

Evaluation of Ferric-chloride (FeCl_3) precipitation Effluent Treatment method in the reduction of organics pollutants from the effluent of Solvent Production Plant (SPP) of a Heavy Water project (HWP)

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Abstract: The Nuclear Organic Solvents are used in varied activities of Department of Atomic Energy in front end and back end of closed nuclear fuel cycle processes of Indian Nuclear Power program. These solvents are being synthesized in various units of heavy water plants. The effluent generated is composed of hypersaline Sodium Chloride (NaCl) or Potassium Chloride (KCl) with organic contaminants. The Chemical Oxygen Demand (COD) parameter which reflects the organic impurities exhibits the values up to 27,000 ppm and didn't fall under the prescribed limit of Central Pollution Control Board (CPCB), India. The effluent treatment method based on FeCl_3 was successful in reducing the COD to the level of 550 ppm and the pH level to prescribed limit but the other parameter measurements exceeded to certain extent than CPCB Industrial wastewater discharge limits. The main objective of the research is to analyze the effectiveness and potentiality of FeCl_3 precipitation method to treat the Solvent Production Plant (SPP) effluents in relevant to the statutory limit of CPCB. The physicochemical characteristics study of effluent before and after treatment initiated the water quality assessment of effective effluent management. This analysis leads to address the complexities of the ferric chloride precipitation method and the requirement of developing an alternative eco-friendly and energy efficient effluent treatment system with simplified treatment processes for sustainable operations in future.

Keywords: COD, Effluents, FeCl_3 precipitation, HWP Tuticorin, SPP

I. INTRODUCTION

The SPP in Heavy Water Plant (HWP) was mainly established focussing in production of solvents like Tributyl Phosphate (TBP), Tri Iso Amyl Phosphate (TIAP), Tri Octyl Phosphine Oxide (TOPO), Di Hexyl Octanamide (DHOA), Mono ester of Di-2-Ethyl Hexyl Phosphonic Acid ($\text{D}_2\text{EHPA-II}$) for important applications in DAE (Department of Atomic Energy) activities in front end and back end of nuclear fuel cycles specifically for the recovery of special nuclear materials^{1,2}. The Industrial activities in manifold were taken up by Heavy Water Board (HWP) with the development and deployment of various activities other than heavy water production through heavy water plants³.

In the production of solvents, the effluents generation was inevitable in the form of hyper saline aqueous solution containing NaCl, KCl with organic traces due to hydrolysis process, alkali and water washing in order to obtain a pure product. The Chemical Oxygen Demand (COD) of the effluent exhibit the range of 26,800 ppm which is multi-fold times higher than the prescribed limit 250 ppm of Central Pollution Control Board (CPCB). The disposal of Industrial effluent with high organic impurities causes nutrient depletion, degrading the water quality and reducing the Dissolved Oxygen (DO) content as a result of affecting the ecosystem^{3,4}. The main objective is disposing effluent after treatment with reduced levels of pollutants concentrations only up to acceptable limits prescribed by the statutory bodies of local and national level

pollution control boards ⁵. The intensive physicochemical characteristics analysis in this research could provide a deep insight to the pollutant concentration of effluent in development of a technically feasible environmentally friendly effluent treatment system ^{6,7}.

Since the effluent from SPP unit of HWP composed of high salts and organic compounds, chemical treatment method was viable to filter the effluents promptly with the main purpose of reducing the Chemical Oxygen Demand (COD) ⁸. A wide variety of methods (like Adsorption, Ion Exchange, Extraction, Wet Oxidation, Stripping, Distillation, Membrane Technology etc.,) are known to treat different types of Industrial effluents related to organic and Inorganic pollutants with its associated advantages and disadvantages ⁹.

The chemical precipitation method is overall considerable successful method in worldwide Industries for reducing the level of organic compounds in effluent ¹⁰. The chemical precipitation method uses high quantity of metal salt solution which enhances precipitation through increasing metal hydroxide and aggregation rate which results in entangling organic pollutants into large aggregates in the method of sweep floc-coagulation process ¹¹. This sweep floc-coagulation process is simple and advantageous in economically driven treatment of possibilities in recovering the over dosage of salt after the treatment using chelating agents ¹².

The factors such as resistance, viscosity of the solution and pressure affects the flow rate in effluent treatment during pumping of effluent to reactor vessels and hence careful consideration of these factors are necessary while improving the efficiency ¹³. The selection of a particular treatment system mainly depends on the degree of treatment required to bring the quality of treated effluents to a permissible level of disposal or reuse ¹⁴. This ensures that the final effluent is safe for disposal or acceptable for specific reuse or recycling. The deep investigation of the effluent characteristics before and after treatment would provide a precious discernment in designing and developing an appropriate effluent treatment system which fulfils the aspects of sustainability and eco-friendly nature ¹⁵.

The primary objective of this research was to evaluate the effectiveness of the ferric-chloride (FeCl₃) precipitation method in reducing the organic pollutant load of the effluent to the minimum acceptable levels. This study presents several important contributions to the understanding and treatment of effluents generated from solvent-production operations at the Heavy Water Plant (HWP). First, the work provides comprehensive physicochemical characterization of real-time effluents from the Solvent Production Plant (SPP), including detailed assessment of organic load, salinity, and hydrolysis-derived impurities. The systematic analysis for effluents associated with nuclear solvent manufacturing processes has not been reported previously.

Second, the study offers a critical evaluation of FeCl₃ based chemical precipitation for this unique high salinity, high COD effluent. The work quantitatively establishes the limitations of this method, including the production of substantial sludge (320

– 560 kg per 7m³ of effluent) and the inability to achieve the statutory COD limits in a single treatment setup. These findings reveal previously undocumented constraints in the applicability of conventional precipitation techniques for this effluent category.

Finally, the study establishes a structured basis for developing alternate or hybrid treatment methodologies tailored to SPP effluent characteristics. By identifying the shortcomings of established precipitation approaches and mapping the specific chemical constraints of the effluent, the work lays the foundation for designing more efficient and compliant treatment systems for specialized waste streams arising from nuclear-industry solvent production.

II. MATERIALS AND METHODS

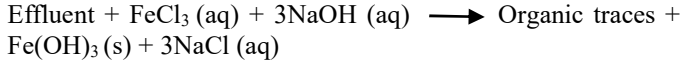
The methods followed in the physicochemical analysis of an effluent (before and after FeCl₃ precipitation treatment method) elucidates the clear aspects of understanding the unique concentration characteristics of effluent. The primary data related to characteristics of effluents were obtained from the lab study of Process Control & Analytical Laboratory (PC & AL) of SPP unit (mostly from the real time effluent discharged from the solvent production site) and the secondary data concerned were retrieved from the FeCl₃ precipitation treatment method in lab study. The overall data associated with quantification of parameters in both feed and treated effluent were analyzed in relevant to the statutory limit of TNPCB Parameters (Table 1) such as density (using Mettler Toledo Weighing Machine), pH (using pH meter LABINDIA), Conductivity (using Conductivity meter LABINDIA), TDS - Total Dissolved Solids (using Standard Glass fibre filtration and evaporation method), Sodium ion Na⁺ (using Flame Photometer ELICO), Chloride ion Cl⁻ (using Argentometric Titration Method), COD (using Redox titration method using reagents of Potassium Dichromate K₂Cr₂O₇, mixture of silver sulphate AgSO₄ and sulphuric acid H₂SO₄, Ferroin indicator [Fe(C₁₂H₈N₂)₃]SO₄). These parameters were estimated in real time mixture of effluent and comprehensive study of different types of effluents from synthesis of solvents like TBP, TIAP, TOPO, DHOA, D₂EHPA-II.

TABLE 1
TNPCB Industrial Wastewater Discharge Limit

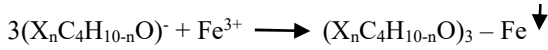
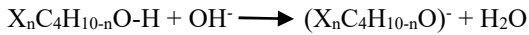
Parameters	Limit
pH	6.5 – 8.5
Conductivity, K (mS/cm)	2.25
TDS (ppm)	2100
Na+ (%)	60
K+ (%)	0.001 – 0.01
Cl- (%)	0.06
COD (ppm)	≤ 250

Mechanism of Chemical Precipitation of FeCl₃

When FeCl₃ is added to the aqueous effluent, followed by pH adjustment to a neutral value using NaOH, the trivalent metal cations undergo hydrolysis, forming positively charged monomeric and polymeric species. These species exhibit a high surface area, enabling them to adsorb negatively charged organic matter, leading to the formation of insoluble precipitates that eventually settle as sludge. For a simplified understanding of sludge generation, the following chemical equation illustrates the role of FeCl₃ in the precipitation process in our study.



In the case of Tri-Butyl Phosphate (TBP) effluent, the predominant butanol derivatives undergo chemical precipitation through the adsorption of butanol ions by metal ions, leading to the formation of metal butanolates.



The pH influences the type of metal hydroxide formed when the metal salt is dissolved in water. The organic effluent precipitation rate increases with increase in pH at very high pH values. This may be due to increased ionization of butanol ions into butanolate ions under higher alkaline conditions. The higher availability of butanolic ions at higher pH conditions increases the conversion of metal ions to metal butanolates.

III. RESULTS AND DISCUSSION

Feed Effluent Physicochemical Analysis

The characteristics of SPP wastewater were analyzed, and the results are presented in Table 2. The wastewater was observed as pale yellow in color, with a measured pH of 8.0. The analysis revealed elevated levels of conductivity (K), total dissolved solids (TDS), sodium (Na⁺), chloride (Cl⁻), and chemical oxygen demand (COD).

TABLE 2
Physicochemical characteristics of an Effluent (Before Treatment)

Mixture of effluents from Solvent	Density (g/cc)	pH	Conductivity K (mS/cm)	TDS (ppm)	Na ⁺ (%)	Cl ⁻ (%)	COD (ppm)
TBP, TIAP, TOPO, DHOA, D ₂ EHPA -II	1.037	8.1	43	28,681	0.98	1.5	26,800

TABLE 3
Physicochemical characteristics of an Effluent (After FeCl₃Treatment)

Mixture of effluents from Solvent	Density (g/cc)	pH	Conductivity K (mS/cm)	TDS (ppm)	Na ⁺ (%)	Cl ⁻ (%)	COD (ppm)
TBP, TIAP, TOPO, DHOA, D ₂ EHPA -II	1.030	6.8	108	72,360	3.1	4.2	550

Most of these parameters exceeded the permissible limits set by the Tamil Nadu Pollution Control Board (TNPCB), the regulatory authority for industrial wastewater discharge in Tamil Nadu, India.

FeCl₃ Chemical Precipitation Treated Effluent Analysis

The chemical precipitation process was carried out by adjusting the wastewater pH to 2, followed by the addition of FeCl₃ solution (20% w/v) with a quantity one third of effluent volume. A caustic solution of sodium hydroxide (NaOH, 20% w/v) was then introduced to facilitate precipitation. The mixture was left to settle overnight for complete precipitation (Figure 1).

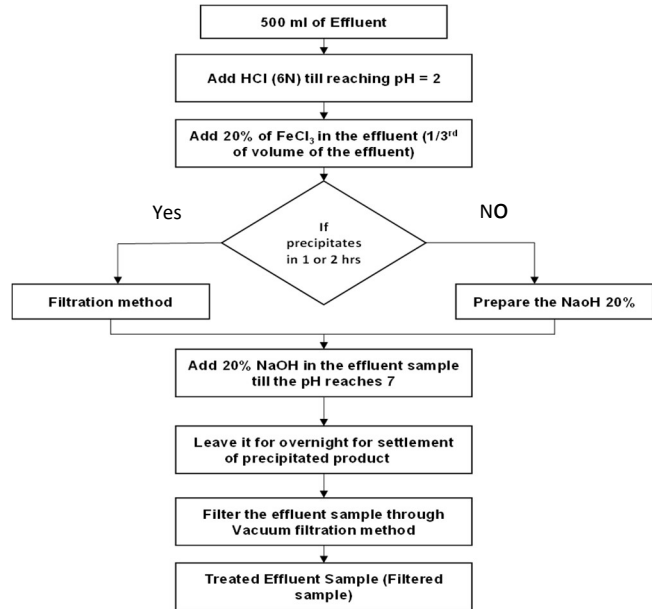


Fig. 1: FeCl₃ procedure in Lab scale method for investigation of the effluent treatment

The addition of FeCl₃ initially formed a dark brown floc, which gradually aggregated into larger particles and settled as sludge. After settling, the supernatant appeared clear and visibly colorless. Physicochemical analysis revealed that the FeCl₃ precipitation treatment effectively maintained pH levels and reduced COD to a reasonable level of 550 ppm (Table 3). However, other parameters showed a significant increase, likely due to chemical interactions between FeCl₃ and NaOH.

The chemical precipitation is highly dependent on the dose of FeCl_3 ¹⁶. The use of high doses of metal salt improves the rate of precipitation by two mechanisms such as: a) increasing concentration of metal hydroxide and aggregation rate, and b) by enmeshing the organic ligands into large aggregates by sweep floc coagulation.

Comprehensive Analysis of FeCl_3 Effluent Treatment for different effluent from solvent synthesis

The effluents in solvent production are generated from various chemical processes in solvent production due to esterification, distillation, substitution reaction (adding sodium as well as medium like Tetra-hydra Furan, Triethyl amine, hexane), alkylation, water washing, recovery through batch distillation, alkali hydrolysis, acid hydrolysis, final water washing, purification of a crude product and cooling & drawl of product. The effluents generated from solvent production primarily consist of sodium salts (NaCl), potassium chloride (KCl), and organic traces of raw materials and nuclear solvents left over from synthesis and production processes. Analysis of SPP effluent samples at the PC & AL laboratory of the Heavy Water Plant (Tuticorin) revealed significant pollutant concentrations (Table 4). The high levels of Chemical Oxygen Demand (COD) and Total Dissolved Solids (TDS) (Figure 2) indicate the presence of organic residues, which are predominantly discharged along with sodium salts NaCl), potassium salts (KCl), and other chemicals used in synthesis and reaction processes.

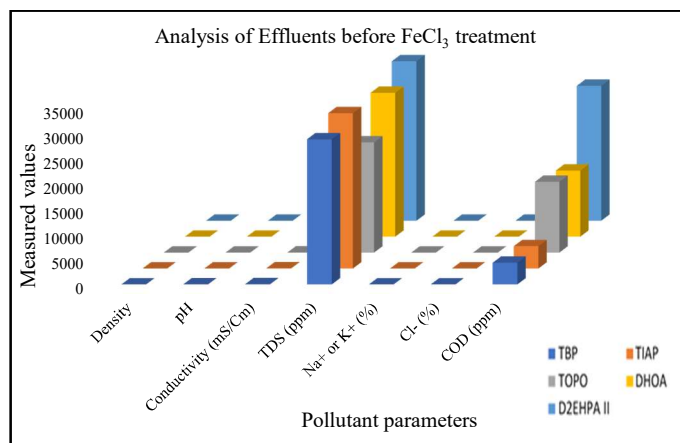


Fig.2: Physicochemical characteristics of an effluent before FeCl_3 treatment

The chemical precipitation process using ferric chloride (FeCl_3) was conducted by adding a predetermined quantity of FeCl_3 to 500 mL of effluent solution, adjusting the pH as described in Section 3.2. The addition of FeCl_3 initially produced a dark brown floc, which gradually formed larger aggregates and settled as sludge. The supernatant, obtained after centrifugation, appeared clearer and lighter in color. It was then filtered using vacuum filtration to separate the water from flocculated coagulants. Laboratory investigations of FeCl_3 treatment on effluents from five different solvent types (Table 4) showed that FeCl_3 effectively reduced pH and COD to acceptable levels but the TDS doubled (Figure 3).

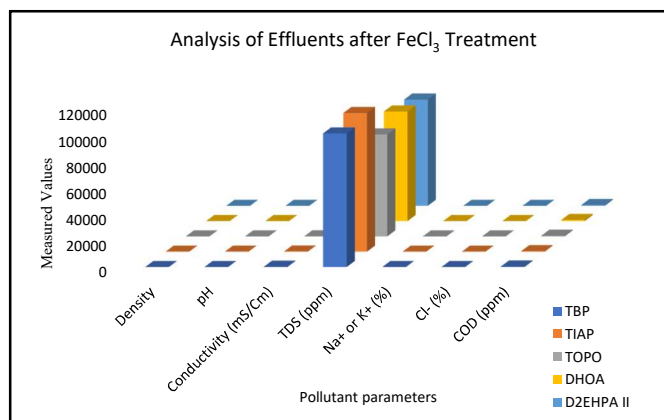


Fig.3: Physicochemical characteristics of an effluent after FeCl_3 Treatment

TABLE 4
Effluent characteristics analysis of before and after FeCl_3 Treatment

Name of the solvent preparation	EFFLUENT PARAMETERS													
	Density (g/cc)		pH		Conductivity (mS/cm)		TDS (ppm)		Na+ or K+ (%)		Cl- (%)		COD (ppm)	
	BT	AT	BT	AT	BT	AT	BT	AT	BT	AT	BT	AT	BT	AT
TBP	1.078	1.092	10.5	7.01	100.7	153.5	67,133.33	102,133.4	4.1	3.72	0.01	6.4	4339	352
TIAP	1.062	1.085	10.4	7.0	102	158.2	68,340	1,05,994	4.5	5.8	0.011	3.5	4482	370
TOPO	1.0108	1.0364	10.9	6.6	32.9	117	21,993.4	78,000	1.4	2.5	0.0085	4.16	14,144	520
DHOA	1.008	1.034	3.15	4.17	68.04	125	45586.8	83750	1.58	2.87	2.4	4.5	13,200	900
D2EHPA-II	1.024	1.0306	8.01	7.6	108	121.1	72000	81137	2.56	2.6	3.0	5.6	2600	600

BT – Before Treatment AT – After Treatment

Laboratory studies estimated that solid waste generation in real time from the FeCl_3 precipitation process ranges between 327 to 560 kg for 7 m³/day of treated effluent makes it complex and cost ineffective. The treatment process and waste generation data are presented in Figure 4 and Table 5.

TABLE 5
Approximate Solid waste generation predicted from PC&AL Investigation

S. No	Effluent from the Solvent	Solid waste (sludge) generated in kg from the effluent treatment
1	TBP	560
2	TIAP	562
3	TOPO	327.6
4	DHOA	378
5	D ₂ EHPA-II	372.96

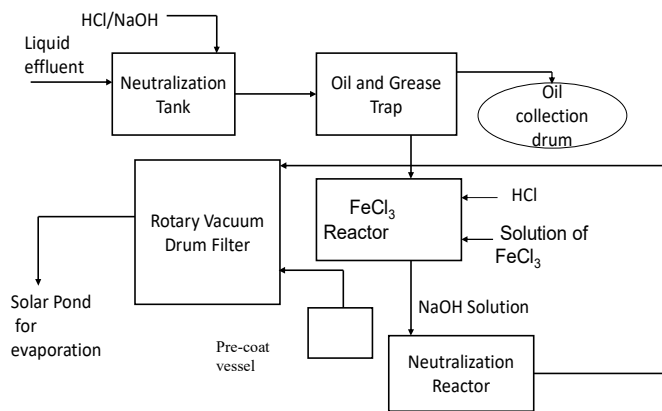


Fig.4: Schematic sketch of FeCl_3 precipitation based Effluent Treatment Method in Industrial Scale

IV. CONCLUSION

This study delivers the comprehensive evaluation of real-effluents generated from the Solvent Production Plant (SPP) at HWP Tuticorin and provides a novel systematic evaluation of the FeCl_3 precipitation method for treating these uniquely challenging, high salinity, high-COD waste streams. The FeCl_3 process achieved a significant reduction of COD – from the range 26,800 ppm to 550 ppm and effectively adjusted the pH, demonstrating its potential suitability of organic load reduction. However, the method was unable to meet the TNPCB requirement of less than 250 ppm COD. The treatment further resulted in substantial sludge generation (327 – 562 kg per 7 m³ of effluent) and caused the Total Dissolved Solids (TDS) to nearly double due to the interaction of FeCl_3 with NaOH during pH neutralization, which increased dissolved ionic species in the treated effluent. Other physicochemical parameters also increased because of the chemicals introduced during the precipitation process.

The novelty of this work lies in identifying and quantifying the limitations of FeCl_3 precipitation specifically for nuclear solvent production effluents – particularly the roles of metal – organic complexation, high salt load, and sweep-floc coagulation in constraining treatment efficiency. These insights, not previously reported for this effluent category, highlight the fundamental challenges of applying conventional precipitation methods to the wastewater.

Overall, the findings establish a critical knowledge base for developing alternative or hybrid treatment systems that can minimize sludge formation, control TDS and other residual pollutants, and offer a more energy-efficient, cost-effective, and sustainable solution for the safe management of effluents from nuclear solvent-production operations.

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