Characterization of coke plant effluent by lysimeter test to evaluate safe disposal to land

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Abstract. The importance of coal carbonization industries is evolving with great interest from the national point of view. In coke ovens, naturally found coal is converted to coke suitable for metallurgical industries. Enormous quantities of liquid effluents produced contain suspended solids high in COD, BOD, phenols, ammonia, and other toxic substances disposed into the water bodies without proper treatment contamination of the aquatic ecosystem. A large coke plant of Steel Authority of India Limited (SAIL) at Rourkela Steel Plant (RSP) has been surveyed for this purpose, and the impact of its effluent on surface water quality is discussed in this paper. The study found that concentrations of BOD, COD, total suspended, and dissolved solids have exceeded the tolerance limit as per I.S.: 2490 effluent water standard (inland surface water). Column lysimeters were prepared by collecting soil from the National Institute of Technology (NIT) campus, Jhirpani riverside, Mandira Dam side, putting it layer-wise into a column, and compacting it carefully to put on the original in-situ conditions. Raw effluents, diluted effluents, and water (as a blank) were applied to the three lysimeters twice a week with a 5cm inundating. The impact of raw and diluted effluent on groundwater quality and soil is also studied and discussed in this paper. The study found that the RSP soil sample and NIT campus soil sample were found more efficient for the disposal of effluents, and it is estimated that 2.73 hectares of land can be irrigated with effluents of the coke plant without deteriorating groundwater and soil quality.

1. Introduction
Coke is produced in coke plants for metallurgical purposes, and in the process of conversion, gas is produced as a by-product. These are responsible for the entire supplies of toluene, benzene, naphthalene, anthracene, and other coal tar products in India, constituting raw materials for manufacturing synthetic dyes, drugs, and high explosives [1]. A large amount of water is used for exhilarating hot coke and washing off gas produced from the oven. Effluents generated from the excitement of coke usually contain suspended matter of coke breeze (broken pieces of coke). Water used for washing gas comes out as ammoniac solid liquor, having a high concentration of phenol, cyanide, ammonia, and other toxic substances. These effluents cause severe surface water pollution in the area [2].

The iron and steel industry is one of the most energy-intensive sectors within the Indian economy. Steel production in India has increased by a compounded annual growth rate (CAGR) of 8% over the last ten years [3]. Each ton of steel production in India consumes 25–60 m³ of water on average, and 5-9 tons of coal is fed as primary raw material. It may be noted that, in developed countries, the water consumption for each ton of steel production varies from 3 to 6 m³, i.e., 8 to 10 times less than that of
the water consumption in India (CPCB 2010) [4]. In an integrated iron and steel industry, wastewater generated from coke oven by-product plants is usually the most polluting.

Coke is produced by pyrolysis of coal, and it is also the primary component in the manufacture of steel. During pyrolysis, the gases produced from the coke oven are cooled further for steel-making purposes [5]. Tar, ammonia, phenols, naphthalene, light oil, and sulfuric compounds are some of the major pollutants found in the condensed water of coke oven gases; some of them, like tar and ammonia, can be recovered in a decanter for other purposes, the liquid left after the recovery is called coke-oven wastewater [6].

The agricultural potential of coke oven wastewater is being neglected in India. Wastewaters are substantial in nutrients, and they can be used in irrigating agrarian lands [7]. Disposal on land could recede pollution on surface water occurring due to removal, and it can also successfully remove the nutrients from the wastewater, thereby providing multistage water treatment and at the same time boosting agricultural growth. Disposal on land will help check the ecological balance of groundwater and control surface water pollution. The main challenge is to utilize all three aspects: chemical, physical, and biological properties of water with minimum unwanted effects on the crops, the characteristics of soil, and the quality of groundwater and surface water runoff. Marinating the aerobic condition under the ground is also possible by limiting the disposal amount of wastewater [8].

Rourkela Steel Plant (RSP), which has six coke oven batteries, effluents from it are considered for treatment. Rourkela does not have varied soil texture, but the various sites were chosen for soil sample collection based on the location and distance from the nearby water body, and a study was performed on it for disposal of effluents. In the process of production of coke by anaerobic carbonization of coal, gas is produced in a considerable quantity. Clean fuel gas is produced by treating this gas in the by-product plant after removing condensable, corrosive, or economically valuable components. The coal chemicals generally have reasonably good selling value. Coke wastewater generated during the washing of coke gas contains major chemicals and hazardous contaminants like ammonia, phenol, cyanide, and sulfide, whereas materials like oil, grease, and tar form an insoluble layer that hinders the access of oxygen from the air.

1.1 Objectives
The aim of the present study was:
- To determine the number of pollutants retained by soil so that the quality of groundwater remains unharmed.
- To construct a lysimeter column for the laboratory scale test.
- To perform tests on leachate by considering parameters such as pH, Temperature, D.O., COD, BOD, Dissolved solids, suspended solids, Total hardness, Ca hardness, and Mg hardness.

1.2 Scope of the study:
The present study focused on the retaining of pollutants by the soil, and the effluent received must be under the limits of disposal of effluent in sewage disposal of facilities.

2. Literature review
The treatment of coke oven wastewater, as one of the most complex and problematic industrial waste streams, is often discussed in the literature and widely investigated by many scientific and industrial R&D centers worldwide. The topics listed below include the previous research works that have been conducted on the treatment of wastewater:
- Industrial wastewater treatment
- Coke oven wastewater treatment

2.1 Industrial wastewater treatment
Biological methods have long treated industrial wastewater. Several studies indicate that physical treatments can remove organic pollutants from the enormous quantity of sewage at a relatively low cost
However, a long residence time is required due to the prolonged process of biodegradation. Autotrophic bacteria that oxidize ammonia during the biological nitrification process and other heterotrophic oxidizing bacteria are normally sensitive to the presence of toxic compounds such as phenol, cyanide, and high concentration of ammonia.

2.2 Coke oven wastewater treatment

In recent publications, electrochemical processes are proposed to decompose and destroy a range of contaminants (cyanides, sulfides, and thiocyanates) present in coke oven wastewater.

Ozyonar and Karagozogly [15] compared treating of pre-treated coke wastewater by electrocoagulation process (E.P.) and electrochemical peroxidation process (ECP) using direct pulse current. They used the air stripping process of ammonia as a physicochemical process for this purpose. A direct pulse current was used to prevent the passivity or polarization of electrodes and increase removal efficiency. They found that ECP was more efficient than E.P. in removing COD, total organic carbon, phenol, cyanide, and thiocyanate, but higher operating costs.

Pillai and Gupta [16] applied anodic oxidation of industrial wastewater from a coke oven plant having cyanide including thiocyanate (280 mg/l), chemical oxygen demand (COD 1520 mg/l), and phenol (900 mg/l) using a novel PbO$_2$ anode. Optimization was performed for maximizing the removal efficiencies of these three parameters simultaneously; those were 99.6%, 86.7%, and 99.7% for cyanide, including thiocyanate, COD, and phenol, respectively.

Water reclamation from coke oven wastewater effluent or introduction of membrane processes arranged in a different model to the coke oven wastewater treatment is also a subject of much research. Fascinating and promising results are obtained.

Kumar and Pal [17] designed an experiment and investigated a new system using forward osmosis–nanofiltration in a flat-sheet crossflow module. The aim was to separate reusable water from coke-oven wastewater with reduced concentration polarization and high flux using low energy. Removal of about 96–98% of cyanide, phenols, NH$_4^+$–N, and chemical oxygen demand from real coke-oven could be achieved along with pure water flux of 46 l/(m$^2$h) in a forward osmosis system under optimized conditions.

Jin et al. [18] investigated a full-scale plant using anaerobic, anoxic, and oxic processes (A1/A2/O), along with a pilot-scale membrane bioreactor (MBR), nanofiltration (N.F.), and reverse osmosis (R.O.) integrated system to treat coking wastewater for industrial reuse over a period of one year. The removal of pollutants (TCN, COD, BOD, ammonium nitrogen, SCN, fluoride) efficiency reached very high values during the A1/A2/O biological treatment stage, and all parameters were further reduced by over 96.0%.

Chang et al. [19] investigated the biological and chemical characteristics of coke-oven wastewater after ozonation treatment through the examination of selected parameters in a bench-scale bubble column reactor. Ghose [20] analyzed the physicochemical treatment of wastewater from the coking plant as a suitable option for the treatment of coke plant effluents.

Vazquez et al. [21] analyzed laboratory-scale activated sludge plants to study the biodegradation of coke wastewater.

3. Land treatment and details of the coke plant under study

Compared to all other methods of treatment, land treatment is the cheapest in some old coke plants, availability of space might be a problem for biological treatment. Disposal to land does not require an expensive wastewater treatment plant. It acts as a primary, secondary, and tertiary treatment for wastewater and helps in controlling surface water pollution. This can help in minimizing the cost of fertilizers and help to grow the important crops in the region. This proves to be economical as well; the cost of irrigation can be checked. Also, groundwater gets restored by using this method.

3.1 The methodology adopted for the study:
3.1.1 Sampling and analysis of coke plant effluent: Wastewater from RSP was collected twice a week on Monday and Friday. Each day at 17:55 hours, they were poured into the Lysimeter; two irrigation per week with 5 cm flooding each. This was continued for a period of one month. The grab sampling method was used for sampling. The leachate and the raw effluent were analyzed by following the technique given in "standard methods for the examination of wastewaters" [11].

3.1.2 Collection of soil samples: Different areas of Rourkela were selected for the Collection of soil samples. Though Rourkela did not have varied soil texture (mostly sandy, loamy soil is found), different places were selected based on the location. The samples were collected from the following areas:

- **NIT Campus**: The soil on the NIT campus was sandy loamy, and the ground is stable and in a sparsely populated area.
- **Jhirpani (Riverside)**: This site was chosen because it was saturated and moving water is always there.
- **Mandira dam**: The soil sample is the same as Jhirpani, but here, the water is stable, and the soil is also saturated.
- **RSP waste disposal site**: RSP was chosen because the waste from industries is disposed of here, which contains a heavy amount of chemicals.

4. Preparation of Column Lysimeters:
The PVC pipes were used for the construction of the column lysimeter, which had a dimension of 2m in length and 0.2m in diameter. It consists of three ports with a diameter of 0.05m, at 0.3, 0.9, and 1.6m depth, which were driven inside lysimeters. One end of each port was connected to the plastic cup fixed tightly used for collecting leachate from each port, and the other end was closed to retain leachate from leaving the Lysimeter. To collect leachate, the top of the pipes in the ports were perforated, and a fine screen, sand, and gravel were placed so that leachate could be collected smoothly, as shown in figure 1 and figure 2(a & b). The soil collected was carefully placed and compacted in the Lysimeter to simulate the original in-situ condition pertaining to stratification and density.
4.1 Disposal of effluent and inspection:
The experiment was conducted in two phases:

**Phase 1:** All three lysimeters were introduced with different types of liquids keeping the soil (NIT Campus) in the Lysimeter the same. Distilled water was introduced in lysimeter No.1, and in lysimeter No.2, diluted effluent of the coke oven plant was introduced. In lysimeter No.3, raw effluent was introduced. There were two irrigations conducted per week in each Lysimeter for a period of one month.

**Phase 2:** In this phase, the raw effluent was used as the liquid, and the soil in each of the lysimeters was changed. Soil from Mandira dam was placed in lysimeter No.4, Jhirpani soil was placed in lysimeter No.5, and soil from the RSP dumping site was placed in lysimeter No.6. The soil was compacted to attain in-situ conditions, and the same procedure for irrigation was followed for the next month.

The leachate from lysimeters 2, 3, 4, 5, and 6 were collected to assess the impact of coke plant effluent on groundwater quality.

4.2 Impact on soil quality:
Soil from different lysimeters after completion of sampling was taken and put into separate pots. For the comparison, the untreated soil sample was also put into the pot alongside, and different seeds were sown into them in equal amounts.

5. Result and discussion
The leachate temperature from all lysimeter tests was found slightly higher than the temperature specified in the effluent water standard. The temperature in the first phase of the experiment was found to be 41ºC for all the three lysimeters taken, and in the second phase, it was 46.1ºC for all the three lysimeters. The limit for disposal in sewerage for effluent is 40ºC, which is being slightly exceeded by effluents from the Lysimeter. However, the pH was found to be 7.5 for Lysimeter with distilled water, 7.48 for Lysimeter with the diluted sample, 7.4 for Lysimeter with raw effluent, and 7.48 for Lysimeter with Mandira dam soil, 8.98 for Lysimeter with Jhirpani soil, and 7.91 for Lysimeter with RSP soil sample. The pH range of all the soil and effluent samples was within the standard range of 5.5 – 9.0 (figure 4). Therefore, considering pH it is safe to dispose of it on land, and considering temperature, it is not suitable.

There is no standard limit for the initial D.O. content of the leachate. The BOD of the samples taken in the first phase was 510 mg/l for distilled water, 520 mg/l for the diluted sample, and 490 mg/l for raw effluent. In the second phase of the experiment, the BOD was found to be 340 mg/l for the RSP sample, 590 mg/l for Jhirpani soil, and 640 mg/l for the Mandira dam. The BOD is found to be very high as compared to the tolerance limit of effluent water standard (figure 5). This shows that survival of aquatic life is not possible due to the lesser amount of dissolved oxygen in the water and the bacteria and other...
micro-organisms are present in very high concentrations. The COD found was also much higher than the limits in the effluent water standard. The COD of distilled water was 1350 mg/l, 1220 mg/l for diluted sample, and 1270 mg/l for Lysimeter with raw effluent (figure 6). In the second phase of the experiment, the COD concentration found was much higher at 1650 mg/l for Lysimeter with Jhirpani soil, and 1650 mg/l for Lysimeter with Mandira dam soil, and 1670 mg/l for Lysimeter with RSP soil sample.

The number of dissolved solids in the first phase of the experiment was found to be below the tolerance limit of the effluent water standard. The number of dissolved solids in the distilled water sample and the diluted sample was 1085 mg/l and 870 mg/l, respectively. But the number of dissolved solids in the raw solid was 985 mg/l, which is lesser in comparison to the two others. However, the standard limit is 2100 mg/l. In the second phase of the experiment, TDS for RSP soil was 1585 mg/l, 8730 mg/l for the Jhirpani soil sample, and 2840 mg/l for the Mandira dam soil sample (figure 3). It is inferred that soil from RSP is suitable for disposal and within limits. TSP found was beyond the tolerance limit in both phases. The Mandira dam soil sample had 10880 mg/l, 21855 mg/l in Jhirpani, 5890 mg/l in RSP, 1565 mg/l in distilled water, 1570 mg/l in the diluted sample, and 805 mg/l in raw effluent. TSP limit for effluent water standard is 100 mg/l.

For measuring the quality of soil, the original soil sample of Mandira dam soil and RSP soil was taken, and the soils from the Lysimeter after treatment were also taken (figure 7 and figure 8). Green seeds were planted in the soil, and the soil was irrigated twice a day because of the hot weather. The growth of the plant was observed for the next 15 days. The plant’s growth in the soils after treatment was healthier than compared to the original soil (figure 9). This shows that it is suitable for plant growth, and the soil is enriched with nutrients also.
Figure 7. Leachate collected from Lysimeter

Figure 8. Soil testing before sowing of seed

Figure 9. Soil testing after sowing of seed

Table 1. Measured parameters

| Parameters            | Distilled water sample (1) | Diluted water sample (2) | Raw Effluent (3) | Mandira Dam Soil Sample (4) | Jhirpani Soil Sample (5) | RSP Soil Sample (6) |
|-----------------------|-----------------------------|---------------------------|-----------------|-----------------------------|-------------------------|---------------------|
| pH                    | 7.5                         | 7.48                      | 7.4             | 7.48                        | 8.98                    | 7.91                |
| Temperature (°C)      | 41                          | 41                        | 41              | 46.1                        | 46.1                    | 46.1                |
| BOD (mg/L)            | 510                         | 520                       | 490             | 340                         | 590                     | 640                 |
| COD (mg/L)            | 1350                        | 1220                      | 1270            | 1650                        | 1650                    | 1670                |
| Dissolved Solids (mg/L)| 1085                        | 870                       | 985             | 1585                        | 8730                    | 2840                |
| TSP (mg/L)            | 1565                        | 1570                      | 805             | 10880                       | 21855                   | 5890                |

6. Conclusion
From the above study, the following conclusions are drawn. With the use of wastewater, the nutrient in the soil was restored, and healthier plants could be grown. However, for direct disposal, it should be treated first for high BOD and COD, and then it can be disposed of on land. It will help in reducing surface water pollution and restoration of nutrients in the soil. For the initial treatment, much lesser space and capital are required, which will reduce the cost of setting up large treatment plants on the plant sites.
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