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Brief communication

Negative effects of cyanide on health and its removal options from industrial wastewater

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ABSTRACT

Water resource scarcity, population growth, pollution of surface and groundwater by discharging toxic wastewater and subsequent diseases may raise the necessity of reusing and treatment of wastewater. Cyanide is one of the toxic materials which can be found in some industrial wastewaters. Strict laws set by international bodies have forced industries to work on developing efficient cyanide removal processes. In addition, at short-term exposure, cyanide could result in rapid breathing, tremors and other neurological effects, but long term exposure it may cause weight loss, thyroid effects, nerve damage and death. Skin contact with liquids containing cyanide may also produce irritation and sores. The application of old methods like alkaline chlorination process has become limited due to toxic nature of intermediate and by-products, and unique methods, such as biological, the iron cyanide precipitation, SO_2/Air, acidification/volatilization and reneutralization, ion exchange and hydrogen peroxide processes are mainly developed and used by their respective companies. In this paper, the negative effects of cyanide on health and its industrial manufacturers as well as cyanide removal processes are briefly discussed.

Keywords: Cyanide, Removal, Industrial wastewater.

INTRODUCTION

The technical definition of cyanide is a triple-bonded molecule with a negative one charge, consisting of one atom of carbon in the +2 oxidation state and one atom of nitrogen in the -3 oxidation state.[1] Generally, cyanide compounds are present in environmental matrices and waste streams as free (HCN, CN^-), simple (Na, K, Ca, Zn, Cd and Ag salts of cyanide) and complex (weak, moderately and strong complexes with transition metals), inorganic (SNO^- and CNO^-) and organic (nitriles) cyanides.[2] At short-term exposure, cyanide could cause rapid breathing, tremors and other neurological effects, but at long term exposure it may cause weight loss, thyroid effects, nerve damage and dead. Skin contact with liquids containing cyanide may also produce irritation and sores.[3] Cyanide with the concentration of 0.05 mg/dl in blood might also result in poisoning and in the concentrations higher than 0.3mg/dl in blood leads to death.[4]

Cyanide can naturally be found in about 2000 sources. Humans are in close contact with cyanide in their daily life through food, drink, smoking, medicines and while using products which contain cyanide.[3] They are

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exposed to certain levels of cyanide due to smoking tobacco (0.5mg/cigarette), respiring exhaust from vehicles (7-9 mg/km), handling certain type of pesticides and insecticides and using cosmetics (e.g. eye blush and lipstick).[1] Some food products may either naturally contain cyanide or cyanide is used for their production. The concentration of cyanide per kg in certain food products has been observed as: salt (20mg/kg), lima beans (100-300mg/100g plant tissue), cassava (104mg/100g plant tissue), wild cherries (140-370mg/100g plant tissue), packed fruit juice (e.g., 0.03-15.84 mg/l in orange and sour cherry), sorghum (250mg/100g plant tissue), almond (297 mg/kg) and almond products (50 mg/kg). Varying quantities of cyanide may be found in other fruits and vegetables such as apricot, strawberry, apple, peach and cauliflower. Some drugs used for curing cancer and hypertension are made of cyanide and cyanide compounds.[1]

Cyanide is commonly found as a contaminant in water and wastewater from various industries including metal cleaning, plating, electroplating, metal processing, mining (extraction of gold, silver, etc.), coke plant, paint and ink formulation, petroleum refining, explosives manufacturing, case hardening, automobile manufacturing, printed circuit board manufacturing, chemicals, pesticides industries and synthetic fibers production and so on.[5] In addition, concentration of total cyanide from industrial wastewater placed in the approximately range of 0.01 to 100 mg/l; for example, in electroplating wastewater cyanide concentration is 15 to 100mg/l and in automobile manufacturing 10 to 250mg/l.[3,6]

To protect the environment and water bodies, effluent containing cyanide from various industries must be treated before discharging into the environment. The USEPA has proposed a limit for drinking and aquatic-biota waters regarding total cyanide which is 0.2 and 0.05 mg/l, respectively, where total cyanide refers to free and metal-complexed cyanides.[7] WHO and Iranian National Standards Organization have determined 0.07 mg/l cyanide in drinking water for standard maximum permissible concentration.[8,9] According to Iranian Environmental Protection Organization, cyanide disposal limit for discharging into surface water is 0.5mg/l and for draining to absorbent wells and agriculture is 0.1mg.[10]

Because of the above-mentioned and potential hazards associated with cyanide, control and remediation of cyanide-contaminated wastewater is usually desired. To reduce the cyanide level for disposal of effluent, several treatment systems have been developed. All these methods are based on cyanide recovery by acidification and/or destruction by chemical oxidation.[11, 12]

The following are mentioned as a brief description of some important removal techniques for cyanide:

- Biological treatment: Under anaerobic as well as aerobic conditions is possible. Aerobic conditions are preferred due to the toxicity of cyanides to methanogenic bacteria under anaerobic conditions. However, attached growth processes and combined processes such as oxic/anoxic proved advantageous for the cyanide detoxification. Some of the microorgamisms which are capable of degrading cyanide are: Kelbesillaoxitoca, Pseudomonas sp., Pseudomonas fluorescence, Citrobacter sp., Trichoderma spp., Fusariumoxysporum, Fusariymsolani, Bacillus pumilus, Stemphylium loti, Rhizipusoryzae, P. Acidovorans, etc.[13-15]

- Alkaline chlorination: Cyanide-containing waste is initially treated with chlorine or hypochlorite to produce cyanogen chloride, which is then hydrolyzed to form much less toxic cyanate at pH>11.

Furthermore, chlorination oxidizes the cyanate to NH3, CO2 and N2. On the other hand, excess hypochlorite is toxic and chlorine can react with organics to form chlorinated compound.[12]

- Hydrogen peroxide: In the presence of soluble Cu2+ catalyst CN- is oxidized to cyanate with H2O2 at pH 9.0 to 9.5. This method operates relatively easily but reagent is costly, and requires accurate measurement of H2O2 chemical dose.[12]

- SO2/air (INCO) process: In the presence of soluble Cu2+ catalyst CN- is oxidized to cyanate with SO2 at pH 8.0 to 9.0. Unlike hydrogen peroxide, this reagent is very cheap and is used over a wide pH range but this process adds sulfates to treated water or wastewater.[16]

- Ozonation: At pH 10.0 to 12.0, ozone with an electrode potential of +1.24v oxidizes CN- to cyanate and in excess, hydrolyzes to produce HCO3- and N2. Similar to H2O2, the cost of process reagent and equipment is high.[17]

- Anodic oxidation: In electro-oxidation, anode metals include graphite platinized titanium and cyanide reaction occurs directly, like 1 and 2 equation:

$$2CN^{-} \rightarrow (CN)_2 + 2e \quad (1)$$

$$(CN)_2 + 4OH^{-} \rightarrow 2OCN^{-} + 2H_2O + 2e \quad (2)$$

- Electro-chlorination: Cyanide oxidized electrochemically in chlorine-based solution. Chlorocyanogen gas is formed as an intermediate and chloride anions are regenerated and serve as catalysis. Temperature should be 40-500C and pH>11. In both of these processes post-treatment by a number of oxidation methods is required.[18]

- Electrodialysis: A potential is applied across two electrodes separated by a membrane permeable to cyanide. Cyanide is placed in the half containing electrode and diffused through the membrane and concentrated in the other half due to its negative charge. This process is efficient but costly.[19]

- Reverse osmosis: Pressure applied on the water to pass through a membrane, which is impermeable to cyanide. This method requires external pressure and power that make this method efficient but expensive.[20]

- Electrowinning: Cyanide complexes reduced to corresponding metals by applying potential across two electrodes immersed in the same solution. Reaction involves the reduction of anions at the cathode. This method is not useful at low concentration of cyanide.[11]

- Hydrolysis/distillation: CN- naturally hydrolyzes in water to form aqueous hydrogen cyanide and further volatilized to form hydrogen cyanide gas at high temperature and pressure, which is captured in absorption-scrubbing tower or vented to atmosphere. Production of hydrogen cyanide gas is one of the disadvantages of this process.[21]

- Acidification/volatilization and reneutralisation (AVR): Cyanide complexes acidified to pH<3. The produced HCN (g) is volatized and absorbed in NaOH and recycled. Metals are precipitated as hydroxides after renaeutralization. AVR requires high acid consumption and specially designed reactor while energy consumption is low.[22]

- Flotation: In ion flotation heteropolar surfactant, usually a cationic amine such as tricapylmethyl ammonium chloride, is added to react with anionic thiocyanate complexes to precipitate as an organic double salt.[12, 21]

- Iron cyanide precipitation: Addition of ferrous iron to react with cyanide to form a variety of soluble and insoluble compounds, which may be nontoxic and highly stable at pH 5.0 to 6.0. Precipitated solids are removed and disposed. This method is suitable for mining industry but disposal of precipitate is difficult.[23]

- Activated carbon: This method is used as packed bed systems with dilute cyanide concentration. Depending on the adsorption characteristic, adsorption of cyanide and metal complexes occurs on the bed. Activated carbon is applied only for low concentration of cyanide and sometimes pretreatment is required; however, this method is effective and efficient.[24, 25]

- Resin: Resins are polymeric beads containing a variety of source functional groups with either chelation of ion exchange capabilities. It is used in packed bed systems for adsorption of metal cyanide complexes but it is difficult to find suitable resin.[26]

- Catalytic oxidation: When adsorption occurs in the presence of oxygen, the carbon will catalytically oxidizes cyanide to cyanate and the presence of catalysts like Cu^{2+} or PbO_2 catalysis increase adsorption of cyanide, and in excess cyanide is hydrolyzed to form HCO_3^- and NH_3. This process is effective in presence of copper or other catalyst but this technology is still developing.[27]

- Caro's acid: Peroxymonosulfuric acid (H_2SO_5), known as Caro's acid used in slurry treatment applications (equation 3), where Cu catalyst is not desirable. This technology is not applicable to all type of site and has not been yet established well.[28]

$$H_2SO_5+CN^- \rightarrow OCN^- + H_2SO_4 \qquad (3)$$

- Photolysis: This enhances reduction/ oxidation reaction by providing energy from electromagnetic radiation to catalyze electron transfer process. Oxidation of CN^- occurs to form OCN^-, then NO_3- and CO_3^{2-} using UV/Visible light and semiconductor-type substrate, e.g., TiO_2, ZnO and CdS. Photolysis is an effective process since the removal process becomes complete and in the reaction, no undesirable by products is formed; however, this process operates difficultly and requires high energy.[27]

CONCLUSION

According to the methods explained for cyanide removal, the application of old processes like alkaline chlorination has become limited duo to toxic nature of by products and unique methods, such as biological process and the iron cyanide precipitation processes, are mainly developed and used by their respective companies. In addition to the conventional SO2/Air process, AVR and ion exchange processes have been receiving worldwide attention. The application of hydrogen peroxide has been increasing, as well. Investigations for development of new processes have been ongoing. In arid climates, evaporation is used to obtain zero discharge. Since the cost of reagents and the degree of required treatment may vary from site to site, cyanide treatment costs are site specific. Some processes may require high capital costs and may provide lower operational costs (e.g., reagent cost, energy and maintenance requirements), while some processes can be implemented to a site with small capital costs, but operation of using these methods might be expensive. During the project planning stage, cost-benefit analyses should be conducted for potential alternative treatment methods to determine the most appropriate process for a given site.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interests.

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