text{Zn}(\text{CN})_3^-$  with a concentration of more than 60% of all Zn-cyanide species. The rest is  $\text{Zn}(\text{CN})_2$  and, to a little extent,  $\text{Zn}(\text{CN})_4^{2-}$ . Other species like  $\text{Zn}(\text{CN})^-$  and  $\text{Zn}(\text{CN})_2\text{OH}^-$  are of minor concentrations. Since iron ferrocyanide is a strong insoluble complex, it can be satisfactory assumed that by increasing pH up to 8, iron ferrocyanide,  $\text{Fe}_2(\text{Fe}(\text{CN})_6)$ , and sodium-zinc hexacyanoferrate  $\text{Na}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ , are formed and precipitated from the solution leaving a small concentration of cyanide in solution according to Eqs. (1) and (3) described.

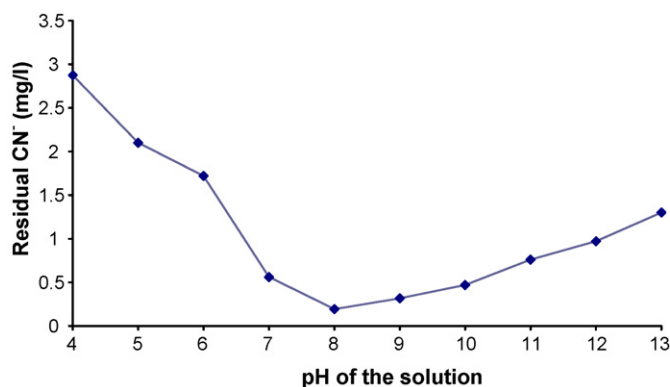
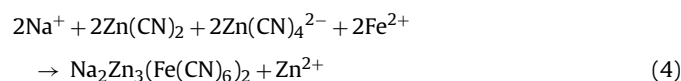
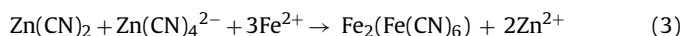
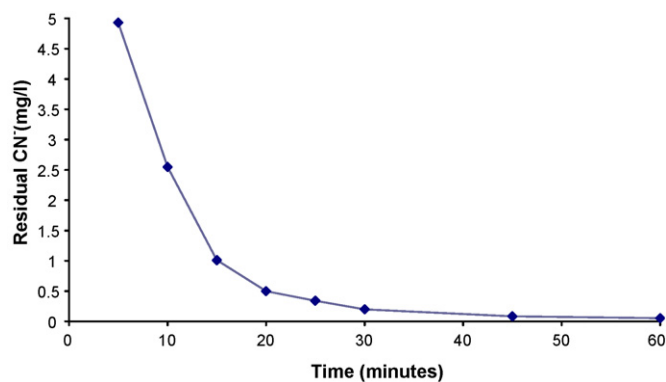


Fig. 4. Effect of pH of the solution on the residual cyanide ( $C_i(\text{CN}^-) = 102 \text{ mg/l}$ ,  $\text{Fe}^{2+}/\text{CN}^-$  molar ratio = 0.96, mixing time = 30 min, mixing velocity = 1600 rpm,  $C_i(\text{Fe}^{2+}) = 60 \text{ g/l}$ ).



**Fig. 5.** Effect of mixing time on the residual cyanide ( $C_i(\text{CN}^-) = 105 \text{ mg/l}$ ,  $\text{Fe}^{2+}/\text{CN}^-$  molar ratio = 1.6, mixing velocity = 1600 rpm,  $C_i(\text{Fe}^{2+}) = 60 \text{ g/l}$ ,  $\text{Fe}^{2+}/\text{CN}^-$  molar ratio = 0.96, pH 8).

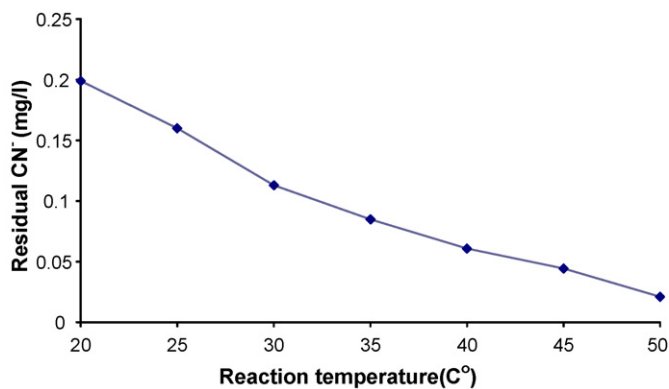
At pH higher than 8, the slight increase in cyanide concentration in solution, after treatment, is attributed to the presence of hydrolyzed soluble Zn-cyanide species like  $\text{Zn}(\text{CN})_2\text{OH}^-$  and  $\text{Zn}(\text{CN})_3\text{OH}^{2-}$ . Besides, at pH above 8, cyanide removal is incomplete due to increased competition of cyanide and cyanide complex ions with hydroxyl ions for a reaction with the iron ions, which leads finally to the precipitation of ferrous ion and complex formation rate decreases with a sensible value [34,35].

### 3.6. Effect of mixing time

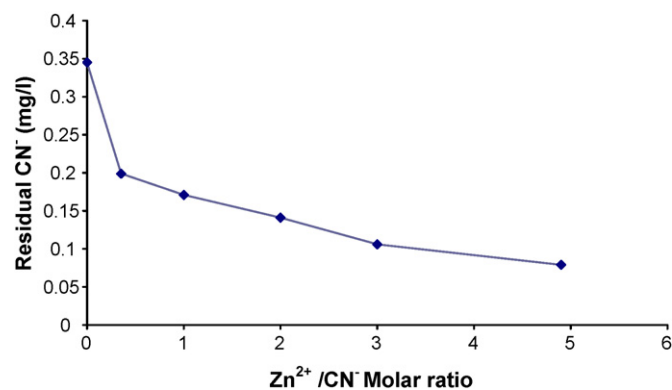
In this set of experiments, the mixing time was adjusted between 5 and 60 min. The concentration of cyanide in the solution was measured as a function of mixing time, and is shown in Fig. 5. Increasing the time of mixing increased the treatment process efficiency. The increase in time of mixing increases the contact time between the reactant species and the rate of collisions increases with time. The optimum value for treatment, in case of  $\text{CN}^-$  initial concentration of 105 mg/l, is 30 min of mixing. As will be shown later, longer time will be needed in case of treating solutions containing higher  $\text{CN}^-$  initial concentration.

### 3.7. Effect of temperature

In this set of experiments, the temperature was adjusted between 20 and 50 °C. The concentration of solution cyanide was measured as a function of temperature, and is shown in Fig. 6, which indicates that increasing the temperature of treatment process increased the cyanide removal efficiency, because the temperature



**Fig. 6.** Effect of reaction temperature on the residual cyanide ( $C_i(\text{CN}^-) = 105 \text{ mg/l}$ , mixing time = 30 min, mixing velocity = 1600 rpm,  $C_i(\text{Fe}^{2+}) = 60 \text{ g/l}$ ,  $\text{Fe}^{2+}/\text{CN}^-$  molar ratio = 0.96, pH 8).



**Fig. 7.** Effect of  $\text{Zn}^{2+}/\text{CN}^-$  molar ratio on the residual cyanide ( $C_i(\text{CN}^-) = 105 \text{ mg/l}$ , mixing time = 30 min, mixing velocity = 1600 rpm,  $C_i(\text{Fe}^{2+}) = 60 \text{ g/l}$ ,  $\text{Fe}^{2+}/\text{CN}^-$  molar ratio = 0.96, temperature = 20 °C, pH 8).

has a pronounced effect on increasing the fraction of collisions that are capable of generating energy in excess of that required to produce the activated state. Thus the rate of reaction increases with temperature.

### 3.8. Effect of $\text{Zn}^{2+}/\text{CN}^-$ molar ratio

In this set of experiments, the  $\text{Zn}^{2+}/\text{CN}^-$  molar ratio was varied between 0 and 4.9. The concentration of cyanide in the solution was measured as a function of  $\text{Zn}^{2+}/\text{CN}^-$  ratio. The stoichiometry of reactions (1)–(4) demands a  $\text{Zn}^{2+}/\text{CN}^-$  molar ratio of 0.167. The effect of variations in the  $\text{Zn}^{2+}/\text{CN}^-$  molar ratio on the treatment process is shown in Fig. 7. At  $\text{Zn}^{2+}/\text{CN}^-$  of 0 there is no  $\text{Zn}^{2+}$  ions to form complex with  $\text{CN}^-$  ions and at  $\text{Zn}^{2+}/\text{CN}^-$  ratios of 0.352 and higher, very low, permissible, cyanide concentration was detected in solution after 30 min of agitation. This means that the optimum ratio is more than two times the stoichiometric ratio, which shifts the reaction to the product side.

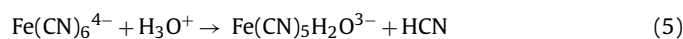
### 3.9. Effect of initial cyanide concentration

Optimum conditions have been applied for several  $\text{CN}^-$  initial concentrations. Two initial concentration ranges were investigated: (1) low range with  $\text{CN}^-$  initial concentration range between 10 and 50 mg/l and (2) high range with  $\text{CN}^-$  initial concentration range between 200 and 500 mg/l. The same treatment procedure was applied for all cases and then cyanide was measured. The results of the low-range concentration are shown in Fig. 8, while the results of the high-range concentration are shown in Fig. 9. As can be noticed from these figures, 30 min of mixing were enough to reach the permissible low level of cyanide concentration for the low range of initial concentration, while 120 min of mixing were essential to reach the permissible low level of cyanide concentration for the high range of initial concentration.

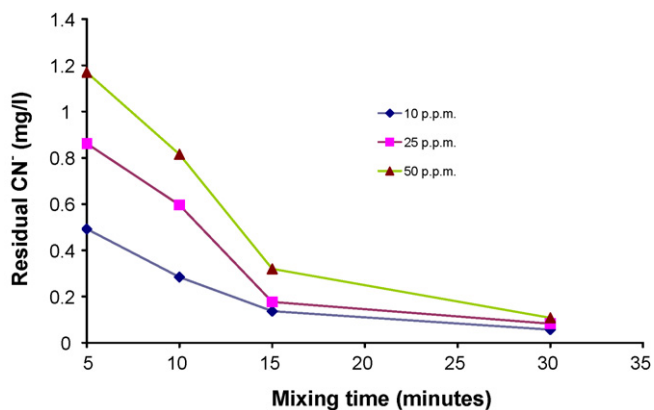
### 3.10. Chemical stability of insoluble complex

It was shown before that iron ferrocyanide,  $\text{Fe}_2(\text{Fe}(\text{CN})_6)$ , and sodium–zinc hexacyanoferrate  $\text{Na}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$  are the main insoluble complexes, which were formed during the removal of cyanide ions using ferrous sulfate. It has been reported [36] that the complex decomposed when contacted with low pH acidic solution, which should be taken into account in any process that places large amounts of complex underground.

The ferrocyanide ion is thermodynamically unstable in acidic solutions, with the following reactions illustrating acid attack:







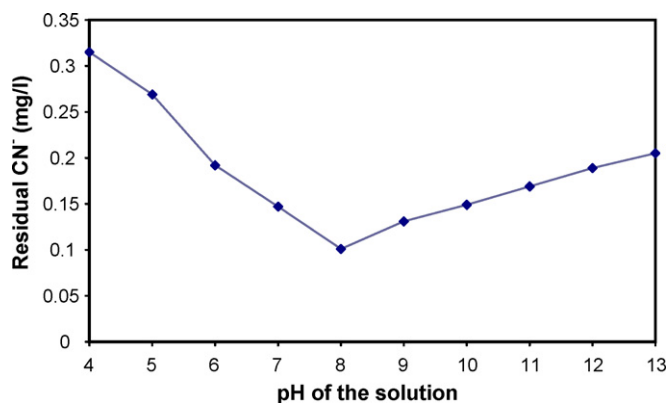
**Fig. 8.** Effect of mixing time on the residual cyanide for low range of initial cyanide concentration ( $C_i$  ( $\text{CN}^-$ ) = 10, 25 and 50 mg/l, mixing time = 30 min, mixing velocity = 1600 rpm,  $\text{Fe}^{2+}/\text{CN}^-$  molar ratio = 0.96, pH 8,  $\text{Zn}^{2+}/\text{CN}^-$  molar ratio = 0.352, temperature = 20 °C).



Willians [37] reported that these reactions, as well as the oxidation of ferrocyanide to ferricyanide, occur relatively rapidly in acidic solutions, particularly after exposure to light or heat. To measure the effect of pH on the solubility of the complex, 0.5 g of the dried complex was added to 1000 ml of distilled water. The pH of the solution was adjusted using  $\text{H}_2\text{SO}_4$  or NaOH and keeping it for a week. Then the concentration of cyanide was measured. The results are shown in Fig. 10. As can be noticed, there is some dissociation of the complex in solution. The released amount of cyanide was found to be minimum at pH 8, which can be attributed to the same explanation given before while studying the effect of pH on cyanide removal. Fortunately, the concentration of cyanide in solution remains within the permissible limits.

### 3.11. Treatment of a real wastewater sample

Optimum conditions for the treatment process have been applied for a real wastewater sample, which was obtained from a galvanic unit of a military factory. The wastewater sample contained 18 mg/l  $\text{CN}^-$  and 12 mg/l  $\text{Zn}^{2+}$ . The residual cyanide after treatment was analyzed according to the method previously discussed. The concentration of cyanide in the solution was reduced from 18.0 mg/l to 0.128 mg/l after 15 min of mixing, showing that this treatment is



**Fig. 10.** Effect of pH of the solution on the dissociation of the formed complex (temperature = 20 °C, time = 7 days, complex concentration = 0.5 g/l).

effective and sufficient. This real waste solution, after treatment, can be discharged directly to the sewer system according to the Egyptian Law decree 44/2000.

## 4. Conclusion

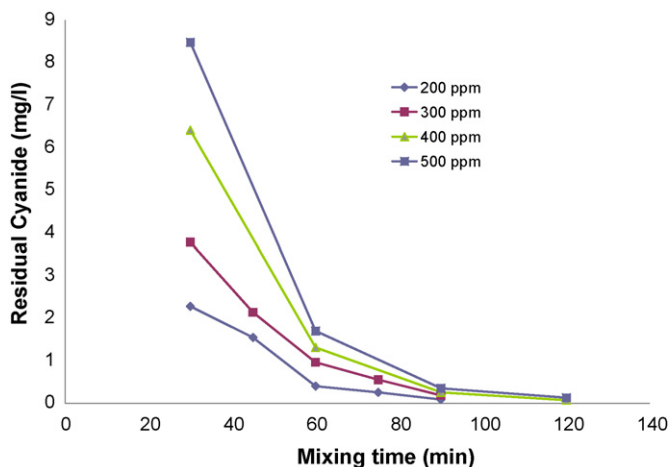
A simple straightforward addition process of  $\text{FeSO}_4$  was successfully used to treat cyanide-containing wastewater. The optimum conditions for the removal of cyanide by adding  $\text{FeSO}_4$  in the presence of zinc ions and the formation of zinc–sodium hexacyanoferrate were found to be at pH of 8,  $\text{Fe}^{2+}/\text{CN}^-$  molar ratio of 1, and mixing velocity of 1600 rpm. The optimum mixing time was found to be related to the initial concentration. As the initial concentration of cyanide increases, the mixing time needed to reduce the concentration of cyanide in the solution to the allowable limits for discharge increases. The increase in temperature was found to increase the cyanide conversion efficiency. The optimum conditions for treating the cyanide containing wastewater by the simple method of adding  $\text{FeSO}_4$ , after being determined, were applied to a real waste sample from galvanization plant. It was proven that this real wastewater, after the simple treatment process introduced in this study, can be discharged directly to the sewage system according to the Egyptian Law decree 44/2000.

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**Fig. 9.** Effect of mixing time on the residual cyanide for high range of initial cyanide concentration ( $\text{Fe}^{2+}/\text{CN}^-$  molar ratio = 0.96, mixing velocity = 1600 rpm,  $\text{Zn}^{2+}/\text{CN}^-$  molar ratio = 0.352, pH 8, temperature = 20 °C).

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