

Optimization of Raw Material usage in Manufacturing of Dye – A Cleaner Production Technique

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ABSTRACT There is no denying the fact that dyestuff industry is the major growth driver all around especially in the textile and chemical industries in the country. India is one of the major supplier of the dyes and dye intermediates from the Asian region and can meet the requirements of the world at large provided adequate incentives and facilities are made available. The dye industry achieved growth rate of 15% during last year. India's share in the world market is estimated at 5-6%. The Share of Gujarat in all Indian export is about 60%. The major markets for Indian dyestuff are the European country, USA, South Korea, Hong Kong. Manufacturer are suffering due to competition in market by the other country like china, so to with stand with them it is necessary to optimize the manufacturing process either Production cost ,Raw material cost or Energy cost which is the ultimate way to stand in competitive market. To achieve the above mentioned thing Cleaner Production is applied. Cleaner Production means economic savings from reduced consumption of raw materials and energy and lower treatment costs as well as other benefits such as a better company image and better working conditions. Fiber reactive dyes are commonly employed for textile dyeing; the use of these dyes can introduce high costs and environmental concerns. For example, their fixation levels can be as low as 50% and high salt levels are typically needed to achieve desired shades. Thus, a mechanism for increasing fixation and exhaustion efficiencies in an economical way would enhance the value of these dyes to the textile industry. With these points in mind, 'Optimization of Raw material usage in Manufacturing of Reactive Dye', one of the cleaner production technique that holds promise for achieving desirable exhaustion and fixation efficiencies. Specifically, the reactivity and affinity of Reactive Blue (Blue RGB) dye. Modified dye is also cheaper than conventional dye. In laboratory study it was determined that modified dye gave the best results in affinity, shade depth assessments and cost.

Keywords—Cleaner production, reactive dye, diazotization, coupling .

I INTRODUCTION:

1.1 INTRODUCTION TO CLEANER PRODUCTION

The primary function of the economic activities is to process input resources (raw materials, energy, water, etc.) into usable outputs. However all the inputs are not transformed into products. The portion that does not get transformed into useful outputs comes out as wastes. This transformation into waste depends on the technology employed and efficiency of the process. However, with the growth of the economic activities, on one hand the withdrawal of resources from nature has increased, while on the other hand the discharge of the wastes into the environment as

amplified. The environmental pollution and ecological degradation first became issues of international concern in the 1970s, when it was recognized that mass production by industry and mass consumption by society are depleting the resources and generating huge amounts of pollutants. Traditionally the focus of environment protection efforts has been upon setting up pollution control equipment to treat liquid effluents or gaseous emissions and bringing down the concentration of pollutants to within the stipulated limits. This concept is appropriately known as "End of Pipe (EOP)" treatment. While this EOP approach has been thought of as the effective method for protecting the

environment, it has, in reality, presented following disadvantages.

- 1) It results in the transfer of pollutant from one medium to another viz. gaseous pollutants into solids (SO₂ into gypsum), liquid effluents to solids (sludge from wastewater treatment plants) or solid wastes into gaseous (incineration) thereby affecting no net environmental benefits. In some instances, this transfer can even increase the risk to human health and the environment.
- 2) It rarely reduces the absolute quantity of the pollutants
- 3) It assumes that the environment has enough capacity to take care of the residual pollution levels by itself.
- 4) It requires huge dead investments and recurring expenses, which makes this concept highly unsustainable at times. For most of the SME's this is just not feasible on account of poor profitability, space constraints etc.

Realizing these drawbacks and looking into further aggravating problems as the pollutant assimilation capacity of the receiving bodies nearing exhaustion, the concerned agencies were forced to go backward in the industrial production processes and there emerged the concept of proactive approach of waste reduction at source in environment protection. In other words, **Cleaner Production (CP)** was realized the need of the day.

What is Cleaner Production?

Cleaner Production focuses on preventing or minimizing the generation of wastes and emissions. The basic idea of cleaner production is that it makes more sense to avoid creating a problem altogether rather than trying to remedy the problem. It is commonly called proactive approach to waste management.

Cleaner Production can be defined as: A new and creative way of thinking about products and the processes that makes them. It is achieved by the continuous application of strategies to minimize the generation of wastes and emissions.

Cleaner Production means economic savings from reduced consumption of raw materials and energy, and lower treatment costs as well as other benefits such as a better company image and better working conditions.

1.2 INTRODUCTION TO DYESTUFF

The synthetic dye industry today is vast and contains many groups of dyeing processes and dyes. From the synthesis of biological stains used in the preparation of microscope slides to the production of acetate

rayon dyes and nylon dyes used in the preparation of commercial textiles, the industry continues to develop new processes and dyes to serve the needs and wants of humanity. One area of early synthetic dye chemistry though, azo dyes, remains one of the largest and most important to the industry. The birth of azo dyes came in 1858, the same year Perkin started his factory for the production of mauve, although their value was not appreciated until Bottiger produced congo red, the first direct cotton dye, in 1884. Johann Peter Griess had made the original discovery that a diazo compound could be derived from the reaction of nitrous acid with aromatic amines. Upon experimentation, he further concluded that this diazo compound could couple to another aromatic amine resulting in the formation of a dye. This area of chemistry has been greatly expanded and refined and now includes trisazo, tetrakisazo and polyazo dyes. The diazonium ion, containing the $-N=N-$ chromophore, serves as a weak electrophile which may perform an electrophilic aromatic substitution on an aromatic ring to produce a vast and diverse array of different dyes. Upon referral to the above discussion of the chemistry behind the colors, one can see how these dyes with their great amounts of conjugated Π bonds serve as excellent dyes. The future of the synthetic dye chemistry appears certain. As the global market continues to expand and western culture proceeds to penetrate even the world's most isolated regions, the demand for inexpensive dyestuffs will continue to rise. It is promising that this demand will be well met as "the possibilities of further synthesis [of dyes] are unlimited." With these prospects in sight for the synthetic dye chemistry, one might say that this industry certainly promises a bright and colorful future.

Ever since the beginning of humankind, people have been using colorants for painting and dyeing of their surroundings, their skins and their clothes. Until the middle of the 19th century, all colorants applied were from natural origin. Inorganic pigments such as soot, manganese oxide, hematite and ochre have been utilized within living memory. Palaeolithic rock paintings, such as the 30,000 year old drawings that were recently discovered in the Chauvet caves in France, provide ancient testimony of their application. Organic natural colorants have also a timeless history of application, especially as textile dyes. Synthetic dye manufacturing started in 1856, when the English chemist W.H. Perkin, in an attempt to synthesize quinine, obtained instead a bluish

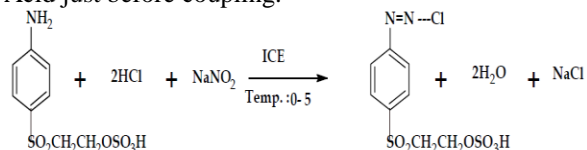
substance with excellent dyeing properties that later became known as aniline purple. Perkin 18 years old patented his invention and set up a production line. This concept of research and development was soon to be followed by others and new dyes began to appear on the market, a process that was strongly stimulated by Kékulé's discovery of the molecular structure of benzene in 1865. In the beginning of the 20th century, synthetic dyestuffs had almost completely supplanted natural dyes.

2. MANUFACTURING PROCESS OF AZO(REACTIVE BLUE 250) DYE:

Manufacturing Process for manufacturing of Reactive blue 250 involves five step processes. The raw material requires for that processes are H-Acid, Vinyl Sulphon, Ortho Anicidine Vinyl Sulphon, Hydrochloric acid, sodium nitrite and Sodium Hydroxide. The processes involve are diazotization and coupling.

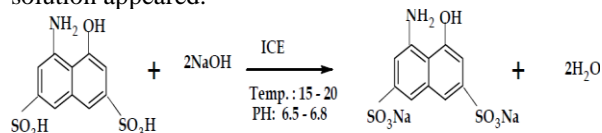
2.1 First Diazotization:-

Vinyl Sulfone (Acetanilide based) charged to an M.S.R.L. reaction vessel along with water and ice to maintain temperature between 0 to 5 °C. Then Hydrochloric Acid was added followed by Sodium Nitrite powder gradually till diazotization completed, which can be confirmed by starch iodide paper. Starch iodine paper will convert in to purple color if diazotization not complete (if excess nitrite will present in reaction mass). If all nitrite will consumed than there will not any change on iodine paper. Any excess nitrite will be removed by adding Sulfamic Acid just before coupling.



2.2 Prepare Clear Solution of H-Acid:-

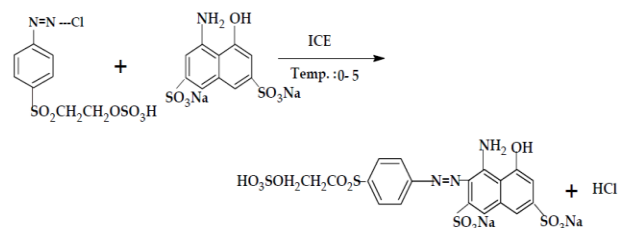
H-Acid (1 Hydroxy 8 amino 3, 6 di sulphonic acid) was charged to a M.S.R.L. reaction vessel along with Caustic lye and maintained at Temperature at 15 – 200 °C and pH at 6.5 to 6.8 stir it till clear brown solution appeared.



2.3 First Coupling:-

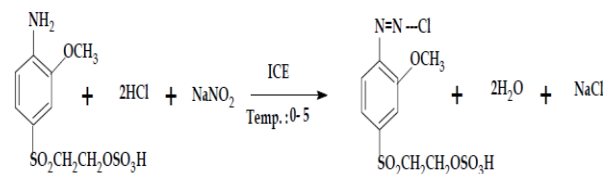
Prepared clear slurry of H-Acid was charged in to the diazotized vinyl sulfone, and stirred for 6 to 8 hrs

keeping the temperature between 0 to 5 °C by adding of ice.



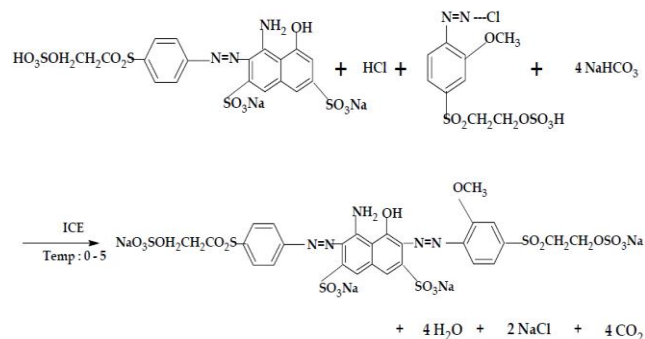
2.4 Second Diazotization:-

As mention in first coupling, Vinyl Sulfone (Ortho Anicidine Based) charged to a M.S.R.L. reaction vessel along with water and ice to maintain temperature between 0 to 5 °C. Then Hydrochloric Acid was added followed by Sodium Nitrite powder gradually till diazotization completed, any excess nitrite was removed by adding Sulfamic Acid just before coupling. Keep temperature between 0 to 5 °C throughout the diazotization reaction.



2.5 Second Coupling:-

Charge diazo of O.A.V.S. to the first coupling mass and stir for 3 hours keeping temperature 0 to 5 °C pH of the coupling mass was raised by addition of sodium bicarbonate and maintained temperature at 0 to 5 °C by addition of ice. Properties of dye (Strength, tone etc.) was checked before starting spray drying, if any correction needed apply. At last transferred batch to spray dryer.



2.6 Spray Drying:-

The standardized dye liquid of reactive Blue 250 is transferred to the spray drying holding tank and spray dry. After drying in to spray dryer the crude dye was packed in plastic bags to avoid contamination from moisture and dust. For some cases it was passed through Reverse Osmosis setup to further purify it and reduce the salt concentration.

3. EXPERIMENTAL WORK:

Experimental work for this study is done at R & D department of Mira Organics Pvt. Ltd. at Ankleshwar. Before taking any raw material for use it was tested in quality control laboratory of the industry. After Preparation of dye dying on cotton is done as per standard procedure. All testing of dye and dyed cotton done with different instrument as per

standard procedure. All Testing Procedure are listed here.

As described earlier experimental methodology is same for all this experiment. Material charged and Product recovered is listed here in the following table, As per Stoichiometric of the reaction the raw material required as per purity listed as shown in the following table: Each batch is taken of 100 Gms of Reactive blue 250. The Software was prepared in Excel for calculation & the same is shown below.

Experiment No :							
Basis :	100 Kgs						
Property	H-Acid	V.S	NaNO ₂	OAVS	Na Salt of H-Acid	Di azo of V.S	NaOH
Mol. Wt in Gms/Mol	319	281	69	311	363	328.5	40
Purity	80%	96%	100%	95%			48%
Density in Gms/cc							
Viscosity in cP							
	Bl Carb	HCl	CO ₂	H ₂ O	NaCl	Di Azo of OAVS	Product
Mol. Wt in Gms/Mol	84	36.5	44	18	58.5	358.5	1021
Purity	98%	30%					
Density in Gms/cc		1.18					
Viscosity in cP							

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Viscosity in cP							

STAGE 1 : Di Azotization of Vinyl sulphon			
Material In		Material Out	
Weight in Kg		Weight in Kg	
Vinyl Sulphon	28.67	Di azo salt of V/S	32.17
HCl	23.83	H ₂ O	20.21
NaNO ₂	6.76	NaCl	6.88
	59.26		59.26

STAGE 2: Na Salt of H-Acid			
Material In		Material Out	
Weight in Kg		Weight in Kg	
H-Acid	39.05	Na Salt of H-Acid	35.55
NaOH	16.32	H ₂ O	12.01
		Impurity	7.81
	55.38		55.38

STAGE 3: First Coupling Mass			
Material In		Material Out	
Weight in Kg		Weight in Kg	
Na Salt of H-Acid	35.55	1st couple	64.15
Di azo salt of V.S	32.17	HCl	3.57
	67.73		67.73

STAGE 4 : Di-azotization of OAVS			
Material In		Material Out	
Weight in Kg		Weight in Kg	
OAVS	32.06	OAVS diazo	35.11
HCl	23.83	H ₂ O	20.21
NaNO ₂	6.76	NaCl	7.33
	131.57		131.57

STAGE 5 : Final Dye Coupling with Neutralization			
Material In		Material Out	
Weight in Kg		Weight in Kg	
Ist Couple	64.15	Dye	100
HCl	3.57	H ₂ O	7.05
Bi-Carb	32.91	NaCl	11.46
Dave diazo	35.11	CO ₂	17.24
	135.75		135.75

OVERALL MATERIAL BALANCE AS PER PURITY :			
Material In (in Kg)		Material Out (in Kg)	
H-Acid	39.05	Dye	100
V.S	28.67	Salt	33.48
NaNO ₂	13.52	H ₂ O	59.48
OAVS	32.06	CO ₂	17.24
NaOH	16.32		
sodium carbonate	32.91		
HCl	47.67		
	210.20		210.20

Figure: Stoichiometric calculation of reaction in Excel Programme

	Materials input							Materials output			
	H-Acid	V.S	NaNO ₂	OAVS	NaOH	Na ₂ CO ₃	HCl	Dye + Salt	H ₂ O	CO ₂	ANY OTHER
Existing Process	39.05	28.67	13.52	32.06	16.32	32.91	40.86	133.48	52.67	17.24	
Exp.-1	39.05	28.67	13.52	31.73	16.32	26.60	40.86	126.00	52.67	17.24	0.84
Exp.-2	39.05	28.67	13.52	31.73	9.72	27.00	40.85	120.00	46.34	24.19	
Exp.-3	38.27	28.67	13.78	32.06	10.62	33.00	40.85	126.00	45.79	24.99	
Exp.-4	37.49	28.67	13.78	32.06	10.34	33.00	40.85	125.00	45.86	24.85	
Exp.-5	37.49	28.67	13.52	32.06	8.73	32.91	28.12	131.92	32.35	17.24	
Exp.-6	374.93	286.69	135.16	320.64	87.32	329.09	281.23	1319.17	323.49	172.38	

4. RESULT AND COST ANALYSIS:

4.1 FINAL PRODUCT ANALYSIS REPORT

EXP NO.	PRODUCT (GMS)	STRENGTH	RESULT	DE	DL*	Da*	Db*
Existing Process	133.48	1		0.56	-0.46	0.33	-0.19
1	126	1.31	FAIL	3.85	-3.81	0.45	0.21
2	120	0.89	FAIL	1.6	1.4	-0.20	-0.74
3	126	1.02	OK	0.59	0.4	0.15	-0.4
4	125	1.04	OK	0.59	-0.56	0.16	-0.13
5	131.92	1.03	OK	0.55	-0.42	0.33	0.12
6	1319.17	1.01	OK	0.54	-0.38	0.31	-0.04

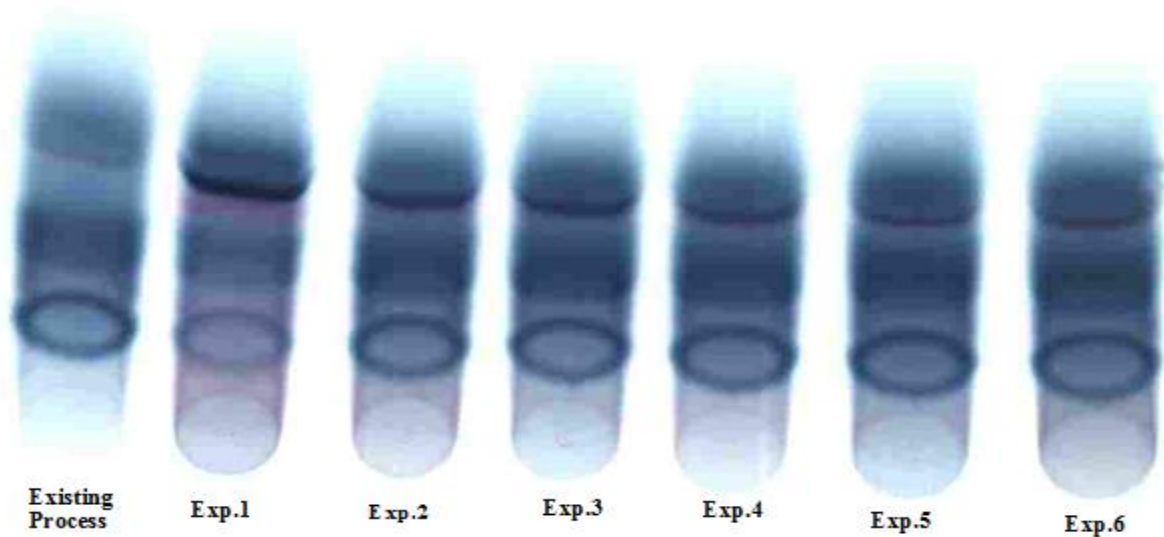


FIG.1 THIN LAYER CHROMATOGRAPHY REPORT OF 2% DYE SOLUTION

4.3 COST ANALYSIS:

Cost analysis of 100 kg of product					
		As per existing method		As per modified method	
Raw material	Cost of raw material in Rs./Kg	Quantity of raw material require in Kg	Total cost in Rs.	Quantity of raw material require in Kg	Total cost in Rs.
H-acid	275.00	39.05	10738.75	37.39	10309.75
V.S.	125.00	28.67	3583.75	28.67	
NaNO ₂	26.00	13.52	351.52	13.52	
OAVS	220.00	32.06	7053.2	32.06	
NaOH	24.00	16.32	391.68	8.73	209.52
Na ₂ CO ₃	11.00	32.91	362.01	32.91	
HCl	2.00	40.86	81.72	28.12	56.24
TOTAL			22562.63		21925.99
DIFFERENCE					636.64

Same selling price with improved dye quality					
		As per existing method		As per modified method	
	Selling price in Rs./Kg	Quantity formed in Kg	Selling price in Rs./Kg	Quantity formed in Kg	
	175.00	133.48	175.00	131.91	
Total revenue	23359.00				23084.25
Difference					-274.25
Overall profit					361.89

**5. CONCLUSION AND FUTURE SCOPE:
CONCLUSION**

- The Raw material cost is reduced to 636.64 Rs. /100 Kg. of dye Produced. For 1 ton of batch

saving is of 6366.40 Rs. company is producing 200 tons of Product/yr, So saving is of 12,73,280 Rs./yr in dye raw material.

- Final production was reduced to 1.18 % as per modified method, but quality of product was of less salt content compared to existing process.
- Selling price of product as per existing process is 175.00 Rs. /Kg. and as per modified method (2% increase) is 178.50 Rs. /Kg.
- Company will make profit of Rs. 186.94 Rs. /100 Kg. of dye selling. It means that Rs. 1869.40 per tons. Thus Rs. 3,73,880 per year. So over all saving per year is Rs. 16, 47,160.
- If company sells product as per existing price (i.e. 175.00 Rs/Kg), then also company will make overall profit of Rs. 361.89 per 100 kg of dye selling. Thus company will make profit of Rs.3618.90 per ton, which amounts to Rs. 7, 23,780 per year.

FUTURE SCOPE:

- ❖ It is recommended that this salt study be expanded to the yellow and red dyes.
- ❖ Future work would most beneficially include an evaluation of the dyes in an actual production setting. With a production it would be possible to evaluate batch to batch repeatability of the dyes and to conduct a more extensive cost analysis.
- ❖ If jacketed reactor with internal cooling coils is designed with suitable chilling brine to control temperature in process, then modified method is more economical than prevalent method.

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