

**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 4, 4'-Diamino Benzene Sulphanilide**



March, 2017

**Central Pollution Control Board**  
(Ministry of Environment, Forest & Climate Change, Government of India)  
**Parivesh Bhawan, East Arjun Nagar,**  
**Shahdara, Delhi – 110032**

**Procedure for grant of authorisation by SPCBs/PCCs for utilization of Hazardous Waste**

- (i) While granting authorisation for utilization of hazardous wastes, SPCBs/PCCs shall ensure the following:
  - a. The waste (intended for utilization) belongs to similar source of generation as specified in SoPs.
  - b. The utilization process is similar to the process of utilization described in SoPs.
  - c. End-use / product produced from the waste shall be same as specified in SoPs.
  - d. Authorisation be granted only after verification of utilization process and minimum requisite facilities as given in SoPs.
  - e. Issuance of passbooks (similar to the passbooks issued for recycling of used oil, waste oil, non-ferrous scrap, etc.) for maintaining records of receipt of hazardous wastes for utilization.
- (ii) After issuance of authorization, SPCB shall verify the utilization process, checklist and SOPs on quarterly basis for initial 2 years; followed by random checks in the subsequent period for at least once a year.  
 In-case of lack of requisite infrastructures with the SPCB/PCC, they may engage 3<sup>rd</sup> party institutions or laboratories having EPA/NABL/ISO17025 accreditation/recognition for monitoring and analysis of prescribed parameters in SoPs for verification purpose.
- (iii) SPCBs/PCCs shall provide half yearly updated list of units permitted under Rule 9 of HOWM Rule, 2016 to CPCB and also upload the same on SPCB website, periodically. Such updated list shall be sent to CPCB half yearly by July and January respectively.
- (iv) Authorisation for utilisation shall not be given to the units located in the State/UT where there is no Common TSDF, unless the unit ensures authorised captive disposal of the hazardous waste (generated during utilisation) or its complete utilisation or arrangement of sharing with any other authorised disposal facility.
- (v) In case utilization proposal is not similar with respect to source of generation or utilization process or end-use as outlined in this SoP, the same may be referred to CPCB for clarification / conducting trial utilization studies and developing SoPs thereof.
- (vi) The source and work zone standards suggested in the SoPs are based on the E(P)A notified and OSHA standard respectively, however, SPCB/PCC may impose more stringent standards based on the location or process specific conditions.

**33.0 Utilization of Spent Sulphuric Acid:**

| Type of HW   | Source of generation  | Recovery/Product  |
|--|---|---|
| Spent Sulphuric Acid-Category 26.3 of schedule-I of HOWM Rules, 2016 | during the production of 4,4-Diamino Benzene Sulphanilide (DABSA) | As a supplementary resource to manufacture 2-NADPSA and 6-Acetyl OAPSA. |

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### 33.1 Source of Waste

The Spent Sulphuric Acid is generated during manufacturing process of DABSA (4, 4-Diamino Benzene Sulphanilide). The chlorosulfonation of acetanilide using Chloro sulphonic acid produces spent acid containing sulphuric acid, hydrochloric acid and other organic impurities. Typical characteristics of the waste is given below:

|                                      |           |
|--------------------------------------|-----------|
| Total Acidity                        | 25.1%     |
| Sulphate                             | 13.82%    |
| Chlorides                            | 3.22%     |
| Acetanilide                          | 0.12%     |
| Acetanilide Sulphonyl Chloride       | 0.58%     |
| Total Organic Carbon                 | 4110 mg/l |
| Lead as Pb                           | 0.06 mg/l |
| Fe as Fe <sub>2</sub> O <sub>3</sub> | 4.8 mg/l  |
| COD                                  | 8480 mg/l |

The aforesaid Spent Sulphuric Acid is categorised as hazardous waste at S.No. 26.3 of schedule-I of HOWM Rules, 2016 which are required to be disposed in authorized disposal facility in accordance with authorization condition, when not utilized as resource recovery.

### 33.2 Utilization Process

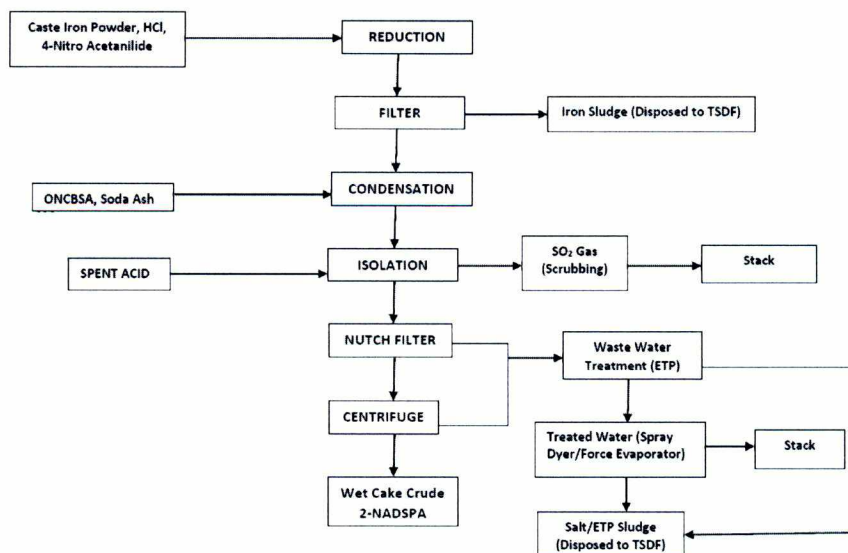
#### a) Utilization in production of 2-NADPSA:

Sodium salt of 2-NADPSA is allowed to react with the Spent Sulphuric Acid in a reactor with constant stirring for 4-5 hours at room temperature. The crude mass is filtered using Nutch filter and further allowed to react with Sodium Carbonate to get Sodium salt of Crude 2-NADSPA. The crude NADSPA is again reacted with spent Sulphuric Acid. Finally, reaction mixture is filtered, centrifuged and dried to get pure 2-NADPSA. Sulphur Dioxide, liberated during the additions of spent Sulphuric Acid, is scrubbed using alkali scrubber. The discharged waste water during the process (i.e. filtration, Centrifuge, drying, washing of floor, reaction vessels, etc.) is treated in Effluent Treatment Plant (ETP).

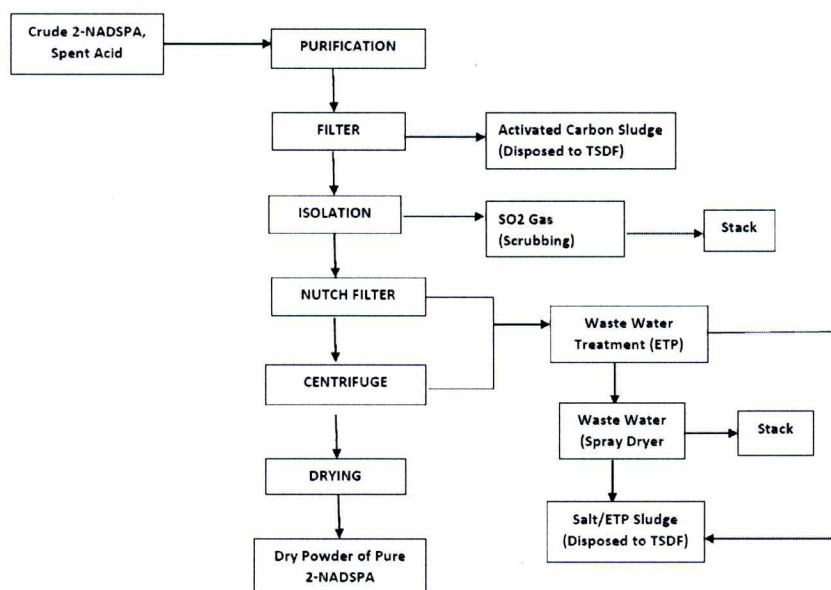
#### Process Flow Diagram of manufacturing of 2-NADSPA

#### Preparation of Crude 2-NDSPA & Isolation

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**Purification of Crude 2-NADSPA & Isolation**

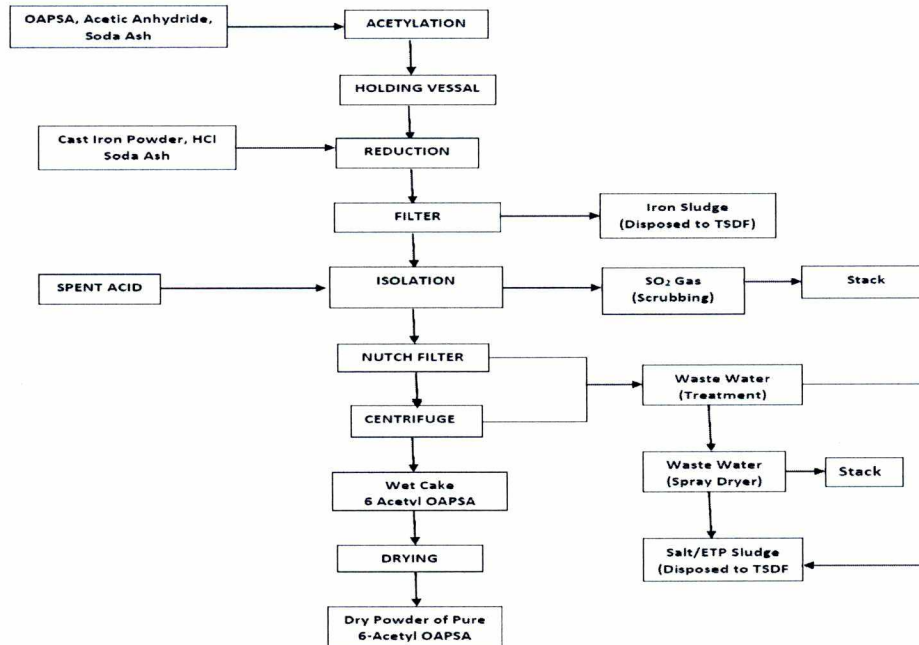


**b) Utilization in production of 6-Acetyl OAPSA:**

The Sodium salt of 6-Acetyl OAPSA is allowed to react with Spent Sulphuric Acid in a reactor with constant stirring for 10 hours at room temperature. The crude mass is filtered using Nutch filtered, centrifuged and dried to get pure 6-Acetyl OAPSA. Sulphur Dioxide is liberated during the addition of Spent Sulphuric Acid is scrubbed using alkali scrubber. The discharged waste water during the whole process (i.e. filtration, Centrifuge, drying and washing etc.) is treated in Effluent Treatment Plant (ETP).

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**Process Flow Diagram of isolation and purification of 6-Acetyl OAPSA**



**33.3 Product Usage / Utilization**

2-NADSPA:

2-NADSPA will be utilized in production textile dyes such as Reactive Blue 161 and Brown 355.

6-Acetyl OAPSA:

6-Acetyl OAPSA will be utilized in leather dyes such as Reactive Blue 160 and Reactive Blue 221

**33.4 Standard Operating Procedure (SoP) for utilization**

This SoP is applicable only for the utilization of Spent Sulphuric Acid generated during manufacturing of 4,4-Diamino Benzene Sulphanilide (DABSA).

- (1) Spent Sulphuric Acid shall be transported in SPCB/PCC authorised acid-proof tankers mounted on vehicles fitted with requisite safeguards ensuring no spillage of the same.
- (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.

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- (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). Chemical process 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 tanks, as the cases may be, through chemical process pump.
- (6) The vent of Spent Sulphuric Acid storage tanks shall be connected to scrubber for treatment using alkaline medium.
- (7) The unit shall provide separate storage tanks for the storage of chemicals and the storage tanks should be at designated place with proper cover and with acid brick lining floors.
- (8) The unit shall ensure that the said utilization process and its associated activities shall be demarcated separately within the unit.
- (9) Spent Sulphuric Acid shall be mixed with 2-NADSPA and 6-Acetyl OAPSA only in closed vessel reactors (isolation vessel) having mechanised stirring system with retention time of 4-5 hours and 10 hours respectively. The mixer shall be kept under covered shed with adequate safety gadgets provided to workers, as well as ensuring proper ventilation in the process area.
- (10) Sulphuric Acid Mist, HCl Vapour and SO<sub>2</sub> are expected to be liberated from the said reactors (isolation vessel) where the Spent Sulphuric Acid is added. Thus, the said reactors (isolation vessel) 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.
- (11) The spray dryer should be attached with Stack. The boiler attached with the spray dryer shall be operated electrically or by fuel permitted by the concerned SPCB/PCC. Depending upon type of fuel, suitable air pollution control device(s) shall be installed with the boiler followed by stack of height as prescribed by the concerned SPCB/PCC.
- (12) 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.

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- (13) 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.
- (14) Treatment and disposal of wastewater:  
The following are the sources of wastewater from utilization process;
- a) Waste water (generated from Nutch filter, centrifuge and Floor washing/reactor wash/vehicle wash/spillages, etc.)
  - b) scrubber bleeds
- The above waste water shall be treated Physico-Chemically by neutralizing with lime followed by clarifier and the treated water shall be subjected to spray dryer or forced evaporator (single or multi effect evaporator) so as to achieve the zero discharge.
- (15) It shall be ensured that Spent Sulphuric Acid is procured from the industries that have valid authorization for the same from the concerned SPCB/PCC as required under Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016.
- (16) The residue generated (from filter press, ETP sludge, scrubber, bag filter, Spray Dryer/forced evaporator, product spillages, etc.) shall be collected and temporarily stored in non reactive drums / bags under a dedicated hazardous waste storage area and be sent to authorized common TSDF or other authorized facility within 90 days from generation of the waste in accordance with the authorization issued by the concerned SPCB/PCC. Such storage area shall be covered with proper ventilation.
- (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) The unit shall provide suitable fire safety arrangements and flame proof electrical fittings.
- (21) 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.

### **33.5 Records/return filing**

*Waste Management Division, CPCB Delhi*

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- (1) The unit shall maintain a passbook issued by concerned SPCB wherein the following details of each procurement of Spent Sulphuric Acid 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 2-NADSPA and 6-Acetyl OAPSA manufactured, hazardous waste generation and its disposal etc. shall be maintained including analysis report of emission monitoring & effluent discharged, as applicable.
- (3) The unit shall maintain record of hazardous waste utilised, hazardous waste 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 concerned SPCB.
- (4) 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.

### **33.6 Standards**

- (1) Fugitive emissions in the work zone:

|                   |   |                            |
|-------------------|---|----------------------------|
| PM <sub>10</sub>  | - | 5.0 mg/m <sup>3</sup> TWA* |
| Hydrogen Chloride | - | 7.0 mg/m <sup>3</sup> TWA  |
| Sulphuric Acid    | - | 1.0 mg/m <sup>3</sup> TWA  |

*Reference: Occupational Safety and Health Standards 1910:1000);*

TWA\* - Time-weighted average

The Permissible Exposure Limit is 8-hour TWA.

- (2) Stack Emissions:

|                     |   |                      |
|---------------------|---|----------------------|
| SO <sub>2</sub>     | - | 50 mg/m <sup>3</sup> |
| HCl Vapour and Mist | - | 35 mg/m <sup>3</sup> |
| Sulphuric Acid Mist | - | 50 mg/m <sup>3</sup> |
| TOC                 | - | 20 mg/m <sup>3</sup> |

- (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

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recognized laboratories and the results shall be submitted quarterly to the concerned SPCB/PCC.

**33.7 Sitting of Industry**

Facilities for processing of Spent Sulphuric Acid shall preferably be located in a notified industrial area or industrial park/estate/cluster and in accordance with Consent to Establish issued by the concerned SPCB/PCC.

**33.8 Size of Plant & Efficiency of utilisation**

Maximum 1.0 metric tons of Spent Sulphuric Acid would be required to produce 0.37 metric tons of each product i.e. of 2-NADSPA and 6-Acetyl OAPSA. Therefore, requisite facilities of adequate size of storage shed and other plant & machineries as given in para 33.10 below shall be installed accordingly.

**33.9 On-line detectors / Alarms / Analysers**

Online detectors/alarms/analyzers shall be installed in case of continuous process operations for HCl Vapour and Mist and Sulphuric Acid Mist.

**33.10 Checklist of Minimal Requisite Facilities**

| S. No. | Requisite Facilities   |
|--------|--|
| 1.     | Storage tank(s) of adequate capacity to store Spent Sulphuric Acid of at least two weeks requirement.<br><br>Such storage tank(s) 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, the storage tank(s) may be below the ground provided it has HDPE liner system beneath the tank and leachate collection system below HDPE liner |
| 2.     | Cool, dry, well-ventilated covered storage shed(s) for Spent Sulphuric Acid storage tanks within premises.   |
| 3.     | Mechanized system for transfer of Spent Sulphuric Acid from tankers to storage tanks and storage tanks to reactor vessels  |
| 4.     | The process units shall have proper ventilation (preferably with ventilation ducts above the process units connected to ID fan with exhaust above roof level).   |
| 5.     | Covered hazardous waste storage space to store hazardous generated during utilization process  |
| 6.     | Reactors (isolation vessel) with suction hood connected via duct to scrubber and stack of adequate height as prescribed by concerned SPCB/PCC  |
| 7.     | Nutch filter   |

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|     |   |
|-----|---|
| 8.  | Centrifuge  |
| 9.  | Dryer (of adequate size operated electrically or by fuel) as permitted by the concerned SPCB/PCC  |
| 10. | Effluent treatment plant comprising of collection tank, neutralization, coagulation & sedimentation and sludge handling unit (Filter/Centrifuge/ Sludge drying bed etc.)  |
| 11. | Boiler (attached with the spray dryer/forced evaporator) operated electrically or by fuel as permitted by the concerned SPCB/PCC. Depending upon type of fuel, suitable air pollution control device(s) shall be installed with the boiler followed by stack of height as prescribed by the concerned SPCB/PCC. |
| 12. | Spray dryer/forced evaporator (single or multi effect evaporator) attached to stack of adequate height as prescribed by concerned SPCB/PCC  |
| 13. | 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.   |
| 14. | Dedicated hazardous waste storage area for temporary storage of hazardous waste generated during utilization process  |

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