Characterization of coke oven wastewater

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Abstract. During manufacture and processing of iron in iron and steel industry various wastewaters are generated, out of which the coke oven wastewater is contemplated to be the most toxic byproduct. Untreated discharge of coke oven wastewater to environment will increase the contamination and may threaten the flora and fauna. Physico-chemical characterization is required to assess the pollution level and to identify the treatment method. In the present research work, coke oven wastewater was collected from iron and steel plant and various physico-chemical characteristics were studied. The study found that concentrations of BOD₅ (73.13 mg/l), COD (540.25 mg/l) and cyanide (27.9 mg/l) exceeded the tolerance limit as per IS: 2490 effluent water standard (inland surface water). Biological treatment may supersede the conventional technologies for safe disposal to inland surface water.

1. Introduction
The Steel and Iron industry is one of the most energy consuming sector of the Indian economy and is scrutinized both locally and globally. In the last decade the production of steel in India has surged by a growth rate of 8% compounded annually [1]. India is 3rd largest producer of steel and largest producer of sponge iron in the world. The world produces 1630 million tons of steel annually of which India contributes 91.46 million tons [2]. In India relatively large quantity of water is consumed to produce steel as compared to developed countries. The reason is for high usage of water is coke; a major component for producing steel consumes around 4000m³ of freshwater for producing 1000 ton of coke. The whole process at the end produces over 1000m³ of extremely hazardous wastewater [3].

The rising demand of steel due to speedy urbanization occurring in the developing world has established a huge demand for metallurgical coke. Carbonization of Coal generates gas and other by-products such as anthracene, toluene, naphthalene, benzene and coal-tar products which comprises the unprocessed materials for the production of various drugs, synthetic dyes and explosives [4]. The effluent produced from the quenching of coke contains large quantities of organic and inorganic pollutants, such as ammonium, sulphate, cyanide, thiocyanate, phenol and polycyclic aromatic hydrocarbons (PAHs) [5]. Due to the complexity in removing the organic matter, treated wastewater discharged from the steel plant cannot achieve the required effluent standard; hence the released effluent becomes an objectionable matter [6].

The coke plants produce polluted effluent generated due to washing of the ammonia stills, which accumulates from the gas coolers as a result of condensation/ sedimentation. The effluents contain cyanide, phenol, ammonia and sulphide which are very toxic to the marine life. The indissoluble pollutants mostly from tar; form a layer in the surface which obstructs the contact of oxygen with air.
Fine suspended particles choke the respiratory organs of fish making it unsuitable to survive. Heavy suspended particles get settled on the bottom of stream and source for further pollution. Inadequate dilution, pyridine, free lime and thiocyanates can also have far-reaching problems to the marine life. Most of the dissolved oxygen (DO) is used up by sulphur compounds, mainly sulphides which also have direct hazardous impacts on aquatic life. Oil and grease form oil slimy which limits the dispersal of oxygen from air into the water [7].

Various probes have indicated that biological treatment can be used to remove organic pollutants in colossal quantities from the wastewater at comparatively very low cost [8]-[12]. However, the biodegradation is very slow and time consuming. Pre-treatment studies [13], [14] like steam chemical coagulation, sludge concentration, stripping, aeration, settling and sometimes dilution under non-identical conditions (anaerobic, anoxic and aerobic) have been used to reduce unfavourable impact on environmental conditions. Treatment of wastewater comprising different combinations of thiocyanate (SCN⁻), ammonia-nitrogen (NH₄⁺–N), cyanide (CN⁻) and phenol compounds is very tough since the contaminants resist the effective removal of each other.

Wastewater can either be reused or recycled through proper wastewater management. Due to rapid increase of population, industrialization and urbanization the accessibility of fresh water had decreased drastically. Hence an honest wastewater management approach is the need of the hour. The new perspective should be focused on enhancing sustainable treatment technologies. Detailed physiochemical and bacteriological characterization is required for identifying the best and optimized treatment for coke oven liquid waste and its proper disposal.

Present study was performed to know the concentration of different organic and toxic parameters of coke oven wastewater. As biological treatment is the least cost method for the treatment of large volume of coke wastewater, we proposed for an attached growth bioreactor i.e. rotating biological contactor system (RBCs). RBC systems are comparatively easy to operate, using discs on a rotating shaft that provide a partially effluent-submerged surface that supports biofilm growth responsible for the degradation of the organic compounds in the wastewater[15].

2. Monitoring protocol

2.1. Sampling site

The effluent collected from coke oven plant is located in Rourkela (22° 26’ 04” N, 84° 85’ 36” E), India. The plant uses water from river the Brahmani and discharges its effluents to the same. Coking temperature ranges from 1050–1100°C for coking hours: 18-20 h.

2.2. Sample collection

Five litres of liquid effluent was collected in morning hour (10-11am) of every week and brought to the laboratory in a plastic jar. Total five numbers of samples were collected. Temperature and pH were performed immediately. The remaining wastewater was properly marked and preserved in the refrigerator at 4°C for further physico-chemical characterization summarized in Table.1. The wastewater sample was acidified by adding H₂SO₄ and alkaline by adding 1N NaOH for testing of phenol and cyanide concentration where the pH targets 3.9-4. The samples were kept for COD determination by 2 ml/l of H₂SO₄ and were examined following the methods [16].

2.3. Analytical methods

Potassium buffer was used for the chemical analysis in order to maintain the pH constant at the required value and phenol standard (Merck). Deionized water was used during experimental steps. All chemicals and reagents used for various physico-chemical analyses were purchased from Merck and Himedia. The physico-chemical tests were conducted using the untreated coke oven effluent samples. Colorimetric method was used to estimate the phenol content from the effluent sample using 4-aminoantipyrine method. Phenol reacts with 4-aminoantipyrine in the presence of potassium ferricyanide to form a coloured antipyrine dye. Chloroform extracts the dye from aqueous solution. The absorbance of the extract was measured at 460 nm using Perkin Elmer make UV VIS Spectrophotometer. Pyridine barbituric acid colorimetric method was used to verify the amount of
cyanide in the effluent sample. The absorbance was read at 578 nm for the complex developed with pyridine-barbituric acid reagent and CNCl. All the procedures followed for the analysis were as per the accordance to the standard [16]. Metallic species of coke oven effluent were determined by using atomic absorption spectrophotometer (Perkin Elmer, AAnalyst 200).

2.4. Data analysis
In this research work, physico-chemical characterized data were used to study spearman rank correlation analysis investigates the relationship among them with the help of software IBM SPSS 24 shown in Table 2. The spearman rank correlation coefficients were determined to measure the relationship between two variables.

3. Results and Discussion
Total 5 numbers of samples were tested for physico-chemical analysis. The procedures followed for analyses were as per the accordance to the standard [16]. The pH of the effluent was found to be moderately alkaline in nature and ranges from 8.2 to 8.5 with an average value of 8.35. The COD concentration of the effluent also exceeded permissible limit of 250 mg/l as per IS code [17]. High value of BOD demonstrated the existence of biologically degradable substances. A high value of dissolved solid content was found as compared to raw water indicating contamination by inorganic salts. Dissolved solid in the effluent was found as 1035 mg/l. The average concentration for phenol and cyanide exceeds the tolerance limit which is 1mg/l and 0.2mg/l, respectively as summarized in Table 1. Mercury, arsenic and iron dominate the metallic species.

| Table 1. Characterization of coke plant effluent |
|-----------------------------------------------|
| Parameters         | Min. value | Max. value | Average | Tolerance limit, IS: 2490 Effluent |
|-------------------|------------|------------|---------|----------------------------------|
| pH                | 8.2        | 8.5        | 8.35    | 5.5-9                            |
| Temperature       | 30 °C      | 33 °C      | 31.5 °C | 40 °C                            |
| BOD <sub>3</sub>  | 63.92 mg/l | 82.34 mg/l | 73.13 mg/l | 30 mg/l                        |
| COD               | 436.7 mg/l | 643.8 mg/l | 540.25 mg/l | 250 mg/l                       |
| Dissolved Solids  | 943.2 mg/l | 1128.4 mg/l | 1035.8 mg/l | 2100 mg/l                      |
| Phenol            | 170.27 mg/l | 192.34 mg/l | 181.30 mg/l | --                             |
| Cyanide (CN<sup>-</sup>) | 25.6 mg/l | 30.2 mg/l | 27.9 mg/l | 0.2 mg/l                      |
| Total Hardness    | 428.7 mg/l | 440.2 mg/l | 434.45 mg/l | --                             |
| Mercury(Hg)       | 28.9 µg/l | 31.08 µg/l | 30.35 µg/l | 10 µg/l                        |
| Lead(Pb)          | 0.031 µg/l | 0.065 µg/l | 0.048 µg/l | 100 µg/l                       |
| Arsenic(As)       | 10.65 µg/l | 15.74 µg/l | 13.19 µg/l | 200 µg/l                       |
| Iron(Fe)          | 0.743 µg/l | 1.338 µg/l | 1.04 µg/l | --                             |
| Zinc(Zn)          | 0.013 µg/l | 0.028 µg/l | 0.020 µg/l | 5000 µg/l                      |
| Nickel(Ni)        | 0.048 µg/l | 0.053 µg/l | 0.050 µg/l | 3000 µg/l                      |

Coke plant effluent consists of huge amount of suspended solids. After quenching the coke, huge quantity of effluents are generated that mainly constitute suspended coke breeze [18]. At the discharge point, river water was found to be turning black due to deposition of coke breezes. So, along with surface water pollution and siltation on the riverbed, a large quantity of valuable coke breeze is being lost every day [19]. Various environmental circumstances will increase the toxicity of phenol. The toxicity level of phenol increases due to lower concentration of dissolved oxygen, increased salinity and increased temperature [20]. High BOD, COD, phenol contents of effluent is prompting acute surface water pollution. The test results unveil that proper treatment of coke oven effluent and strict adherence of the norms is required before discharging to surface water bodies.

After identifying the different parameters present in coke oven wastewater, a low cost biological treatment method for the better removal of the organic pollutants can be proposed.
Spearman rank correlation (Table 2) shows significantly good correlation between phenol and COD. Cyanide shows mainly inverse correlation with other physico-chemical parameters.

Table 2. Spearman rank correlation matrix between different parameters present in coke oven wastewater

|          | pH      | Temperature | BOD     | COD       | Phenol   | Cyanide |
|----------|---------|-------------|---------|-----------|----------|---------|
| pH       | 1       | 0.162       | 0.359   | 0.289     | 0.162    | -0.379  |
| Temperature |       |             |         |           |          |         |
| BOD      | 1       | -0.527      | -0.73   | -0.667    | -0.111   |         |
| COD      |         | 1           | 0.205   | 0         | 0.527    |         |
| Phenol   |         |             |         | 1         | -0.892*  | -0.46   |
| Cyanide  |         |             |         |           | 1        | -0.667  |

*Correlation is significant at the 0.05 level (2-tailed)

Spearman rank correlation has performed between different parameters such as pH, temperature, BOD, COD, Phenol and cyanide to identify the relationship and common sources between them. In this study the effluent is collected from coke-oven plant. This correlation analysis will help to determine dependency on existence for parameter. It is one of the vital step to select its appropriate treatment method as removal of one parameter shows the possible removal of related parameter.

4. Conclusion

The physico-chemical characterization was analysed using real coke oven wastewater collected from steel plant. Most of the physico-chemical parameters such as COD, BOD, Phenol and Cyanide concentration exceeded the limit prescribed for disposal on inland surface as per IS code [16]. There is a need to identify the low cost eco-friendly technology to treat the coke oven wastewater for its further disposal or reuse.

5. References

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