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Research Article

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Pharmaceutical Effluent Reduction through Recycling of Methylene Dichloride by Using Green Process and Treatment Methodology

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Abstract: Pharmaceuticals industries are majorly consuming methylene dichloride as one of the solvent. After pharmaceutical processing, hazard wastes of effluent are being generated. Hazard wastes are highly harmful to environment and health. Hazard waste stream of methylene di chloride had been identified as spent solvent which have been incinerated or selling from the industry. Experimental evidence had been created to find the best possible solution to convert the specific stream of hazard waste in to pure methylene dichloride which will be recycled into the process. The study aimed to find the optimum methodology and commercial scale application of the process to get pure quality of methylene di chloride from waste stream. Treatment technology developed and focused with three fundamental treatment steps. The primary treatment involves treating of the spent waste with calcium chloride which removes the moisture and followed by simple distillation operation. It helps to removes major moisture and elimination of salts. Secondary treatment involves treating with molecular sieves to achieve the moisture almost to anhydrous level. Third treatment had developed with carbon treatment to remove color in the recovered solvent. Tertiary treatment ensures for meeting the clear liquid and matches with fresh solvent. The developed process provides the better yield and better process control with less emission mechanism. Recovered methylene dichloride sample was tested with various analysis tools, which were meeting all defined quality parameters. The major advantage of the developed process had been achieved all quality parameters and it can be scaled up for the commercial application with less cost of operation.

Keywords: Pharmaceutical waste, Adsorption, molecular Sieve, Spent waste of methylene dichloride, Waste reduction, Carbon.

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1. INTRODUCTION

Pharmaceuticals organization is growing multifold in India due to the business favoring and cost of the products. Two states of India namely, Telangana and Andhra Pradesh yields approximately 42% of the annual gross pharmaceutical production[1]. Hyderabad is the hub of highest producers of pharmaceutical products and intermediates[2]. Based on the production volume, pharmaceutical industries are generating various effluents and hazardous wastes. Reagents and different solvents are being used in pharmaceutical industries for the manufacturing of API or intermediate products. After completion of the process waste solvent (Hazard waste) is being generated .It can be sold or incinerated[3]. Methylene dichloride is one of the commonly used Solvent in Pharmaceutical Industry. Methylene di chloride (MDC) can be produced by two major methods. One was direct chlorination of methane and the other was Hydro chlorination of methanol. The direct chlorination of methane yields methylene chloride by the direct Reaction of excess methane (natural gas) with chlorine at a high Temperature (340-370°C) and at a pressure slightly above one Atmosphere, producing methyl chloride, methylene chloride, chloroform, and carbon tetrachloride as co products. Hydro chlorination of methanol involves the vapor-phase reaction of hydrogen chloride and methanol with the addition of a catalyst at 180-200°C to the hydro chlorination reactor, (maintained at 350°C) which yields methyl chloride. The exit gases from the reactor pass through a quench tower, scrubber, and drying tower prior to yielding methyl chloride. Methyl chloride then undergoes further chlorination, stripping, and distillation to yield MC and chloroform[4]. Process flow and consumption pattern of methylene dichloride had been described in figure 1. Basically methylene dichloride is one of the raw materials used in the manufacturing of pharmaceutical products. After manufacturing of the product, spent hazard waste of methylene di chloride had been generated as effluent from the process. Methylene Di chloride is the chlorinated solvent which is more harmful to environmental and health[5-6]. It is highly carcinogenic in nature[7]. The boiling point of the solvent is low and tendency to evaporate. This solvent leads for the vent emission and environmental pollution and followed by the energy requirement for the fresh solvent manufacturing.

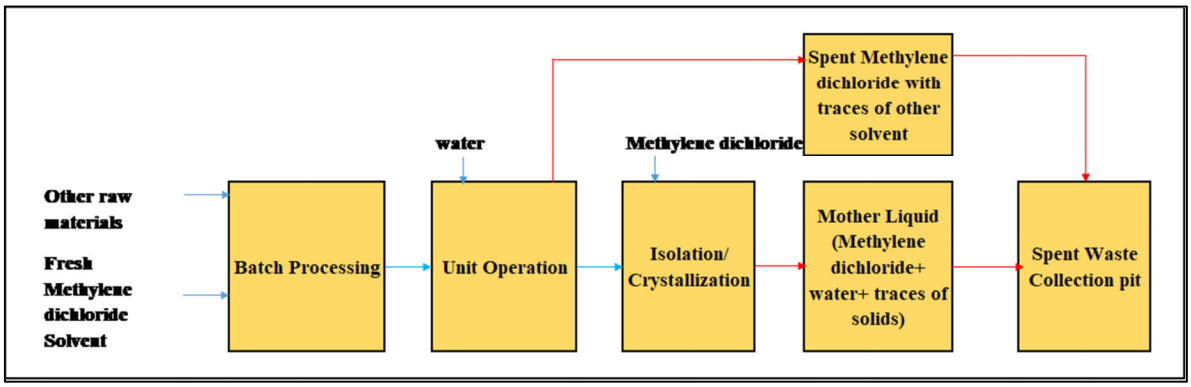

Fig 1: Existing Process flow pattern

Hazards are catered with Liquid, solid and solvent waste, powder waste and spent mixed solvent. Waste water is being treated in the ETP and spent waste solvents are sold for the incineration or to other industries. Solid waste is being incinerated or sent for the land filling. Analysis had been carried out to identify the source of effluent and hazard waste as methylene di chloride. As there were many Practical difficulties and due to composition, the mixer is not recycled to the process and it is being burnt in the incinerator and some of the cases spent wastes were sold to other industries. The mother liquor generated as effluent was further treated through a sequence of steps in order to attain the recyclable quality of methylene dichloride against fresh solvent. The solubility of Methylene di chloride is 0.15% at 25 C and the specific gravity at 25 C is 1.326. Methylene dichloride is non-flammable [8]. Hence, the present study has been described to optimize a suitable sequence of methods for treating hazardous waste streams to fresh recyclable quality.

2. MATERIALS AND METHODS

2.1 Materials

Materials used for this research include fresh Methylene di chloride, water, synthetically saturated methylene di chloride and water, effluent generated from industries, calcium chloride, Molecular sieves and carbon.

2.1.1 Qualities of Materials consumed

Material - Calcium chloride – Grade (Anhydrous) commercial grade, Molecular sieves – 3 A, Activate carbon – Powder form and commercial grade.

2.2 Source of Hazard Waste Generation

As part of preventing effluent generation and providing the solution for the key industrial issue, it had been analyzed; Process flow and consumption pattern of methylene dichloride had been plotted and described in the flow chart. Based upon the process understanding two effluent source points are mixed together which was going as a spent hazardous waste.

2.3 Hazard Waste Characterization

The Characterization of Hazard waste was essential for planning and effective method creation for treating the process. The characteristics of the hazardous waste had been varying as for the mother liquor and distillate. The characteristics of hazard waste vary from place to place and depend on varying solvent addition, process condition and addition of components and Reagents. Characterization of

Hazard waste was done to determine the physical properties and chemical composition. Tools used for characterizing the hazard waste were Gas Chromatography (GC), Moisture content Analyzer, Measuring jar. Hazard waste is characterized as follows.

Physical Properties: Specific gravity is about 1.4 and slightly yellowish in color.

Chemical Composition: Purity of waste stream : > 98.1% and traces of suspended solid particles.

2.4 Methodology to convert the Hazard waste into pure compound

The methodology for converting the hazardous waste into recyclable quality of methylene dichloride is by treating primarily with calcium chloride [9] followed by adsorption of molecular sieves along with carbon treatment. Adsorption was one of the methods used for liquid-liquid or liquid-solid interface[10-11]. 3A molecular sieve provides effective reduction in water content resulting in single digit ppm[12]. Activated carbon was used for various applications which include solvent recovery, separation of gases, and dye removal from industrial wastewater[13]. Here, in this present study it was used for color removal.

2.4.1 Primary Treatment with Calcium chloride

Experiment was conducted in a round bottom flask at 25 C and at atmospheric pressure where we initially added 100 g of waste stream of methylene dichloride whose moisture content is about 0.16% and 3 g of Calcium Chloride. The process was optimized with different qualities such as varying calcium chloride quantity (3, 5 gram), holding contact time of (10, 20, 30 minutes) with agitation speed of 200 RPM. The mixture was stirred after addition of calcium chloride and allowed to settle. The aqueous and organic layer were separated and organic layer quantity was distilled out to remove the chlorides and traces of salts.

The aqueous and organic layer was separated with help of separator. Organic layer was collected and measured. Total quantity was heated with 40 to 45 deg and distillate collected separated receiver .Methylene Di chloride vent loss is possible during distillation. Loss can be avoided for providing better cooling in condenser.

2.4.2 Secondary Treatment with molecular Sieves (Adsorption)

The distilled organic layer was treated with 3A molecular Sieves in a round bottom flask at 25 C and atmospheric pressure. The adsorption study was optimized by conducting three set of experiments by taking initial concentration of 50 ml of distilled layer and varying parameters of loading range (0.2, 0.1, 0.06 g/ml), amount of equivalent adsorbent (10, 5, 3 gram), and residence time (1, 2, 15 hours). The final moisture content was found by using KF Titration method. The moisture content of fresh methylene dichloride is 0.02%. If the moisture content complies the sample was processed for carbon treatment.

2.4.3 Process Validation of secondary Treatment (adsorption)

Based on the experimentation, validation of the concept was done with higher volume of distilled layer i.e. 2500 ml of distilled layer where 150 grams of adsorbent was added. The loading range was 0.06(g/ml) which is much lesser in range. The experimentation was kept for varying contact time of 1, 2 and 15 hours where at each time interval the sample is tested for moisture content by KF and noted.

2.4.4 Tertiary Treatment with carbon

If the moisture content of the adsorption process complies, the carbon treatment was processed to remove color in order to meet fresh solvent specification. Carbon treatment is low cost[14] methodology for color removal. The Experiment was conducted by taking 2 g of activated carbon for 100 ml of Methylene di chloride and string for a period of 20 minutes and filtered. The recovered methylene dichloride was submitted for Gas Chromatography (GC) to check purity.

2.4.5 Desorption of molecular sieves

Desorption is important unit operation for our study[15]. The objective of desorption is to remove the moisture from the molecular sieve and activate the adsorbent for further cycle. As part of the lab scale developmental procedure and process, adsorbed molecular sieves are loaded into the clean trays. The loaded trays were kept initially under nitrogen atmosphere in order to displace all air in the system. After evacuation of the air, vacuum was applied to bring the system below atmospheric condition. Vacuum tray drier having heating element . Heat is being supplied and temperature attained upto 160^{0}C The basic concept behind this was to remove unbound moisture from the adsorbent. The heating was continued for the five hours and at each time interval of 1 hour the weighing was done.

3. RESULTS

Based on the experimental workouts with evidence the primary, secondary and tertiary treatment which helps to achieve the results of the lower level of moisture, color and meeting the Residue of Ignition not detected.

3.1 Results of Primary Treatment

Based on the experimentation, it was noted that the moisture reduction is relatively about 0.08% and the solvent recovery is nearly about 80%. The data clearly states that the residual traces of solvent were found to be not detected. Primary treatment experimentation results are tabulated and described in Table 1. As part of the Process and additional calculation, standard deviation data has arrived for the moisture content. The optimized primart treatment process of moisture content average value is 0.085 % and standard deviation P value reporting as 0.007638.

Table 1: Experimentation results of primary treatment

Run	Waste stream	Initial Moisture content	Calcium Chloride	Agitation Speed	settling time	Distilled quantity	Effluent	Final Moisture content (%)	ROI
	(ml)	(%)	(g)	(Rpm)	(min)	(ml)	(ml)		
1	100	0.16	3	200	10	80	20	0.10	ND

2	100	0.16	3	200	20	79	21	0.08	ND
3	100	0.16	3	200	30	80	20	0.08	ND
4	100	0.16	5	200	10	85	15	0.09	ND
5	100	0.16	5	200	20	83	17	0.08	ND
6	100	0.16	5	200	30	83	17	0.08	ND

ROI: Residue on Ignition

3.2 Results of Secondary Treatment

As described in the methods and materials chapter, the 3 sets of optimization trials (DOE) and validation were conducted and the results were tabulated below. From the data it was noted that the reduction of moisture was about 0.01% and meeting the fresh methylene dichloride specification of about NMT 0.02%. Based process optimization and condition, 0.06 g/ml of adsorbent and the contact time of 2 hours are finalized and results were tabulated in table 2. Key process parameters of loading and contact time of the process had been included as part of compilation.

Table 2: Design of Experiments results of Secondary treatment

Run	Distilled MDC (ml)	Adsorbent quantity (g)	Initial Moisture Content (%)	Loading Range (g/ml)	Contact Time (hour)	Final Moisture Content (%)	Treated MDC (ml)
Set I optimization: Varying Contact Time and Loading Range							
Run 1	50	10	0.1	0.2	1	0.03%	47.5
Run 2	50	10	0.1	0.2	2	0.02%	47.5
Run 3	50	5	0.08	0.1	1	0.02%	47.6
Run 4	50	5	0.08	0.1	2	0.02%	47.3
Run 5	50	3	0.08	0.06	1	0.01%	48.3
Run 6	50	3	0.08	0.06	2	0.01%	48.2
Set II optimization: Varying Contact Time and Keeping Loading Percentage Constant							
Run 7	50	3	0.09	0.06	1	0.02%	48.4
Run 8	50	3	0.08	0.06	2	0.01%	48.1
Run 9	50	3	0.08	0.06	15	0.01%	48.3
Run 10	50	3	0.08	0.06	1	0.02%	48.4
Run 11	50	3	0.08	0.06	2	0.01%	48.2
Run 12	50	3	0.08	0.06	15	0.01%	48.4
Set III optimization : Contact time Optimization							
Run 13	50	50	0.08	0.06	2	0.01%	48.4
Run 14	50	50	0.08	0.06	2	0.01%	48.3
Run 15	50	50	0.08	0.06	2	0.01%	48.4
Run 16	50	75	0.08	0.06	1	0.02%	48.4
Run 17	50	75	0.08	0.06	1	0.02%	48.4
Run 18	50	75	0.08	0.06	1	0.02%	48.2

MDC: Methylene dichloride

3.3 Process Validation of secondary Treatment

The loading Percentage was about 0.06 and extended contact time of 5 hours found sufficient for attaining desired moisture level. To demonstrate the process parameter and consistency of the process conditions, validation was adopted for the developed process and summarized in the table 3.

Table 3: Experimentation results of process Validation of Secondary Treatment

Run No.	Waste stream (ml)	Initial Moisture content (%)	Molecular Sieves (g)	Loading Range (g/ml)	Time (hours)	Water content (%)	Treated MDC (ml)
Run 1	2500	0.15%	150	0.1	5	0.05%	2410
Run 2	2500	0.15%	150	0.06	5	0.1%	2415
Run 3	2500	0.15%	150	0.06	5	0.08%	2418

MDC: Methylene dichloride

This adsorption process will help to meet the specification and elimination of the effluent for the proposed composition of the solvent ratio. This solvent was tested with the process of the intermediates and it met the specification of the intermediates. As part of the Process and additional calculation, standard deviation data has arrived for the moisture content. The validated process of moisture content average value is 0.0467 % and standard deviation P value reporting as 0.0287

3.4 Tertiary Treatment with carbon

After carbon treatment, it was noted that the Methylene dichloride was colorless. The results were tabulated in table

4 and it was found meeting the defined specification. Recovered methylene di chloride samples are represented in the figure 2. The Solvent Identification test was confirmed by Gas Chromatography (GC) and Gas Chromatography Mass Spectrometry (GC-MS) and results were reported in fig3&4.

Table 4: Experimentation Results of Tertiary Treatment

S.No	Input (ml)	Carbon Quantity	Output (ml)	Purity (%)	Description	pH	Moisture content (%)
1	100	2	95	>99	Colourless	5.7	0.01
2	100	2	96	>99	Colourless	5.9	0.01
3	100	2	95	>99	Colourless	5.5	0.01

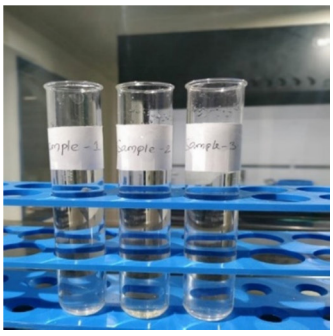

Fig 2: Recovered Methylene di chloride Samples

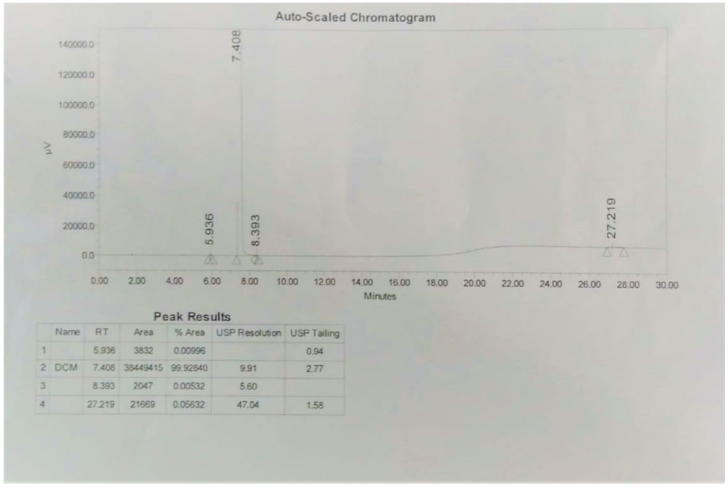

Fig 3: Recovered Methylene dichloride Sample Gas Chromatogram

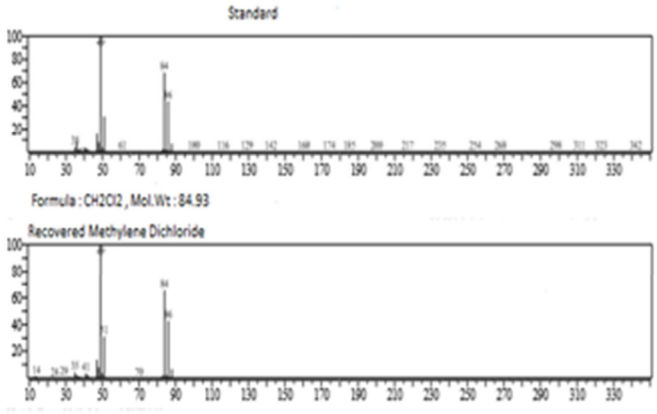

Fig 4: GC-MS of Standard vs. Recovered Methylene dichloride

4. DISCUSSION

4.1 Industrial perspective – Scale up of the process

Experiment had been conducted with different methodologies and achieved the best possible fit of adsorption with carbon treatment to convert the effluent to pure compound which will be recycled to the process. Data analysis explains that the reduction of moisture with minimum time and minimum loss of product was achieved by adsorption process. Treated effluent had been meeting the moisture content and color and quality. The defined process

was simple and commercially adoptable for this particular stream and concept can be extrapolated for the similar characteristic of the methylene di chloride waste. The cost of the project implementation would be highly feasible and easily adoptable. The defined process would not generate the additional load to effluent treatment plants. .The proposed framework is more economically[16] viable and implementable in commercial scale considering the huge amount of Methylene di chloride waste stream generation in the pharmaceutical industry, the commercial scale level design of adsorption column process had worked out and details are as follows.

4.2 Scale up- PART A (Primary and secondary treatment)

4.2.1 Primary Treatment with Calcium chloride

Hazard waste streams of methylene di chloride consist of the moisture and traces of salts. The prime steps to remove the salts and moisture content were done by calcium chloride. Batch reactor is suitable equipment to perform the batch dehydration followed by distillation of the organic layer. It helps to achieve the moisture reduction level of 0.08% and removal of the sulfates.

4.2.2 Secondary Treatment with adsorbent

Adsorption System was built in the process to achieve the moisture in PPM level. Primary treatment gives the moisture of 0.08 % and further reduction would take place in the secondary treatment. Methylene chloride dryer proposed to have a two -column adsorption system with thermal swing regeneration facility. The column was filled up with 130 Kg of type 3 A molecular sieves Effluent stream of Methylene di chloride (Distilled) feed was cooled by cooler to below atmosphere and then taken into the adsorption column from bottom to top at a flow rate of 200 -250 LPH. After continuous feeding for 8 hours the first tower will go for regeneration for 16 hours as per the process by the supplier. One tower can process the maximum of 2200 L of Methylene chloride in 24 hours with 8 hours processing time and 16 hours regeneration time In the meantime the second column can be used for the dehydration of methylene di chloride at 200 -250 L/Hours for 8 hours and then regeneration of molecular sieves for 16 hours. The feed stream was passed through one of the tower while the other tower will be regenerated. Moisture would be absorbed by molecular sieves. Dried methylene dichloride is available from the top in a single pass which would be collected in the product tank.

4.2.3 Derivation of Column Height Calculation

To handle the commercial scale effluent, column height is essential to perform adsorption and desorption. To design the column height and operating the following parameters are considered. Material of construction of the column - stainless steel (SS316) – pH is neutral.

Bulk density of 3 A molecular sieves[17] = 779 kg/m^3 (kg: kilogram, m:meter)
Mass of 3 A molecular Sieves = 130 kg
Volume= Mass/ Bulk Density = 130/779 = 0.167 m^3
Volume occupied by Molecular Sieve=0.167 m^3
Considering 30% excess Volume for Design Purpose =0.167 X 1.3 =0.217 m^3
Basic formula for calculation is $\pi XD^2Xh/4$.

Assuming the Diameter as 0.2642 m, the height is calculated to be 3.96 m. Commercial scale design proposal matrix has been formulated which is described in table 5.

Table 5: Design Summary of Adsorption Column

Design Proposal Matrix		
Adsorption Column Design Considered (Design of Adsorption)		
Material of Construction for the Equipment	Stainless Steel SS316	
Design Considered– Spent waste	2000	Liter/Day
Pure Compound generated after adsorption Process	1936	Liter/Day
Expected % - the recovered methylene di chloride	96	%
Column Diameter	0.2642	meter
Column Height	3.96	meter

4.3 Scale up- PART B (Carbon leaching treatment)

Primary and secondary treatment indents to remove the moisture and salts in the hazard waste effluent of methylene di chloride. After treatment, methylene dichloride was found to be colored. To remove the color, it was treated with carbon to achieve color less liquid. The unit operation of the carbon treatment can be done in the simple batch reactor. Moisture removed methylene dichloride was leached with the carbon in the single stage and filtered in the sparkler filter at commercial scale level.

4.4 Scale Up-Desorption procedure

Desorption temperature had been identified through with Experimentation. Desorption setup consists of the air heater which will heat the air up to 160 C and pass in the column of the tower. Hot nitrogen would be passed on the column for 8 -10 hours with the temperature of 160 C. It would be passed continuously as per the proposed scheme. Due to hot air, methylene di chloride removed through evaporation and solvent will be removed. The temperature would gradually increase and evaporation would take place. Temperature would be monitored by the indicator and useful to measurement and it would be cooled by passing the cool air the same circuit. The overview of the equipment design and overall flow chart had been represented for the commercial scale manufacturing unit in Fig 5 & 6.

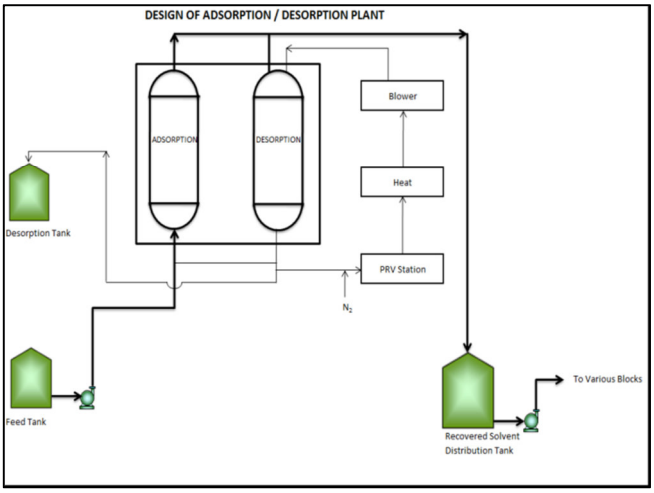

Fig 5: Design of Commercial scale equipment - Adsorption and Desorption Scheme

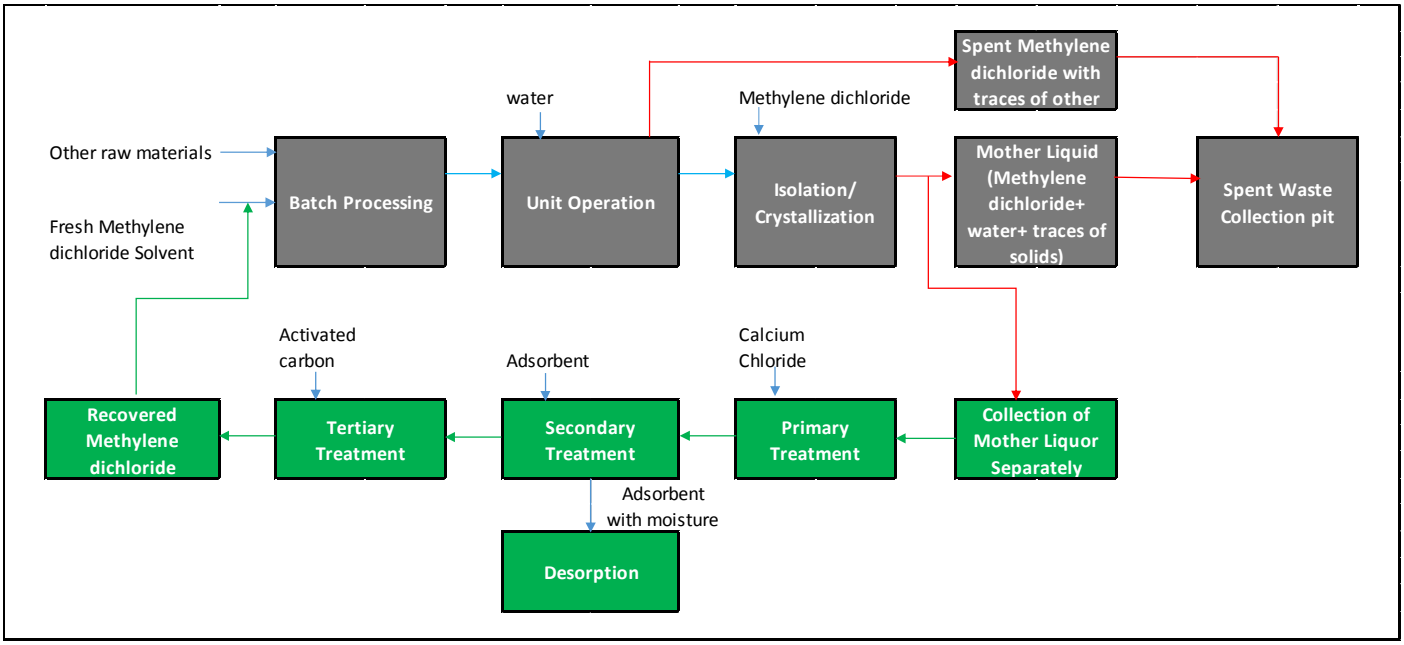

Fig 6: Proposed Process flow Diagram

5. CONCLUSION

The present investigation describes the specific industrial hazard waste to pure methylene dichloride recovery. Methodology have been reported that a combination of treatment process and procedure have been well established with an experimental approach. Results are falling under the specification of purity greater than 99 % and 0.01% of moisture with colorless liquid after carbon leaching. The concept was demonstrated with three validation experiments of process and procedure. Pure methylene di chloride specification achieved and confirmed with the identification test of GC and GCMS. Pure methylene di chloride can be recycled into the intermediate steps of the pharmaceutical process which gives the direct benefit of recycling of the waste stream. The overall advantages would be avoiding the waste of solvents discharge and controlling the environmental hazard, purchasing of fresh solvent in the pharmaceutical industry. The operation of the treatment process was very simple at commercial Scale level and expected higher yield from the developed process. Desorption procedures were well defined during experimentation. The operational cost was cheaper to recycle the solvent as comparatively purchasing of the fresh solvent. The capital investment and food print was very low for the proposed design. We have been accounting the indirect benefit of the fresh water and energy consumption for the manufacturing of the solvent. From a commercialization perspective the design of the system has been designed. The process can be automated completely without manual interventions. The particular developed process pertained to the defined waste solvent Stream which can be extrapolated for different methylene dichloride and chlorinated waste solvents.

6. AUTHORS CONTRIBUTION STATEMENT

Mr. Thanigaivelu S devised the project, conceptual and framework followed by design the experiments, worked out the results mapping and commercial scale analytics with regards to this work. Dr. K. Ramamohan Reddy verified the method of approach, analysis and supervised the works. Both authors discussed the methodology, results and contributed to the final manuscript.

7. CONFLICT OF INTEREST

Conflict of interest declared none.

8. REFERENCES

1. Choudhury Atun Roy, Veeraraghavan Arutchelvan. Treatment of highly concentrated effluent generated from intermediate chemical and bulk drug industries renovated with tertiary removal. Int J Environ Sci Nat Res. 2018 June;12(2):29. doi: 10.19080/IJESNR.2018.12.555831.
2. Changing Markets Foundation and Ecostorm. Hyderabad's pharmaceutical pollution crisis: heavy metal and solvent contamination at factories in a major Indian drug manufacturing hub. 2018; p.12-3 68-9.
3. Chea John D, Lehr AL, Stengel JP, Savelski Mariano J, Slater C Stewart, Yenkie KM. Evaluation of Solvent Recovery Options for Economic Feasibility through a Superstructure-Based Optimization Framework. Ind Eng Chem Res. 2020 March 3;59(13):5931-44. doi: 10.1021/acs.iecr.9b06725.
4. Safriet Dallas. Locating and Estimating Air Emissions from sources of methylene chloride. United States Environmental Protection agency. p. EPA-454/R-93-006:5-18; 1993 February. Available from: https://www3.epa.gov/ttn/chief/le/methlncl.pdf [cited 18/8/2020].
5. US Environmental Protection Agency. Methylene chloride (dichloromethane) 75-09-2, hazard summary-created in April 1992; revised in January 2000, 1-https://19january2017snapshot.epa.gov/sites/production/files/2016-09/documents/methylene-chloride.pdf.
6. United States Environmental Protection Agency. Introduction to hazardous waste identification (40 CFR Parts 261), solid waste and emergency response. 2005 EPA530-K-05-012;5305W:1-3.
7. Shestakova Marina, Sillanpää Mika. Removal of dichloromethane from ground and wastewater: a review. Chemosphere. 2013 Aug 12;93(7):1258-67. doi: 10.1016/j.chemosphere.2013.07.022, PMID 23948610.
8. Smallwood Ian McN. Oxford: Blackwell Publishing Science Ltd. p. 386; 2002. Solvent Recoveryhandbook. 2nd ed. Available from: http://aevnmont.free.fr/SACH-Books/Organic%20 Chemistry/Solvent%20Recovery%20Handbook-Ian%20Smallwood.pdf [cited 18/8/2020].
9. Burfield DR, Lee K, Smithers RH. Desiccant efficiency in solvent drying. A reappraisal by application of a novel method for solvent water assay. *J. Org. Chem.* 1977; 42(18): 3060–65. doi: 10.1021/jo00438a024.
10. Mohammed MA, Shitu A, Tadda MA, Ngabura M. Utilization of various Agricultural waste materials in the treatment of Industrial wastewater containing Heavy metals: AR. Int Res J Environ Sci. 2014 March; 3(3):63.
11. Dabrowski A. Adsorption--from theory to practice. Adv Colloid Interface Sci. 2001;93(1-3):135-224. doi: 10.1016/s0001-8686(00)00082-8, PMID 11591108.
12. Williams DBradley G, Lawton Michelle. Drying of organic solvents: quantitative evaluation of the efficiency of several desiccants. J Org Chem. 2010;75(24):8351-4. doi: 10.1021/jo101589h. PMID 20945830.
13. Abdur M, Daud Nik, Nik Daud NN. A review on activated carbon: process, application and prospects. Journal of Advanced Civil Engineering Practice and Research. tad da, M.A. and Ahsan, A. and Shitu, A. and ElSergany, M. and Arunkumar, T. and Jose, Bipin and Razzaque. 2016 June;2(1):10.
14. Saleem J, Shahid UB, Hijab M, Mackey H, McKay G. Production and applications of activated carbons as adsorbents from olive stones. Biomass Conv Bioref. 2019;9(4):775-802. doi: 10.1007/s13399-019-00473-7.
15. Smith Julian C, Harriott Peter, McCabe Warren L, Unit Operations of Chemical Engineering. New York: McGraw-Hill, Inc. Vol. 815; 1993. 5th ed. Available from:https://evsujpiche.files.wordpress.com/2014/06/unit-operations-of-chemical-engineering-5th-ed-mccabe-and-smith.pdf [cited 18/8/2020].
16. Richardson Paul, Steven Alan, Kargbo Robert, Nawrat Christopher C, Mateos Carlos, Zlota Andrei A, Knight John. Some Items of interest to process R&D chemists and engineers. Org Process Res Dev. 2020 May 5;24(5):874-83. doi: 10.1021/acs.oprd.0c00197.
17. Abdel-Rahman Zaid A, Mahmood Abdulrahman M, Ali Ahmed J. Ethanol-water separation by pressure swing adsorption (PSA). Iraqi J Chem Petrol Eng. 2014 Jul; 15(2):2.