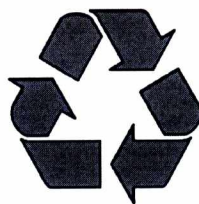


Standard Operating Procedure and Checklist of Minimal Requisite Facilities for utilization of hazardous waste under Rule 9 of the Hazardous and Other Wastes (Management and Transboundary movement) Rules, 2016

Utilization of Spent Sulphuric Acid generated during manufacturing of col 313 dye using Anthraquinone



cpcb

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Central Pollution Control Board
(Ministry of Environment, Forest & Climate Change, Government of India)
Parivesh Bhawan, East Arjun Nagar,
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21.0 Utilization of Spent Sulphuric Acid:

| Type of HW | Source of generation | Recovery/Product |
|---|---|---|
| Spent Sulphuric Acid Category: 26.3 of HOWM Rules, 2016 | Spent acid generated during manufacturing of col 313 dye using Anthraquinone. | Ferrous Sulphate Hepta-hydrate (FeSO ₄ .7H ₂ O) |

21.1 Source of Waste:

Spent Sulphuric Acid is generated during manufacturing col. 313 dye using Anthraquinone. In this process spent sulphuric acid is generated as filtrate after crystallisation of Anthraquinone. This Spent Sulphuric Acid is categorised as hazardous waste category 26.3 of Schedule-I of HOWM Rules, 2016. This hazardous waste is required to be disposed in authorized disposal facility in accordance with authorization condition, when not utilized as resource recovery.

Typical characteristic of spent acid generated is given below;

Acidity: 34%

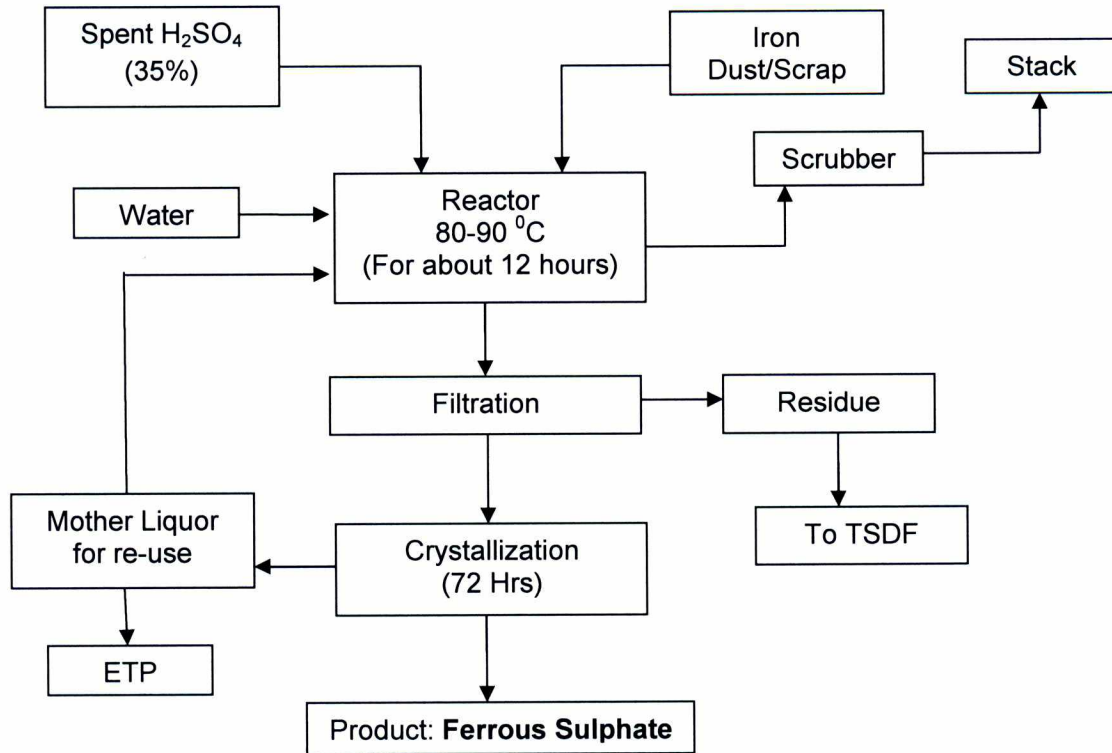
Anthroquinone – 0.4%

Water – 65%

21.2 Process of Utilization:

The utilization process involves reaction of iron dust/scrap with Spent Sulphuric Acid solution (34%) in a reaction vessel and agitated for about 12 hours at temperature 80-90 °C. Water is also added to the reaction vessels during charging of reaction for completing the reaction and finally to obtain a process liquor comprising ferrous sulphate and acid solution. The process liquor is drained through suction pumps to a holding tank and it is filtered in a filter press to separate the ferrous sulphate liquor and residue/filter cake. The resultant filtrate is subjected to crystallization in crystallizer vessel (open or closed) for about 72 hours to obtain final products i.e. Ferrous Sulphate Hepta-hydrate (FeSO₄.7H₂O). The residue/filter cake generated shall be sent to TSDf for final disposal. The mother liquor from the crystallization vessel is drained by gravity and collected in separate collection tank and it is reused in the process until the density of mother liquor is between 1300-1350 kg/m³, if the density of mother liquor exceeds 1350 kg/m³, it is concentrated and the same will be treated in ETP after certain period of time (4-5 months) by neutralizing with lime.

Process flow



21.3 Product Usage / Utilization

Ferrous Sulphate Hepta-hydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) recovered from above process can be used only for industrial purposes and not for treating water for drinking purposes or agriculture applications.

21.4 Standard Operating Procedure (SOP) for utilization

This SOP is applicable only for the utilization of Spent Sulphuric Acid generated from Anthraquinone manufacturing industries to produce Ferrous Sulphate by adhering to following;

- (1) The Spent Sulphuric Acid should be transported in acid-proof tankers mounted on vehicles fitted with requisite safeguards ensuring no spillage of the liquid waste.
- (2) There should be a designated space for unloading of Spent Sulphuric Acid into a rubber lined storage tank. The receiving storage tank shall be placed above the ground and contained with low raise parapet/bund wall & acid proof floor with

slope to collect spillages, if any into collection pit. Alternatively, storage tanks for Spent Sulphuric acid may be below the ground provided it has HDPE liner system beneath the tank and leachate collection system below HDPE liner. In the event of leachate detection in the leachate collection system, corrective measures shall be taken immediately.

- (3) The unit shall install storage tank under cool, dry, well-ventilated covered storage shed(s) within premises, as authorized by the concerned State Pollution Control Board/Pollution Control Committee under Hazardous and Other Wastes (Management & Transboundary Movement) Rules, 2016 so as to eliminate rain water intrusion.
- (4) There shall be no manual handling of the hazardous wastes (Spent Sulphuric Acid). Acid proof pump shall be used for transfer of Spent Sulphuric Acid through pipelines to the reaction vessel.
- (5) The entire process area shall have leak-proof and acid proof floor tiles with adequate slope to collect spillages, if any, into a collection pit. The spillages from collection pit shall be transferred to ETP or reaction tank, as the cases may be, through acid proof pump.
- (6) The vent of Spent Sulphuric Acid storage tanks shall be connected to scrubber for treatment using alkaline medium.
- (7) There shall be proper arrangement for storage of iron dust demarcated away from reaction vessels.
- (8) Acid fume/vapour is expected to be liberated from the reaction tanks where iron dust is added to Spent Sulphuric Acid. Thus, the said reaction tanks shall be connected with hood over it to suck acid fume/vapour. The hood shall be maintained under suction followed by treatment in scrubber using alkaline medium.
- (9) The unit shall maintain proper ventilation in the work zone and process areas. All personnel involved in the plant operation shall wear proper personal protective equipment (PPE) such as Chemical goggles, full-face shield, or a full-face respirator, Impervious gloves of chemically resistant material (rubber or neoprene), Body suits, aprons, and/or coveralls of chemical resistant material and impervious boots of chemically resistant material.
- (10) The treated acid fume/vapour shall comply with emission norms and shall be dispersed into atmosphere through stack of minimum height of 6 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher.
- (11) The process liquor from reaction tank shall be transferred to filter press through chemical process pump. The filtrate from filter press shall be crystallized in crystallizer vessel (open or closed) mounted above the ground. Further, storage

tank of mother liquor from crystallization shall be mounted above the ground and contained with low raise parapet/bund wall & acid proof floor with slope to collect spillage, if any into collection pit.

Crystallization shall not be carried out in open tray arrangement.

(12) The Ferrous Sulphate Hepta-hydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) manufactured of utilizing aforesaid hazardous waste shall not be used in drinking water purification or agriculture applications and the same shall be used only for industrial purposes. The unit shall, therefore, label the product i.e. Ferrous Sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) as "to be used only for industrial purposes, not be utilized for water treatment or agriculture applications".

(13) Treatment and disposal of wastewater:

The following are the sources of wastewater from utilization process;

- a) Spent mother liquor containing ferrous sulphate (generated after numbers of recycling of mother liquor)
- b) scrubber bleeds
- c) Floor washing/reactor wash/vehicle wash/spillages, etc.

The above wastewater shall be disposed as given below;

- Physico-Chemical treatment by collection, neutralization, settling and filtration and treated effluent shall be evaporated in single or multi effect evaporator so as to meet zero discharge.

Or

- The waste water may be sent for disposal to authorized common hazardous waste incinerator.

Or

- The waste water may be sent to Common Effluent Treatment Plants for disposal.

(14) It shall be ensured that Spent Sulphuric Acid is procured from the industries who have valid authorization for the same from the concerned SPCB/PCC as required under Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016.

(15) The hazardous waste (viz. filter press residue, ETP sludge, residue from scrubber, product spillages, MEE residue, if any etc.) generated from utilization process shall be collected and temporarily stored in a dedicated hazardous waste storage area sent to TSDF within 90 days from generation of the waste. Such storage area shall be covered with proper ventilation.

- (16) The residues generated from filter press, ETP Sludge, scrubber, product spillages, MEE residue, if any, etc. shall be disposed as hazardous wastes through common TSDFs as per conditions stipulated under consent/authorization issued by concerned SPCB/PCC.
- (17) Transportation of Spent Sulphuric Acid, and residues generated during utilisation shall be carried out by the sender or receiver (utilizer/TSDF operator) as per the authorization issued by concerned SPCB/PCC under the Hazardous and Other Wastes (Management & Transboundary Movement) Rules, 2016.
- (18) Prior to utilization of spent sulphuric acid, the unit shall obtain authorization for generation, storage and utilisation of Spent sulphuric acid from the concerned State Pollution Control Board under the Hazardous and Other Wastes (Management & Transboundary Movement) Rules, 2016.
- (19) In case of environmental damages arising due to improper handling of hazardous wastes including accidental spillage during generation, storage, processing, transportation and disposal, the unit shall be liable to implement immediate response measures, environmental site assessment and remediation of contaminated soil/groundwater/sediment etc. as per the "Guidelines on Implementing Liabilities for Environmental Damages due to Handling & Disposal of Hazardous Wastes and Penalty" published by CPCB.
- (20) During the process of utilization and handling of hazardous waste, the unit shall comply with the requirements in accordance with the Public Liability Insurance Act, 1991 as amended, wherever applicable.

21.5 Records/Return Filing:

- (1) The unit shall maintain a passbook issued by concerned SPCB/PCC wherein the following details of each procurement of Spent Sulphuric Acid waste shall be entered:
 - Address of the sender
 - Date of dispatch
 - Quantity procured
 - Seal and signature of the sender
 - Date of receipt in the premises
- (2) A log book with information on source and date of procurement of each type of the said hazardous wastes, quantity, date wise utilization of the same, quantity of ferrous sulphate manufactured, hazardous waste generation and its disposal etc. shall be maintained including analysis report of fugitive and emission monitoring, as applicable.

- (3) The unit shall submit quarterly and annual information on hazardous wastes consumed, its source, products generated or resources conserved (specifying the details like type and quantity of resources conserved) to the concerned SPCB/PCC
- (4) The unit shall maintain record of hazardous waste utilised, residues generated and disposed as per Form 3 & shall file annual returns in Form 4 as per Rule 20 (1) and (2) of the Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016, to SPCB/PCC.

21.6 Standards

- (1) Emissions of Sulphuric acid mist in stack connected to reaction tank shall not exceed $30\text{mg}/\text{Nm}^3$. However, SPCB/PCC may prescribe stringent standard.
- (2) Fugitive emissions in the work zone shall comply with following standards
Sulphuric acid – $1.0\text{ mg}/\text{m}^3$ TWA*, $3\text{ mg}/\text{m}^3$ STEL*

** Time-weighted average (TWA), Short-term exposure limits (STEL).*

The Permissible Exposure Limit is 8-hour TWA.

A short-term exposure limit (STEL) is the acceptable average exposure over a short period of time, usually 15 minutes as long as the Time weighted average is not exceeded.

A ceiling limit is one that may not be exceeded for any period of time, and is applied to irritants and other materials that have immediate effects.

- (3) Monitoring of specified parameters for fugitive emission shall be carried out quarterly for the first year followed by at least annually in the subsequent year of utilization. Fugitive emission for specified parameters shall be carried out by NABL accredited or ISO17025/EPA recognized laboratories and the results shall be submitted quarterly to the concerned SPCB/PCC.

21.7 Siting of Industry

Facilities for processing of Spent Sulphuric Acid should preferably be located in a notified industrial area or industrial park/estate/cluster.

21.8 Efficiency of utilisation

About 16 tons of Spent Sulphuric Acid and about 5 tons of Iron dust are required to produce 19 tons of Ferrous Sulphate Hepta-hydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). Hence, requisite facilities of adequate size shall be installed accordingly as mentioned under para 21.10 below.

21.9 On-line detectors / Alarms / Analysers

Online detectors/alarms/analysers shall be installed in case of continuous process operations for acid mist.

21.10 Checklist of Minimal Requisite Facilities:

| S.No. | Requisite Facilities |
|--------------|---|
| 1. | Earmarked unloading area (for transfer of Spent Sulphuric acid from tanker) contained with low raise parapet/bund wall & acid proof floor with slope to collect spillages, if any, to collection pit. |
| 2. | Acid proof lined tanks for storage of Spent Sulphuric Acid |
| 3. | Storage tank (s) should be of such size/capacity that it can store at least two weeks requirement of the said hazardous waste to be used as raw material. |
| 4. | Well-ventilated covered storage shed(s) within the premises for Spent Sulphuric Acid storage tanks |
| 5. | Chemical process (acid proof) pumps for transfer of Spent Sulphuric acid from tanker to storage tank and transfer subsequently to process area. |
| 6. | Mechanical means for transferring of acids/liquid chemicals to the reaction vessels |
| 7. | Leak-proof and acid proof floor tiles with adequate slope to collect spillages, if any, in the entire working area. |
| 8. | Collection pit for collection of spillages from aforesaid working area and unloading area. |
| 9. | Reaction tank of adequate capacity along with hood for suction of acid fumes/ mist from the reaction tank and channelizing to scrubber |
| 10. | Facility for preparation of alkaline medium (for use in scrubber) and its storage tank |
| 11. | Separate collection tank for Spent mother liquor containing ferrous sulphate |
| 12. | Separate storage shed(s) of adequate size for store iron dust/scrap |
| 13. | Scrubber followed by stack of minimum height of 6 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher. |
| 14. | Stacks to have sampling port, platform, access to the platform etc. as per the Guidelines on Methodologies for Source Emission Monitoring published by CPCB under Laboratory Analysis Techniques LATS/80/2013-14. |
| 15. | Filter press |
| 16. | Crystallizer Vessel (Open or Closed) |
| 17. | Drying platform/hot air dryer of adequate size/area for drying Ferrous Sulphate crystals |
| 18. | Effluent treatment plant of adequate capacity comprising of collection tank, neutralization and sludge handling unit (Filter/Centrifuge/ Sludge drying bed, etc.) |

Standard Operating Procedure and Checklist of Minimal Requisite Facilities - Utilization of Spent Sulphuric Acid generated during manufacturing of col 313 dye using Anthraquinone

| | |
|-----|------------------------------------|
| 19. | Sludge drying bed of adequate size |
| 20. | Single or Multi Effect Evaporator |

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