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Letter to Editor

Cyanide Removal from Industrial Wastewaters

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Abstract

Efficiency of the physical-chemical cyanide removal process from wastewaters flowing out of landfill sites generated in the course of pesticides production as well as from coke-making wastewaters has been estimated. Results of free cyanides removal in laboratory and industrial conditions by application of coagulation with iron salts (III) ($FeCl_3$; $Fe_2(SO_4)_3$), flocculation and additionally floatation for coke-making wastes have been discussed. Reactions of complexing and precipitation of cyanides with iron cations (III) or (II) depending on the pH value have been compiled. Results of free cyanides removal from wastewaters with application of sodium hypochlorite obtained in laboratory examinations have been provided.

Keywords: free cyanide, total cyanide, industrial wastewaters, cyanide complexes

Introduction

Cyanide are toxic chemical compounds present in industrial effluents generated by chemical, galvanic, metallurgical and coke industry. Due to their toxicity, it is necessarily to purify wastewaters containing cyanide before directing them to the receiving waters.

The term 'cyanide' [1], according to scientific English literature, refers to one of three classes of cyanide, and it is critical to define the given class of cyanide that is to be removed in a treatment plant. There are main categories of cyanide as determined based on analytical methods. The three classes of cyanide are: (1) total cyanide; (2) weak acid dissociable (WAD) cyanide; and (3) free cyanide as shown in Figure 1.

Total cyanide includes weak and moderately strong metal-cyanide complexes (WAD) with free cyanide and relatively non-toxic, strong cyanide complexes with iron. Cyanides' complex ions with metals are classified depending on bonding strength of the central atom (metal, cation) with ligand (anion CN^-). The notion of free cyanide relates to the most toxic cyanide compounds including only the uncomplexed forms of cyanide, which are the cyanide anion and molecular hydrogen cyanide.

The notion of free cyanide, in commonly applied Polish scientific terminology [3], relates to hydrogen cyanide (HCN), its salt (CN^-) and some metal-cyanide complexes of zinc, cadmium and partly copper. Different definitions of free cyanide determine conditions and procedures for cyanide analyses. It makes it impossible to execute the comparison of the analytic results obtained in country and abroad.

Cyanide treatment processes which remove cyanide from wastewaters are classified as either a destruction-based process or a recovery based process. Various procedures exist for treating cyanide and they comprise physical and/or chemical and also biological methods. These methods include membranous processes, distillation, adsorption, flotation and extraction. Cyanide destruction takes place also as a result of biological, catalytic, electrolytic, and chemical or photocatalytic oxidation. Cyanide treatment can also be conducted by complexation methods and precipitation of insoluble compounds. Reactions occurring during complexation and cyanide precipitation by means of ions of iron have been presented below.

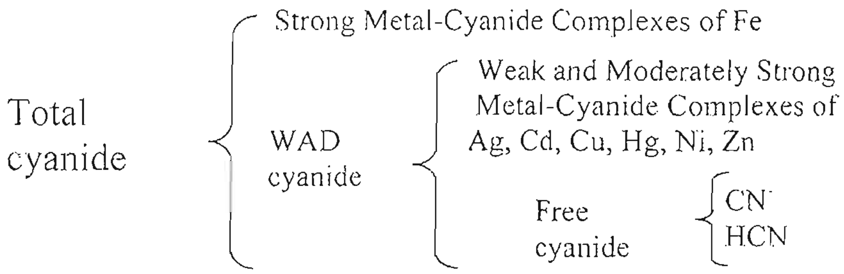

Fig. 1. Classification of cyanide compounds [2].

Cyanide reacts with iron ions forming different soluble and insoluble chemical compounds with lower toxicity than primary compounds. As a result of adding ions of iron (II) or (III) (ferrous (Fe^{2+}) or ferric (Fe^{3+}) cations) to cyanide solutions (depending on pH) the following complexes are formed: hexacyanoferrate (II) ion ($[Fe(CN)_6]^{-4}$) or hexacyanoferrate (III) ion ($[Fe(CN)_6]^{-3}$) in accordance with reactions (1) and (2).

for pH > 8.5 $Fe^{+2} + 6\,CN^- = [Fe(CN)_6]^{-4}$ (1)

for pH 5-6 $Fe^{+3} + 6\,CN^- = [Fe(CN)_6]^{-3}$ (2)

Furthermore, depending on pH reaction and oxidation degree of iron ions added or present in excess, the following insoluble complex iron salts can be created: iron (III) hexacyanoferrate (II) – $Fe_4[Fe(CN)_6]_3$ (Prussian blue), iron (II) hexacyanoferrate (II) - $Fe_2[Fe(CN)_6]$ (Berlin White), iron (III) hexacyanoferrate (III) - $Fe[Fe(CN)_6]$ (Berlin Green), iron (II) hexacyanoferrate (III) - $Fe_3[Fe(CN)_6]_2$ (Prussian brown). The process of forming insoluble complex iron salts takes place in accordance with the reactions presented below (3-6).

for pH = 3-4

$3[Fe(CN)_6]^{-4} + 4Fe^{+3} = Fe_4[Fe(CN)_6]_3\downarrow$ (3) [4]

$[Fe(CN)_6]^{-4} + 2Fe^{+2} = Fe_2[Fe(CN)_6]\downarrow$ (4) [4]

for pH = 3–5

$[Fe(CN)_6]^{-3} + Fe^{+3} = Fe[Fe(CN)_6]\downarrow$ (5) [5]

$2[Fe(CN)_6]^{-3} + 3Fe^{+2} = Fe_3[Fe(CN)_6]_2\downarrow$ (6) [2]

The ranges of pH for some reactions, discussed in the literature as well as in this paper, concern values for which the reaction proceeds in optimal conditions.

This publication is aimed at presenting the estimation of free cyanide removal process from wastewaters flowing out of landfill sites generated during pesticides production and also from coke plants wastewaters.

Experimental Procedures

Free cyanide removal from wastewaters of landfill sites

The out-of-service landfill site of wastes generated during pesticides production is drained and the effluent waters are passed through a drainage ditch. Part of the wastewaters (leachate waters without cyanide) is directed to postproduction wastewaters treatment plant. The implemented treatment technology consists in chemical pre-treatment cleaning (through coagulation and flocculation method) and adsorption on activated carbon [6]. The possibility of introducing an additional wastewaters stream – leachate waters contains cyanide to the existing wastewaters treatment plant was considered. This concept required confirmation of the possibility of cleaning them from pollutants in accordance with the technology applied.

Special attention was paid to free cyanide reduction, because their level in leachate waters exceeded the value permissible and acceptable by Polish legal regulations for disposal of industrial wastewaters to receiving waters (under 0.1 mg/dm^3). For that purpose, laboratory examinations of coagulation and flocculation processes for leachate waters (with reagents used in wastewaters treatment plant) as well as research of static and dynamic adsorption on activated carbon have been conducted. The possibility of free cyanide removal from leachate waters through sodium hypochlorite has been also examined.

Leachate waters susceptibility tests on iron (III) salts coagulation ($FeCl_3$, registered trade mark of Roflok S.C) and flocculation process supported by anion-polymer N71605 have been carried out according to JAR-TEST method. The amount of free cyanide in wastewaters used in laboratory examination equalled 0.91 mg/dm^3 (pH - 6.6). The best pollution removal results have been received using optimal Roflok S.C coagulant dose of 50 mg/dm^3 and 1 mg/dm^3 of flocculent N71605. Through those operations free cyanide content has been reduced to 0.43 mg/dm^3. Free cyanide removal rate in previously tested coagulant doses (50; 100 mg/dm^3) and flocculent doses (0.5;1 mg/dm^3) ranged between 45 and 53%. The most important fact is that the coagulation and flocculation process application cannot assure free cyanide removal to the permissible value (0.1 mg/dm^3).

For the examinations of static and dynamic adsorption on activated carbon F-200, wastewaters after coagulation and flocculation process was used. Activated carbon of this type did not adsorb free cyanide. Concentration level decreased from the value of 0.43 to 0.39 mg/dm^3 during laboratory examinations, but it does not depend on adsorption process, but rather on their tendency to volatilise.

Due to the fact that in laboratorial wastewaters cleaning technology simulation tests the sufficient level of removal of free cyanide was not obtained, another free cyanide removal technique was applied – oxidation through sodium hypochlorite (NaOCl). The tests consist in crude wastewaters chlorination with theoretical dose of NaOCl (1mg CN^- = 3.41 mg active Cl) as well as with a dose two and a half times larger. Free cyanide oxidation rates varied and equals: from 8% to 37% (using theoretical dose) and from 45% to 63% (using the 2.5x larger dose). In both cases, no satisfactory free cyanide level (under 0.1 mg/dm^3) in treated wastewaters was obtained.

Free cyanide removal from coke plant wastewaters

The coke plant wastewaters are characterised by varied content of organic and non-organic compounds like: phenols, cyanide, thiocyaniates, ammonias, sulphides, thiosulphates, chlorides, tares, oils, fatty acids, pyridine-alkalis, benzene derivatives, etc. Those wastewaters are multi-stage cleaned [7, 8], including mechanical removal of the insoluble pollutants, extractive dephenolisation, removal through free and bound ammonia distillation methods, and mechanical-chemical-biological treatment. For the sake of efficient and proper operation of biological treatment as well as for attaining high efficiency of wastewaters treatment, it is necessary to remove inhibitors from the wastewaters, since they have negative impact on activated sludge microorganisms. Those compounds contain for example: polycyclic aromatic hydrocarbons (PAH), diffused and dispersed coal tar remains, cyanide and sulphides. That kind of pollutants are partly removed before biological wastewaters treatment by physical and chemical methods, often called wastewaters pre-treatment.

The effectiveness of free cyanide removal in the coagulation, sedimentation and flocculation processes taking place in a pre-treatment unit has been described below.

The first step of the wastewaters treatment is coagulation and flocculation conducted in a slow and fast mixing chamber and then sedimentation of the suspended matter formed in a settling tank. In the coagulation process (pH was maintained around 5.5 – 6) was used the iron (III) sulphate of trade mark PIX 113 in the amount of 800 mg/dm^3 as a coagulant and flocculent -- polymer N71683 in the amount of 1.0 mg/dm^3. The free cyanide content in the inflow to the coagulation step varied between 24.9 and 33.11 mg/dm^3, while on the outflow from the settling tank, it was formed within the range of 3.72 to 11.99 mg/dm^3. The effect of free cyanide removal obtained remained within the range from 51.8 to 86.6 %.

The next step of wastewaters cleaning is flotation with dissolved air, also called pressure flotation. Flotation system consists of a blending chamber and a saturation and flotation tank. Reagents dosed to the blending chamber were as follows: organic coagulant N77135 ca. 20 mg/dm^3 dose and polymer N71684 ca. 1 mg/dm^3 dose, while directly before the blending chamber, also the iron (III) sulphate was dosed in the amount of 500 mg/dm^3. This process took place with pH similar to previous operations (coagulation, flocculation). As a consequence of the precipitation and suspendded particles distribution from the wastewaters as a result of the dispersed phase removal on the surface and constant floating sludge removal, consecutive free cyanide concentration reduction was obtained on the outlet of the flotation system. Concentrations of free cyanide in influent ranged between 3.72 and 11.99 mg/dm^3 and concentrations in effluent ranged between 1.96 and 6.59 mg/dm^3. The removal rates were moderate and ranged between 26.2 and 55.8%.

Discussion of Results

The results of free cyanide removal presented clearly show that there is a possibility of free cyanide concentration decreasing in previously described processes, i.e. iron (III) salts coagulation ($FeCl_3$; $Fe_2(SO_4)_3$), flocculation and (additionally for coke plant wastewaters) pressure flotation.

During the coke plant wastewaters coagulation process (PIX 113 in a number of 800 mg/dm^3) with the pH between 5.5 and 6, free cyanide complexation with ions of iron (III) (Fe^{+3}) (according to reaction (2)) proceeds. As a result of this complexation, hexacyanoferrate (III) ion ($[Fe(CN)_6]^{-3}$) is formed. This complex, with the presence of iron (III) ions (according to reaction (5)), created an insoluble salt of iron (III) hexacyanoferrate (III) - $Fe[Fe(CN)_6]$. Moreover, during this process (in the range of the optimal pH for correct coagulation with iron (III) salts), colloidal iron (III) hydroxide precipitates (in a floccules form) which absorbs undesirable organic contaminations (they can inhibit biodegradation processes). The coagulant iron (III) sulphate (PIX 113) contained insignificant amount of iron (II) ions (0.4% by weight). In accordance with this fact it was possible to form the insoluble iron (II) hexacyanoferrate (III) - $Fe_3[Fe(CN)_6]_2$ through precipitation of iron (II) ions with complex hexacyanoferrate (III) ion (according to reaction (6)).

A similar process of free cyanide complexing, using iron (III) chloride ($FeCl_3$) and then cyanide ions complexes precipitation process to their insoluble iron salts, takes place during laboratory examination of effluxents from wastewaters flowing out of landfill sites.

Activated carbon Chemviron F-200 (which was used in the static and dynamic adsorption) did not cause concentration reduction of free cyanide. Moreover, because of specific chemical composition of those effluents, the oxidation process of the free cyanide contained by means of sodium hypochlorite (NaOCl), proceeded with medium efficiency (average reduction of 50%) despite the fact that the amount of oxidant was 2.5 times larger than the stechiometric dose.

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