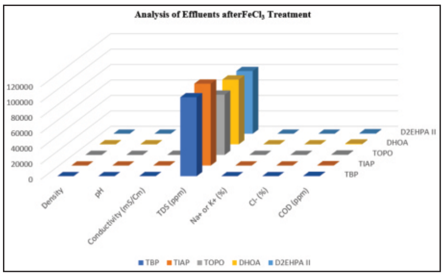
अपशिष्ट उपचार विधि

5

विलायक उत्पादन संयंत्र अपशिष्ट की भौतिक रासायनिक विशेषताएँ और इसकी अपशिष्ट उपचार विधि

ए.एस.जे. हैमिल्टन[1]*, एम. श्रीनिवास[1], एस. सुकुमार[2] एवं जी. वेंकटेसु[2]*
[1]बिट्स पिलानी, हैदराबाद, भारत
[2]भारी पानी संयंत्र, तूतीकोरिन, भारत



$FeCl_3$ उपचार के बाद एक अपशिष्ट की भौतिक रासायनिक विशेषताएं।

सारांश

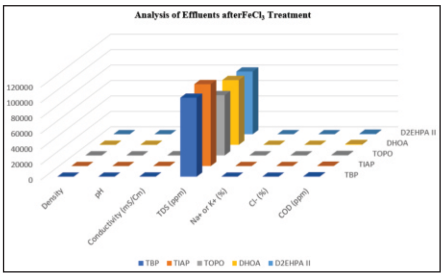
भारी जल संयंत्र (एचडब्ल्यूपी) के अंदर काम करने वाला विलायक उत्पादन संयंत्र (एसपीपी), संवृत नाभिकीय ईंधन चक्र प्रक्रमों के अग्र भाग और पश्च भाग जैसी विभिन्न नाभिकीय ऊर्जा गतिविधियों के लिए विलायक के संश्लेषण में महत्वपूर्ण भूमिका निभाता है। विलायकों के उत्पादन से सोडियम क्लोराइड के साथ जलीय घोल के रूप में कार्बनिक अवशेष के साथ पोटेशियम क्लोराइड लवण अपशिष्ट उत्पन्न हुआ है । उपचार से पहले अपशिष्टों से रासायनिक ऑक्सीजन मांग (सीओडी) 2000 से 14000 ppm की बहुत उच्च सीमा प्रदर्शित करती है, लेकिन फेरिक क्लोराइड ($FeCl_3$) उपचार के बाद एक बार के $FeCl_3$ अवक्षेपण में 350 ppm से 900 ppm की सीमा में स्तर को क्रमिक रूप से कम हुआ है और साथ ही 2100 वर्ग मीटर सतह क्षेत्र के साथ सौर तालाब में छोड़े गए उपचारित अपशिष्ट विसर्जन किया गया और उत्पन्न लवणों का उपयोग कई फ्रेंचाइज़ी गतिविधियों में किया जाएगा। $FeCl_3$ का उपयोग कर रासायनिक उपचार सीओडी को कम करने में सफल सिद्ध हुआ और pH के स्तर को 6 से 7 की सीमा में नीचे लाया है लेकिन किसी भी तरह से टीएनपीसीबी (तमिलनाडु प्रदूषण नियंत्रण बोर्ड) की निर्धारित सीओडी सीमा के साथ संरेखित नहीं है जो कि 250 ppm से कम है। यह अध्ययन अपशिष्ट की भौतिक रासायनिक विशेषताएँ सटीक प्रदूषक सांद्रता स्तर और मौजूदा अपशिष्ट उपचार को निर्धारित करती हैं जो प्रदूषक सांद्रता को सफलतापूर्वक कम करने में व्यवहार्य है और इस अध्ययन में प्राप्त परिणाम भविष्य में एक उन्नत अपशिष्ट उपचार प्रणाली विकसित करने हेतु एक डेटाबेस के रूप में काम करेगा।

Effluent Treatment Method

5

Physicochemical Characteristics of Solvent Production Plant Effluent & its Effluent Treatment Method

A.S.J. Hamilton[1]*, M. Srinivas[1], S. Sukumar[2] and G. Venketesu[2]*
[1]BITS Pilani, Hyderabad, INDIA
[2]Heavy Water Plant, Tuticorin, INDIA



Physicochemical characteristics of an effluent after $FeCl_3$ treatment.

ABSTRACT

The Solvent Production Plant (SPP) functioning inside the Heavy Water Plant (HWP), plays a crucial role in synthesizing solvent for various Atomic Energy activities like front end and back end of closed nuclear fuel cycle processes. The effluent generated from the production of solvents is in the form of aqueous solution with sodium chloride, potassium chloride salts with organic traces. The Chemical Oxygen Demand (COD) exhibits a very high range of 2000 to 14000 ppm from the effluents before treatment but after the Ferric Chloride ($FeCl_3$) treatment the level has been successively reduced in the range of 350 ppm to 900 ppm in one time $FeCl_3$ precipitation as well as the treated wastewater discharged to the solar pond with 2100 m^2 surface area and generated salts will be scrapped and used the same in several franchise activities. The Chemical Treatment of using $FeCl_3$ was successfully proved in reduction of COD and brings down the level of pH in the range of 6-7 but anyhow not aligned with the prescribed COD limit of TNPCB (Tamil Nadu Pollution Control board) which is less than 250 ppm. The physicochemical characteristics of effluent in this study determines the precise pollutant concentration level and the existing effluent treatment viable in reducing the pollutant concentration successfully and the results obtained in this study would serve as a database for developing for future scope of developing an advanced effluent treatment system.

KEYWORDS: *SPP, HWP Tuticorin, Effluents, $FeCl_3$ precipitation, COD*

**Authors for Correspondence: A.S.J. Hamilton & G. Venketesu*
E-mail: p20220429@hyderabad.bits-pilani.ac.in & gm@tut.hwb.gov.in

Introduction

The Solvent Production Plant (SPP) in Heavy Water Plant (HWP) was mainly established intended in production of solvents like Tributyl Phosphate (TBP), Tri Iso Amy Phosphate (TIAP), Tri Octyl Phosphine Oxide (TOPO), DI Hexyl Octanamide (DHOA), Mono ester of Di-2-Ethyl Hexyl Phosphonic Acid (D_2EHPA-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.

Role of Heavy Water Plant in Solvent Production and the Effluents Generation

In the production of solvents, the effluents generation are inevitable in the form of hyper saline NaCl, KCl with organic traces due to hydrolysis, alkali and water washing in order to obtain a pure product. The Chemical Oxygen Demand (COD) of the effluents ranges from 2000 to 14000 ppm which is multi-fold times higher than the prescribed limit 250 ppm of Tamil Nadu Pollution Control Board (TNPCB). The current R&D studies were undertaken to treat the effluents by Chemical treatment through Ferric chloride precipitation method. This Ferric chloride ($FeCl_3$) precipitation process is in successful reduction of COD level but not aligned with the limit of TNPCB in a single step precipitation. The sludge generated out in the $FeCl_3$ precipitation treatment from the SPP is calculated as around 400 MT per annum.

In the purview of R& D studies carried out with the effluents of SPP, it is clearly noticed that the areas mandate to focus are the concept of green chemistry, sustainability, eco-friendly and economically feasible to determine an alternate effluent treatment system suitable to the prescribed limit of TNPCB (Tamil Nadu Pollution Control Board) and Central Pollution Control Board (CPCB).

Methods and Materials

The methodology followed in studying physicochemical characteristics of an effluent elucidates to ensure the right quality and quantity of effluents and studying thoroughly with all the aspects into consideration [1]. The various factors which are to be considered for the discharge of effluents for any purpose are:

- The quantity of effluents discharged per day [2].
- Seasonal variation in quantity as well as quality [3].
- Analysis of important parameters suitable to the prescribed limit of Pollution Control Agencies [4].
- Influence of Industrial wastewater in environmental impacts and ecological imbalance [5].
- Cost involved in continuous supply of discharge in post treatment and cost effectiveness in sludge disposal [6].

The primary data related to n-butanol effluents were taken from the lab study of PC & AL of SPP unit (mostly from the n-butanol traces discharged in solvent production shown in table 1) for the purpose of calibration assessment and the secondary data concerned with the quantification of parameters like density (Mettler Toledo Weighing Machine), pH (pH meter LABINDIA), Conductivity (Conductivity meter LABINDIA), TDS - Total Dissolved Solids (Standard Glass fibre filtration and evaporation method), Sodium ion Na^+ (Flame Photometer ELICO), Chloride ion Cl^- (Argentometric Titration Method), COD (standard titration method using reagents of Potassium Dichromate $K_2Cr_2O_7$, mixture of silver sulphate $AgSO_4$ and sulphuric acid H_2SO_4, Ferroin indicator $[Fe(C_{12}H_8N_2)_3]SO_4$). These parameters were estimated in simulated samples of effluent from production of TBP, TIAP, TOPO, DHOA, D_2EPHA-II.

Ferric Chloride Precipitation ($FeCl_3$) Precipitation Method of Treating Effluents from SPP

The mechanism of removal of organic contaminants in saline solutions were done by using Ferric Chloride ($FeCl_3$) precipitation method [7,8]. In the lab study addition of $FeCl_3$ in the aqueous medium of effluent and further adjusting pH to neutral value, the trivalent metal cations hydrolysed to form positively charged monomeric and polymeric species that have a very large surface area and they tend to adsorb negatively charged organic matter and form insoluble precipitates which eventually settle down as sludge.

In our present study for simple understanding of sludge generation, the following equation may suffice the context of $FeCl_3$ role in chemical precipitation.

$$\text{Effluent} + FeCl_3\,(aq) + 3NaOH\,(aq) \rightarrow \text{Organic traces} + Fe(OH)_3\,(s) + 3NaCl\,(aq)$$

$$xFe^{3+} + yH_2O \rightarrow Fe_x(OH)_y^{(3x-y)+} + yH^+$$

The chemical precipitation of butanol derivatives most predominant effluent from Tri Butyl Phosphate (TBP) effluent is through the adsorption of butanol ions by metal ions to form metal butanolates.

$$X_nC_4H_{10-n}O\text{-}H + OH^- \rightarrow (X_nC_4H_{10-n}O)^- + H_2O$$

$$\downarrow$$

$$3(X_nC_4H_{10-n}O)^- + Fe^{3+} \rightarrow (X_nC_4H_{10-n}O)_3 - Fe$$

The pH influences the type of metal hydroxide formed when the metal salt is dissolved in water. The earlier studies influence the pH on chemical coagulation [8]. 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. The chemical precipitation is highly dependent on the dose of $FeCl_3$. 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 [8]. The lab investigation of Ferric Chloride ($FeCl_3$) precipitation procedure is followed by the flowchart below in Fig.1.

Table 1: Preliminary study from Butanol effluents (before and after treatment).

Parameters	Density (g /cc)	pH	Conductivity (ppm)	TDS (ppm)	Na^+ (%)	Cl^- (%)	COD (ppm)
Before $FeCl_3$ treatment	1.045	7.3	88	58,667	2.0	2.0	8000
After $FeCl_3$ treatment	1.058	6.9	142.9	95,473	5.6	3.2	556

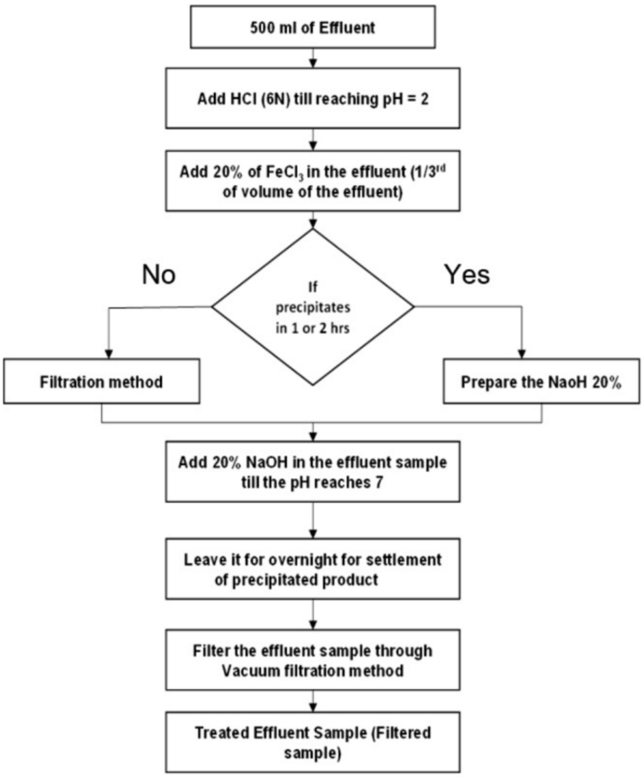


Fig.1: $FeCl_3$ procedure in Lab scale method for investigation of the effluent treatment.

Results and Discussion

The effluents from the Solvent Production Plant (SPP) of a Heavy Water Plant (HWP) Tuticorin were analyzed in Process Control and Analytical (PC & AL) Laboratory and results were estimated in both pre and post $FeCl_3$ precipitation method according to the pollutant concentration of each solvent effluent category and solid waste generated from the $FeCl_3$ precipitation of the effluent discharged at the disposal site.

The effluent management system of ETP (Effluent Treatment Plant) in a SPP unit envisaged to control and monitor effluents from the well-planned laboratory studies of physicochemical characteristics before and after $FeCl_3$ treatment (Table 2).

Effluent Generation and Analysis of parameters of an effluent before $FeCl_3$ treatment

The effluents generated from the solvent production due to the process of 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 predominant nature of the effluents mainly composed of Sodium salts (NaCl) and organic traces of nuclear solvents left out in the chain of synthesis in process operation and production of solvents. The sample analyzed from the effluents of SPP in the PC & AL laboratory of Heavy Water Plant (Tuticorin) clearly pointed the pollutant concentration (Table 2) and the high range of COD and TDS (Fig.2) indispensably shows organic traces mainly discharged with the effluents of sodium salt (NaCl) as well as other chemicals used for synthesis operation and reaction processes.

Analysis of Parameters of an effluent after $FeCl_3$ Treatment

The chemical precipitation was brought about by mixing a predetermined quantity of Ferric Chloride ($FeCl_3$) to 500 ml effluent solution at a particular pH as per the method studied in the section 3. The addition of $FeCl_3$ initially produced dark brown floc which eventually forms larger aggregates and settles down as sludge.

The precipitate can be separated from the solution by filtration (vacuum filtration method). The supernatant obtained from the centrifugation was clear and lighter in colour. The characteristics of effluents from the five solvent types have been investigated in laboratory methods of $FeCl_3$ chemical treatment method (Table 4). It was observed that the addition of $FeCl_3$ reduced the pH and COD to a reasonable level (Fig. 3). It is predicted that the solid waste generated from the precipitation ranges from 370 to 565 kg for the $7m^3$/day of effluent discharged after treatment (table 3) to the solar pond of surface area 2100 m^2 in real time effluent treatment. It is of most important concern that the COD of sludge ranges from 850 to 900 pm but there is no concern for the environmental effects from the sludge since the sludge is being scrapped and sold to other chemical or cement industries for further extraction of useful source for reuse in further operations. The

Table 2: Pollutant concentration analysis before and after $FeCl_3$ Treatment.

Name of the solvent preparation	EFFLUENT PARAMETERS													
	Density (g/cc)		pH		Conductivity (mS/cm)		TDS (ppm)		Na^+ (%)		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

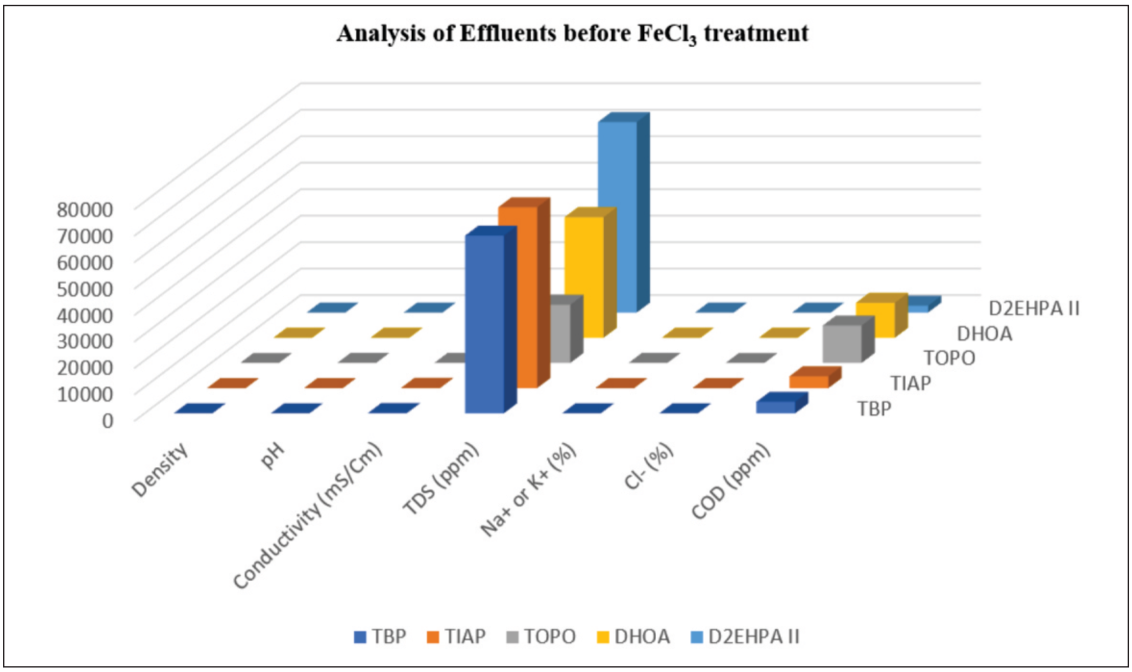


Fig.2: Physicochemical characteristics of an effluent before $FeCl_3$ treatment.

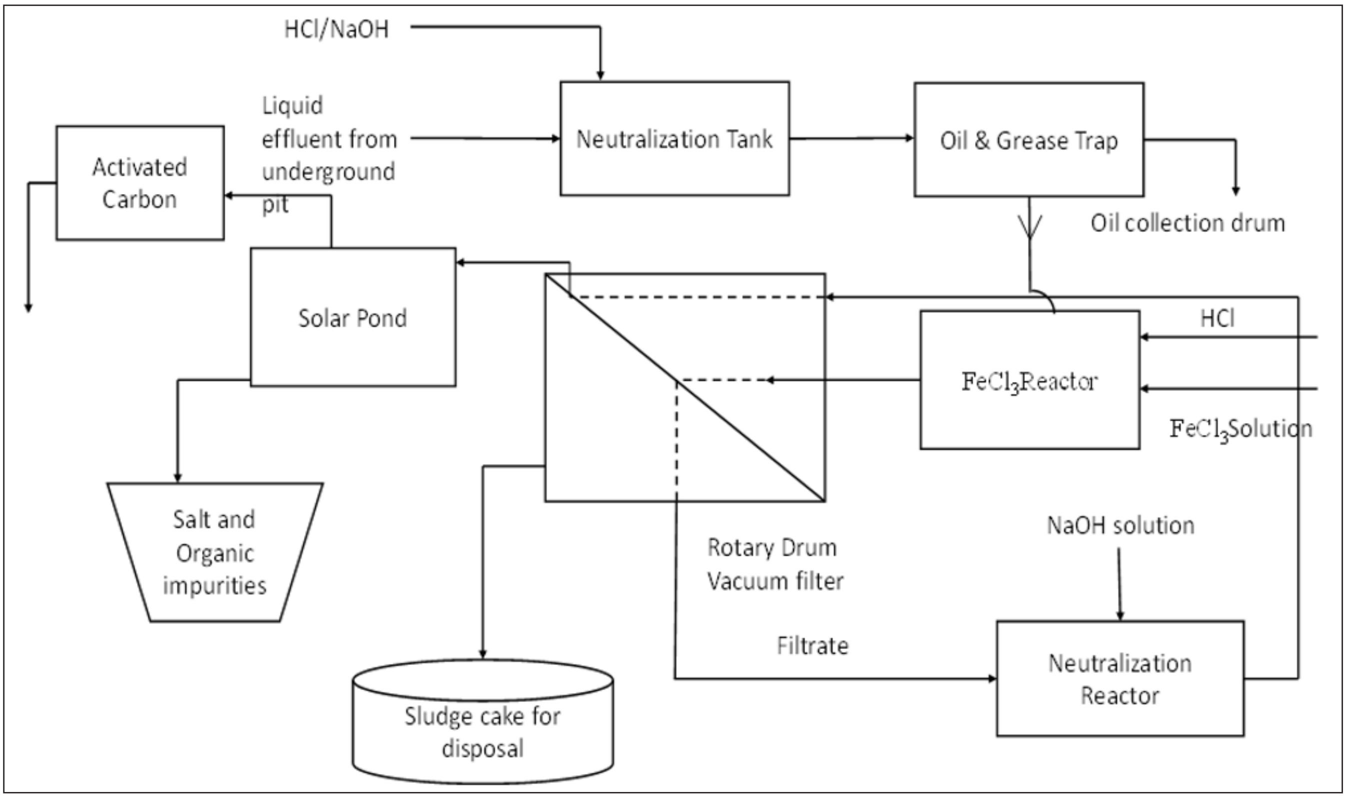


Fig.3: Schematic diagram of Ferrichloride ($FeCl_3$) based Effluent Treatment Plant in SPP.

schematic of Ferrichloride ($FeCl_3$) precipitation method used in the Effluent Treatment Plant (ETP) of Solvent Production Plant (SPP) is shown in the Fig. 2.

Comparative analysis of an effluent before and after $FeCl_3$ treatment

The SPP effluents before and after treatment comparative analysis gives a clear picture about the successful Ferric chloride ($FeCl_3$) precipitation method in reduction pH and COD but there is a noticeable increase in other parameters especially TDS due to the reagents used in the $FeCl_3$ process of

Table 3: Approximate Sludge Generation (ferric oxides) from $FeCl_3$ chemical treatment method.

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	D2EPHA-II	372.96
6	TBP	560

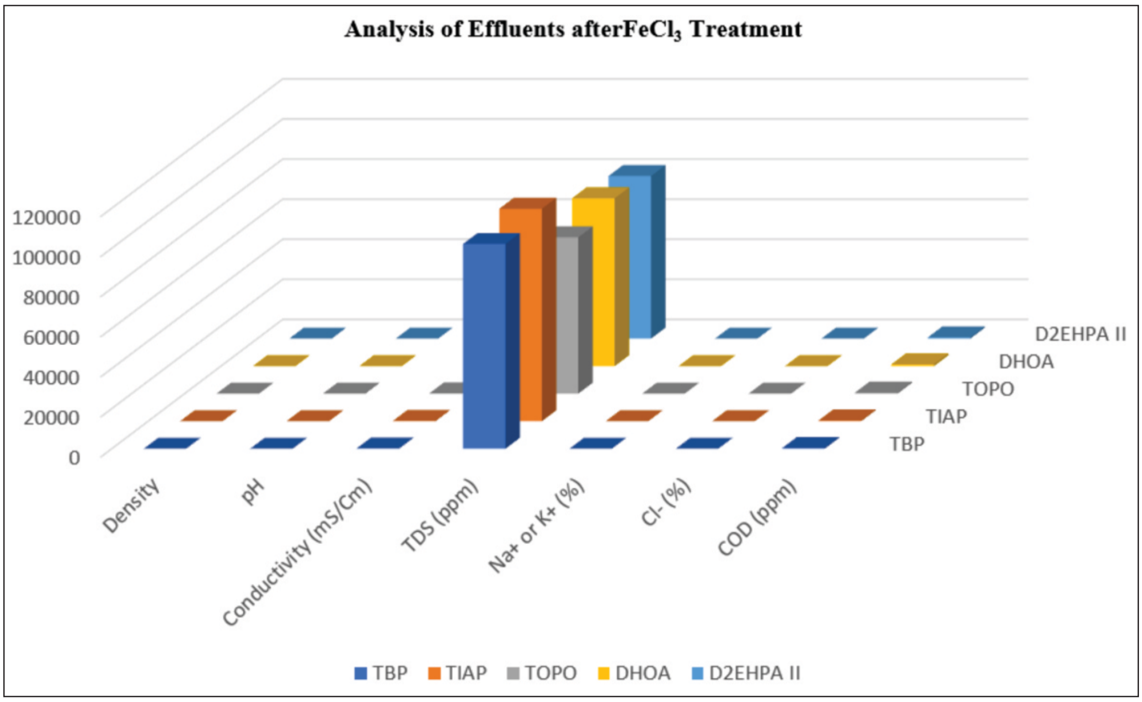


Fig.3: Physicochemical characteristics of an effluent before $FeCl_3$ treatment.

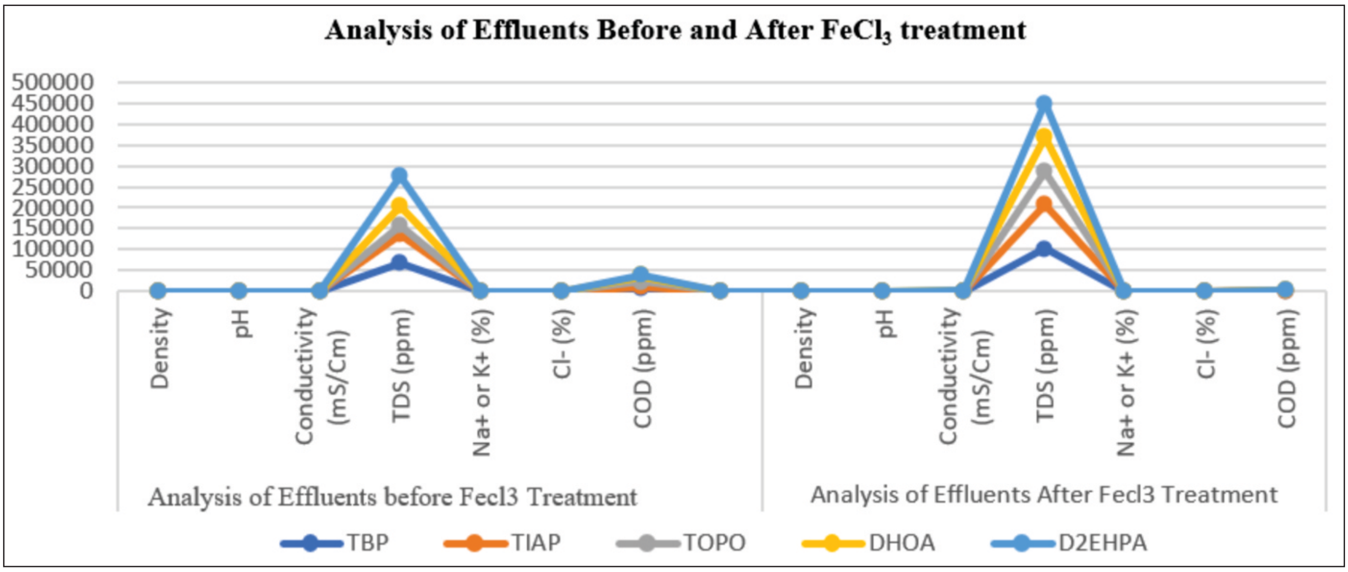


Fig.4: Comparison of SPP Effluents before and after $FeCl_3$ Treatment.

chemical treatment.

The remarkable changes in COD reduction level and pH neutrality (Fig.4) in the discharge of effluents after $FeCl_3$ treatment determines the chemical treatment method in SPP is somewhat successful in reducing the organics at the time of discharge but the parameters the Conductivity, TDS, Na^+, K^+, Cl^- foresighted the possibilities of enormous amount of salts and sludge caused by the FeCl3 precipitation method.

Conclusion

The studies of the proposed research gives a significant view of different types of solvent production processes associated with the effluent generation in SPP unit of HWP Tuticorin. From the physicochemical characteristics of SPP effluents before and after treatment indicated that the localized polluted water mainly composed of organic traces and hyper saline in nature. The acidic hydrolysis, alkali wash from Na_2CO_3 (Sodium Carbonate) and NaOH (Sodium Hydroxide) in solvent production processes leads to the generation of effluents and the current effluent treatment method of $FeCl_3$ (Ferric chloride) precipitation method was successful in reducing the main parameter of COD (Chemical Oxygen Demand) ranges of 320 – 900 ppm from higher level of 14000 ppm but not fulfilled the standard of meeting the statutory limits of Tamil Nadu Pollution Control Board (TNPCB) COD level of 250 ppm. It is widely believed and anticipated that the multiple treatments of $FeCl_3$ method requirement would suffice the soaring level of COD to the acceptable limit of State Pollution Control Board (SPCB – TNPCB) as well as Central Pollution Control Board (CPCB). Furthermore, the $FeCl_3$ precipitation chemical treatment induces coagulation of dissolved solids and flocculates it to settle down as sediment at the end of the treatment processes. The associated solid waste generated for the $7m^3$ of effluent per day from the ETP of SPP unit ranges from 327 to 562 kg per batch of solvent production process and the quantity may differ depends upon the requirement of solvent production in levels. The treated effluent discharged to the solar pond of surface area 2100 m^2 formed as solid waste left after evaporation of discharged wastewater; the solid waste is composed of hyper saline particles contaminated with traces of organic waste would be scrapped to either reuse in extraction of organic materials in chemical or cement industries in the nearby vicinity of Tuticorin. The Environmental indicators analyzed in this study would serve as a data base of future comparative analysis with other developed effluent treatment systems with a main aim of reducing the COD level to the TNPCB limit while eliminating the sludge or residual waste in post treatment of effluent.

References

[1] Gray N., Water Technology. 3rd edition. London: CRC Press; 2017.

[2] APHA. Standard Methods for the Examination of water and waste water. 21st edu. Washington, DC. American Public health Association; 2005.

[3] American society for Testing of Materials. 1969. Manual on water (3rd edu.,) ASTM, Philadelphia, U.S.A.

[4] Journal of Toxicology and Environmental Health (Hemisphere Publishing Corporation, 1025, Verment Avenue, N.W., Washington D.C., 20005, U.S.A.

[5] Ihsan Hamawand, 'Energy Consumption in Water/ Wastewater Treatment Industry - Optimisation Potentials', Energies Journal 2023 MDPI, Basel, Switzerland vol. 16: 24-33.

[6] Sachchida Nand Singh, Gaurav Srivastav and Arun Bhatt, Physicochemical Determination of Pollutants in Wastewater in Dheradun, Journal: Current World Environment, vol. 7 (1),133-138 (2012).

[7] Roohollah Noori, Ronny Berndtsson, Majid Hosseinzadeh, Jan Franklin Adamowski, 'A Critical Review on the Application of the National Sanitation Foundation Water Quality Index', Journal: Environmental Pollution, Elsevier Publication, Vol. 244, 575-587(2019).

[8] Water Quality Analysis of PC and AL Laboratory of SPP, HWP Unit, 2023.

[9] N. Kumara Swamy, Pratibha Singh and Indira P. Sarethy, 'Precipitation of Phenols from Paper Industry Wastewater using Ferric Chloride'. Journal of Chemisty: vol. 4, No.2(2011), 452-456.

[10] Kavindra Kumari Kesari, Ramendra Soni, Pooja Tripathy, 'Wastewater Treatment and Reuse: A Review of its applications and health implications'. Water Air Soil pollution (2021) 232: 208.