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Review Article

EVALUATION OF VARIOUS METHOD AND EFFICIENCIES FOR TREATMENT OF EFFLUENT FROM IRON AND STEEL INDUSTRY—A REVIEW

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This study reviews waste water characterization of iron and steel industry and treatment procedures involved in these industries. The production of iron from its ores involves powerful reduction reaction in blast furnaces. Cooling waters are inevitably contaminated with products especially ammonia and cyanide. Production of coke from coal in coking plants also requires water cooling and the use of water in by-products separation. Contamination of waste streams includes gasification products such as benzene, naphthalene, anthracene, cyanide, ammonia phenols, cresols together with an array of more complex organic compounds known collectively as Poly Aromatic Hydrocarbons (PAH). Different treatment techniques has been utilised in order to reduce pollution mainly caused by organic compounds and aromatics. These techniques were UV-photolysis, hydrogen peroxide and ozone oxidation, electro-oxidation, etc. The efficiency of the combination between bioreactors and UV process was also tested.

Keywords: Iron and steel, PAH, COBP, BOD, Oxidation techniques

INTRODUCTION

In an Integrated Iron and Steel Industry, wastewater generated from Coke Oven by-product Plant is considered to be the most polluting. This wastewater contains toxic chemicals like phenol, cyanide and ammonia, which are harmful to the receiving water bodies when discharged untreated/partially treated (www.steel.gov.in).

In recent years, due to increasing water scarcity, stringent regulation and public awareness, the industry is in the process of upgrading or installing new wastewater treatment methods for proper treatment of wastewater. The major water polluting units are the coke-ovens and bye-product plants from which highly contaminated toxic wastewater containing phenol and cyanide is generated. Other effluents contain high amounts of oil, grease and BOD. Among the wastes from all the operational units, spent liquor from ammonia stills, is the most polluting.

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The type of effluent generated in the steel industry depends upon the process of the product and byproduct. However, the generated effluent can be controlled by adopting latest techniques. Following are the various units from where effluent is generated in the steel industry.

PIG CASTING

While casting pig iron, heavy lime solution is sprayed on the moulds of the pig casting machine to prevent sticking of pig iron in the moulds and to ensure release of it after the metal has solidified and the moulds are inverted. Water is sprayed on the moulds and pigs for cooling. This cooling water contains solid particles (scale and sand with high settling velocity). The wastewater from the casting machine is led to the settling pits for removal of solids and effluents with high pH (around 10) are either-recycled after-correction of pH or discharged.

STEEL MAKING

In the electric arc furnace process, the collected gases are ducted to Bag house/wet scrubber/ESP. Water is used for cooling the furnace and certain components of the electric gear. This water leaves the furnace at a higher temperature. Suspended solids in the water are in the range of 1000-5000 mg/l. Where wet scrubbers are used, process water is piped to thickeners where suspended solids settle down and clean water is recycled.

In Continuous Casting process, the wastewater is produced in the apron spray zone and machinery cooling is normally contaminated with mill scale and oil leakages from the machinery. This water is treated in scale pits where scale and oil is removed. In hot and cold rolling operation, the primary rolling mill effluent containing scale and debris (10 to 20 mesh size) at 100-200 mg per liter and oil at 10-25 mg per liter drop into the flumes below the stands. Some oil also sticks to the scale. Otherwise, it is non-emulsified.

The wastewater from Secondary Mills is very similar to that of primary mills which contains mostly scale from the rolling operations and some oil as leakage from the machinery. The wastewater from pickling operations contains strong spent solution, rinse water and water used in fume scrubbers. Water used in fume scrubber is generally encountered when acid other than sulphuric or phosphoric is used as an industrial cleaning hygiene measure.

In the Coating process, the wastewater originating varies considerably depending on the plating material used. The spent solution and rinse water are the main sources of wastewater. Besides, effluents containing harmfull pollutants are also generated from coke oven byproduct plants.

IMPACT OF STEEL INDUSTRY EFFLUENTS ON WATER BODIES

The major pollutional effects of the untreated wastewaters of steel industry if discharged into the receiving water bodies are: toxicity to aquatic life, reduction of D.O., silting due to suspended solids, taste and odor problems, temperature rise affecting the dissolved oxygen and aquatic life and formation of oil slicks due to floating oil. Toxicity to aquatic life due to ammonia, phenols (monohydric, Polyhydric and derivatives of phenols) and cyanide is well known. With the rise of pH value, the concentration of free ammonia increases. Hence, ammonia toxicity is particularly severe at high pH. Due to discharge of biodegradable organic substances from COBP plant into the water bodies, the soil and water bacteria utilize the organic matter as source of carbon and Dissolved Oxygen (DO) in the water for the respiration requirement. Considerable quantities of suspended and colloidal matter in the discharge reduces the penetration of sunlight, resulting in reduction of photosynthetic activity, an essential feature of self purification of polluted water bodies. Suspended and colloidal matter can also smother bottom dwelling aquatic organisms affecting the life of water bodies/streams and may lead to heavy siltation which affects the flow. Entrapped oil and grease from the effluent lead to formation of ugly oil slicks and iridescent, colour which cause poor aesthetics. Oil slicks also reduce the diffusion of oxygen from the atmosphere to water affecting self purification. Where steel plants are located on the coasts, wave action invariably brings back oil and grease to the shore and spoil the beaches. Coal-tar from coke oven and byproduct plants creates maximum physical problems. Light tar floats on water and attaches itself to anything on its way giving an ugly appearance and heavy matter settles down choking the pipes and cavities in waste treatment units. Phenolic substances in coke oven wastewater are known to create taste and odor problems even at 0.002 mg/l level when chlorinated. Fish living in water containing non-toxic level of phenol are found to be affected. Soluble iron and manganese are known to give rise to bad taste in drinking water even at 0.1 mg/l. Hot uncontaminated effluents in steel plants can reduce DO level and decrease the solubility of oxygen. Nearly 2/3 of water consumed in steel plants is used for heat exchange only and requires' no treatment except cooling. This water should be segregated, cooled and recirculated recalculated (Comprehensive Industry Document Series, 1998; and Industrial Waste Water Treatment).

TREATMENT

In an Integrated Iron & Steel Industry (IISI), wastewater generated from Coke Oven Byproduct (COBP) Plant is considered to be the most polluting stream. This wastewater contains toxic chemicals, like phenol, cyanide and ammonia, which are harmful to the receiving waterbodies when discharged untreated. Realizing the adverse impacts on the receiving environment, the pollution control authorities have notified discharge norms exclusively for COBP wastewater, as shown in Table 2.

In recent years, due to increasing pressure from pollution control authorities, the industry has responded by upgrading or installing new wastewater treatment plants. In existing plants, this COBP wastewater is treated by biochemical oxidation of cyanide, ammonia and phenol. These Effluent Treatment Plants are commonly known as Bio-chemical Oxidation and dephenolisation plants or BOD plants. Apart from treatment, it is also necessary to mi minimize discharge of wastewater and concentration of pollutants at the source itself. Different oxidation techniques has been utilised in order to reduce pollution, mainly cased by organic compounds,

Table 1: Toxic Effects Caused by Various Pollutants Generated from Effluent of Iron and Steel Plant

Class of Pollutant	Notes	Toxic Effect	Dysfunction
Heavy Metals	70 friendly trace element, likes iron and zinc, but 12 poisonous heavy metals, such as lead, mercury, cadmium, nickel	Poisonous interference to the enzyme systems and metabolism of the body	Blood and cardiovascular, eliminative pathways, endocrine, energy production pathways, enzymatic, gastrointestinal, immune, nervous, reproductive, and urinary system
Aromatics Compounds	Molecular weight aromatics are less toxic than higher molecular weight PAH. This is directly linked to the ability of compounds to bioaccumulate	PAH have different type of toxic action, depending on the compound, the exposure (acute or chronic), the organism and the environmental compartment	Non-polar narcosis, phototoxicity, biochemical activation that, in turn, may result in mutagenicity, carcinogenicity and teratogenicity
Surfactants	Increase the apparent aqueous solubility of PAHs and other hydrophobic compounds by micellar formation	Enhance the bioavailability and stimulate the biodegradation of PAHs	Negative impact on the survival of heterotrophic nanoflagellates and ciliates at very low concentrations
Cyanides	Readily diffusible through epithelium, the routes of cyanide excretion are formation of SCN (major) or CNO (minor)	Toxicodynamic effects can vary depending on the dose, route and speed of administration, chemical form of the cyanide, and other factors including the physical condition of the recipient	Lethal toxicity after inhalation of hydrogen cyanide gas, ingestion of cyanide salts or cyanogens, or percutaneous absorption of cyanide from high-concentration solutions; affects many functions in the body (i.e., vascular, pulmonary, central nervous, cardiac, endocrine)
Fluorides	Is readily absorbed, concentrates where calcium is found in the largest amounts	Intake of 20-40 mg/day can inhibit the important enzyme phosphatase	Osteoporosis and arthritis, cancer, infertility, brain damage, hip fractures

Source: European Commission (2008)

aromatics. These techniques were UV-photolysis, hydrogen peroxide and ozone oxidation, electro-oxidation. Advanced oxidation techniques have been tested on untreated coke-oven wastewater and demulsification splitting plant discharge. Main aim of the application of the oxidation treatment process on coke oven wastewater was the reduction of PAHs under Law limits:

UV-Photolysis and H_2O_2 Oxidation: different percentage of COD reduction (15-40%) have been obtained depending on pH, time of photolysis or H_2O_2 concentration. Variation of solution colour and precipitation of solids were observed during the trials. No additional effect has been observed combining these two techniques. High concentration of H_2O_2 are necessary to reach high PAHs removal.

Table 2: Integrated Iron and Steel Plant: Wastewater Discharge Standards [2]

S. No.	Coke Oven Byproduct Plant Parameter (mg/l)	Concentration in mg/l Except pH (Not to Exceed)
1.	pH	6-8
2.	Suspended Solids	100
3.	Phenol	1
4.	Cyanide	0.2
5.	B.O.D, 3 day 27 °C	530
6.	COD	250
7.	Ammonia Nitrogen	50
8.	O&G	10

Source: Comprehensive Industry Document series (1998)

By Ozonolysis: COD reduction value higher than 40% have been obtained after 6 hour working with a ozone concentration $\geq$ 5.6 g/h. Variation of solution colour, precipitation of solids, formation of fumes and foam were observed: humic acids have been judged to be the cause of these phenomena.

H_2O_2-O_3 and UV-O_3 Oxidation: The synergic effect of both techniques reduced the COD more than the single ozonolysis (after 3 h, COD reduction was respectively 45% and 37% respect 22% obtained with single ozonolysis).

Trials have been conducted utilising activated carbon for adsorbing PAHs from coke-oven wastewater. Although results showed high removal efficiency, the total hydrocarbon concentration still remained higher than law limit for water discharge in river, so the combination with oxidizing techniques is recommended.

In order to reduce organic compounds concentration in untreated demulsification wastewater and to enhance their biodegradability, the following techniques have been tested which are as follows (European Commission, 2008):

- UV-photolysis: only a DOC-reduction of 8% was determined,
- H_2O_2 oxidation: 0.1% and 1% of hydrogen peroxide have been utilised but no effects on biodegradability increase were obtained.
- Electro-oxidation: because of the gas formation, the addition of an antifoaming agent was necessary. DOC reduction 16% was determined after 18 h of electro-oxidation.

The best performance, in terms of increased biodegradability, has been obtained with the combination between bioreactor and UV.

The effluents from coke-ovens and by-product plants are treated by biochemical oxidation of cyanide, ammonia and phenol. The treated effluent from BOD plant may be recycled for use in quenching hot coke in coke-ovens. The two most common processes used for the treatment of CO effluents are trickling filter and activated sludge process. Complete Mixed Activated Sludge System (CMASS) is also used for the treatment. The CMASS operates at low substrate concentration and hence can tolerate the toxic waste.

Wastewater management in COBP involves, firstly, reduction in pollutant load in process wastewater and, secondly, proper operation and maintenance of the BOD plant to obtain the desired performance. Treatment of COBP wastewater is achieved by giving physico-chemical (primary treatment), followed by biochemical treatment.

The primary treatment consists of equalisation and physico-chemical separation of suspended, dissolved or emulsified oils and tar. Biochemical treatment is given in Activated Sludge Process (ASP) or Trickling filters. The biological treatment is achieved in multiple stages to meet the prescribed norms. The performance of BOD plants depend on proper design, inlet concentrations of pollutants, type of treatment units, operation and maintenance, availability of trained manpower, etc. These wastes can be treated in admixture 50-50 with raw sewage with a view to bring the toxicity of phenol to acceptable levels. It can also be treated biologically without addition of sewage but it is advisable to dilute it with water or some non-toxic wastes so as to keep the phenol level less than 200 mg/l and preferably below 100 mg/l. For destruction of phenol, activated sludge process is commonly adopted. Although earlier investigations showed that high rate trickling filters resist shocking loads (hydraulic as well as organic), recent findings have proved that in the case of toxic it is the Complete Mixed Activated Sludge System (CMASS) that can best resist shock loadings as it has tendency to equalize flows as well as concentrations. The CMASS operates at low substrate concentration and hence can tolerate the toxic waste better. The conventional activated sludge system working on plug flow basis is likely to be more effective than the high rate trickling filters. Extended aeration activated sludge system which normally works on CMASS principle would operate best as the organic loading is usually low and there is much higher microbial mass per unit of toxic matter fed to the unit. For biological treatment, wastewater is to be cooled if it is hot. It should be ensured that nutrients required by the micro-organism are available.

CARBON TREATMENT METHOD

Trace concentration of phenol from wastewater from COBP can be removed by adsorption on granulated carbon. This process can be directly applied to undiluted effluents from the ammonia still, final cooler blow down, light oil decanter liquor and fractional ion condensate without previous biological treatment. In addition, all the streams which have been bio-treated and diluted can further be carbon treated. Therefore, carbon treatment is either an alternative or an adjunct to biological treatment. Efficiency of carbon treatment in comparison to bio-treatment is furnished in Table 3 (Industrial Waste Water Treatment).

Table 3: Efficiency of Carbon Treatment to Bio-Treatment

Parameters	% Efficiency of Untreated Stream	Removal Biotreated Stream
BOD	80	72
Phenols	90	81
Cyanide	90	81
Ammonia	0	0
Suspended Solids	90	81
Sulphide	100	90
Oil	90	81

TAR AND LIQUOR PLANT

The tar and liquor plant handles the flushing liquor that circulates between the byproduct plant and the coke oven battery. It also processes the wastewater that is generated by the coke making process and which results from coal moisture and chemically bound water in the coal. The flushing liquor flows into tar decanters where the tar separates out from the water and is pumped to storage for later sale. Heavier solid particles separate out from the tar layer and these are removed as Tar Decanter Sludge (TDS). The aqueous liquor is then pumped back to the battery, with a portion bled off from the circuit which is the coke plant "excess liquor" or waste water. This contains ammonia and, after the further removal of tar particles, it is steam stripped in a still. An alkali such as sodium hydroxide is added in the still to decompose ammonia compounds dissolved in the liquor. The ammonia vapor from the still is then either fed into the coke oven gas upstream of the ammonia removal system, or the still itself is often integrated into the ammonia removal system. Either way, the ultimate fate of the ammonia removed from both the coke oven gas and the waste water is the same. The stripped still effluent is either discharged to a municipal seweror it can be treated in an on-site biological effluent treatment plant to remove residual ammonia, phenol and cyanides (The Coke Oven).

CONCLUSION

In conclusion, the review on different type of iron and steel making wastewater has highlighted that the most abundant pollutants are heavy metals and organic compounds especially PAHs, oils and surfactants. Significant concentration of cyanides and fluorides have been also found respectively in coke-oven wastewater and pickling spent bath.

Various oxidation techniques coupled with activated carbon treatment found quite effective in PAH reduction. Concerning demulsification splitting effluents, single biological treatment has obtained a maximum DOC reduction 70%) and its combination with the UV-photolysis has obtained a maximum DOC reduction 87%).

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