Molasses Based Spentwash Decolorization By Coagulation & Flocculation

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Abstract- Decolorization of molasses spent wash has always been a great challenge to the environmental engineers all over the globe. Coagulation and flocculation methods are used for the treatment of spent wash followed by biomethanation for the removal of melanoidin pigments which are responsible for brown color of the spent wash. Decolorization is achieved by applying coagulation and flocculation process as the polishing treatment for molasses spent wash on bench-scale. Important operating variables, including coagulant type and dosage, solution pH, mixing conditions as well as the type and dosage of polyelectrolytes investigation based on the maximum removal efficiencies of chemical oxygen demand (COD) and color, residual turbidity and settling characteristics of flocs is used. Individual effects are also studied for maximum removal of color as well as turbidity, transmittance, COD reduction, total dissolved solids (TDS), sludge formation and volume reduction after the treatment. Cost of treatment and cost recovery options are also discussed.

***Key Words*:** Molasses spent wash, decolorization, coagulation and flocculation, melanoidin, COD reduction, etc.

1.INTRODUCTION

As molasses spent wash is heavily polluting environment and is very difficult to treat by normal and traditional methods due to extreme level of pollutants present in higher concentrations. Disposal of molasses is a major issue due to its high viscosity, dark brown color also deterioration of molasses spreads a bad odour in nearby areas. These molasses in earlier days were valueless and were treated as waste. In 1960's a new concept of ethanol distillery were introduced and molasses were used as raw material for these industries[12]. Today molasses have acquired tremendous demand with prices ranging from 3,500–6,000 INR per m^3 tonne depending upon availability in the market. Due to the strict norms and policies of Central Pollution Control Board(CPCB) and State Pollution Control Board (SPCB) on new establishment of distillery and to run existing distilleries, they need proper treatment before disposal into environment.

In Uttar Pradesh, Central Government is strictly monitoring distilleries for zero liquid discharge and strict policies have to be followed by factories near Ganga river belt which is a part of Clean Ganga Project. As per the norms of CPCB and SPCB for environmental clearance new distilleries need spent wash incineration boilers, biomethanation system and evaporator system for zero spent wash discharge.

Combination of aerobic and anaerobic processes, are normally effective in reducing biochemical oxygen demand (BOD) of molasses spent wash[4]. However, the brown color remains due to the presence of melanoidin pigments. Melanoidins are formed during the Maillard reaction between amino compounds and carbohydrates, having anti-oxidant properties which render them recalcitrant to biodegradation[8].

Physicochemical processes such as carbon adsorption, chemical oxidation have been tested for the decolorization of molasses wastewater[2]. Specific microorganism, especially white rot fungi have been found capable of degrading melanoidins[7]. The shortcomings of these methods include unstable decolorization efficiency, operational difficulty and occasional formation of hazardous by-products/ secondary pollutants. Till date no suitable method has been successfully developed for the polishing treatment of full-scale molasses spent wash.

Alternative to these methods, we are using coagulation and flocculation methods for treatment of spent wash which are most widely practiced for the removal of colloidal particles and natural organic matters (NOM) from water and waste water[5].

In the last decades, the awareness of environmental issues has increased among the society considerably. In the field of spent wash treatment a decrease in nutrients being discharged into surface waters is required as pointed by the Urban Water Directive (91/271/EC). There is an increasing

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need to improve the effluent quality of domestic as well as wastewater treatment processes.

Variables, such as solution pH, coagulant type and dose are well recognized as significant influential factors[5]. Rapid mixing conditions are suggested as most important parameter in the whole coagulation step as well. This treated spent wash can be used for agricultural purposes or reuse in industrial processes to minimize the environmental impacts.

The objective of this study is to investigate major operating conditions to enhance melanoidins removal from biologically treated molasses spent wash by coagulation and flocculation. Operating variables including solution pH, coagulant type and dosage, rapid mixing parameters and coagulant aids (synthetic polyelectrolytes) were optimized on the basis of COD and color reduction, residual turbidity, and the settling characteristics of flocs formed.

In order to deal with these issues, research is focused on finding and improving technologies for decolorization of molasses spent wash. So from our side this is an attempt to decolorize molasses spent wash which can be used for the betterment of society and environment as well.

2. MATERIALS AND METHODS:

2.1 Waste water:

Molasses based spent wash was collected from 50 KLPD capacity distillery situated near Shrirampur, Dist.-Ahmednagar(MH). This unit runs in batch operation, in which spent wash is used for biomethanation before disposal into the environment. This factory has full-scale two-staged biological treatment facility. Raw molasses spent wash is initially mixed in buffer tank before being fed into anaerobic systems comprising of an acidic hydrolysis phase and an internal circulation reactor. Anaerobically treated effluent is then introduced to an activated sludge system. Raw spent wash samples are collected from a single batch of aerobically treated effluents and stored in refrigerator at 5ºC till experimentation. The primary coagulants aids in increasing the settling rate, reduce costs, improve the finished water quality and provide better dewatering characteristics of sludge. Although several studies have been conducted on the decolorization of molasses spent wash by coagulation and more detailed work is still required for process optimization in order to improve coagulation efficiency.

2.2 Experimental setup:

Conventional coagulants, including Polyaluminium chloride ($AlCl_3 \cdot 6H_2O$), ferric chloride ($FeCl_3 \cdot 6H_2O$) and Alum of analytical grade are used for preparing concentrated solutions of 2% by dissolving into distilled water. Cationic polyacrylamide (CPAM) is used as coagulant aids and is commercially available and prepared as solutions with the concentration of 1g/L. Information about the speciation of both polyelectrolytes is not provided by the suppliers.

After coagulation, sample is treated with CPAM which is very well known for color and COD reduction. The dose of CPAM was optimized by collecting supernatant samples. In this case performance is determined from improvement observed in turbidity, transmittance, color reduction and TDS[1].

2.3 Coagulation efficiency:

Coagulation/flocculation tests were conducted using a conventional jar test apparatus. In each run, 1000 ml sample was then poured into a 1000 ml plastic cylinder along with coagulant and the coagulation began with rapid mixing of 150 rpm for 1min, followed by slow stirring of 60 rpm for 10 min. The sludge thus formed was then allowed to settle. Finally, supernatant was withdrawn with help of plastic syringe from near 2 cm below the liquid–air interface for chemical analysis. All the experiments were carried out at ambient temperature of 23–25°C. On the basis of COD reduction coagulation efficiency is determined.

3. RESULTS AND DISCUSSION:

3.1 General Molasses Characteristics:

General properties of molasses composition are mentioned in Table-1 as per Indian standards. Also the characterization of molasses using chromatography is shown in Fig-1.

3.2 General Spentwash Characteristics:

Molasses and water are taken in ratio of 1:3 to which 10% yeast inoculum is added and allowed to ferment for 24 hours. During the fermentation process the sugars are reduced to alcohol and the remaining sugars are generally unfermented sugars which are polysaccharides. The alcohol is separated from sample by distillation and the remaining waste water is now referred as spent wash. General analysis of spent wash is done and mentioned in Table-2.

3.3 Coagulation Efficiency:

All the experiments were carried out at ambient temperature of 23–25⁰C. On the basis of COD removal coagulation efficiency was determined.

Formula:

$$\%\ Coagulation\ Efficiency = \frac{Initial\ COD - Final\ COD}{Initial\ COD} \times 100 \quad \ldots\ldots\ldots(3.3)$$

Table-1: Molasses analysis by ISI methods

Sr. No.	Test Name	Results Obtained	Standard Range	Unit
1	Total Reducing Sugars (TRS)	47.54	45-55	%
2	Un-Fermentable Sugar (UFS)	6.44	4.0 – 6.0	%
3	Fermentable Sugar (FS)	41.10	40.0 – 50.0	%
4	pH (10% solution)	5.47	4.5 – 5.0	-
5	Total Volatile Fatty Acids (TVA)	4834.28	< 5000	ppm
6	Color (0.1% solution)	0.239	NMT 0.3	OD @ 0.375
7	Settleable Sludge	13.95	< 20	%
8	Brix	87.3	85-90	º Brix
9	Specific Gravity	1.437	1.36 – 1.52	g/mL
10	Pol	26.128	25-32	%
11	Sucrose Purity	29.90	25-30	%
12	Total purity	46.96	40-50	%
13	Sulphur content	1.028	2 - 6	% w/w

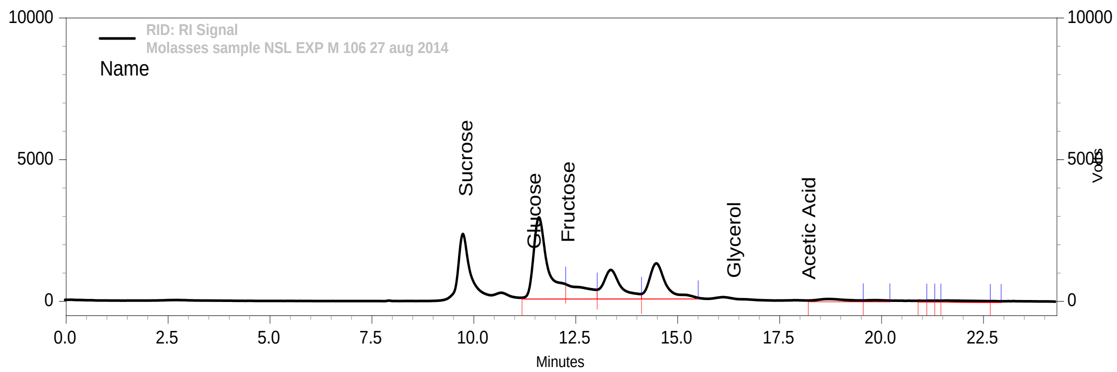

Fig.-1: Chromatogram of molasses characterization

Table-2: Analytical analysis of molasses spent wash

Sr. No.	Parameters	Value	Average value	Units
1	pH	4.2-4.8	4.75	-
2	Settle able solids	1.8-3.5	2.5	(mL/L)
3	Suspended solids-SS	8540-9815	9322	(mL/L)
4	Total Solids-TS	31900-32830	32345	(mL/L)
5	Total Fixed residue at 550 C	2937-3200	3150	(mL/L)
6	Total Volatile residue	28963-29630	29220	(mL/L)
7	Chemical oxygen demand-COD	100000-130000	120000	(mg O_2/L)
8	Biological Oxygen Demand	45000-55000	50000	(mg O_2/L)
9	Total Kjeldahl nitrogen-TKN	950-1100	990	(mL/L)
10	Residual sugars	1.5-2.0	1.40	(%)
11	Total Volatile acids	1500-2000	1720	ppm

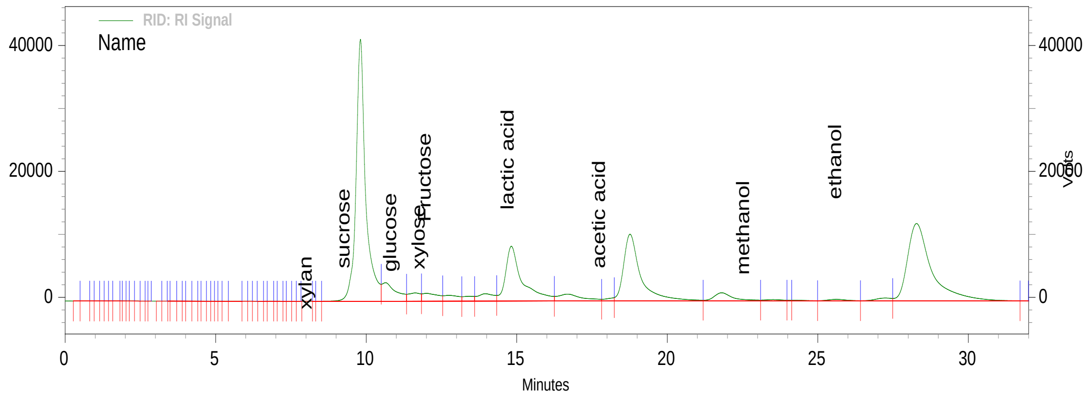

Fig.-2: Chromatogram of spent wash characterization

Table-3: Percentage Coagulation Efficiency

Sr. no.	Coagul-ant used	Initial COD of Spent Wash	After treatment COD	Coagulation efficiency (%)
1	FeCl3	1,39,500	85,095	39
2	Lime	1,39,500	94,860	32.1
3	Alum	1,39,500	99,045	29
4	PAC	1,39,500	83,700	40

3.4 Flocculation by using Polyacrylamide:

Polyacrylamide is used as flocculant which directly helps in treatment of spent wash but dosage of flocculant required is high (refer Table-4). Thus primary treatment is done by coagulation methods using lime and alum to reduce the dosage of the focculant. Both studies are done to optimize dosage of coagulant and flocculant.

Table-4: Flocculation study by using polyacrylamide

Sr. no.	Wt. (gm)	Blank wt. of filter paper (gm)	Wt. of filter paper @ 105^0 C (gm)			Final wt. (gm)	TDS (ppm)	Color Inten-sity at 420 Nm (IU)	Transm-ittance (%)	Turb-idity (%)	Vol. of filte-rate (ml)
			2 hrs	4 hrs	8 hrs						
Control	0	0	0	0	0	0	11500	4.900	4.6	31.2	100
1	1	2.814	6.544	6.531	6.012	2.198	4000	0.892	46.9	5.5	78
2	2	2.414	6.616	5.889	5.419	2.005	3300	0.598	55.7	7.6	74
3	3	2.214	8.614	7.401	6.819	1.578	3000	0.371	72.4	3.9	70
4	4	2.655	10.14	8.918	8.311	1.656	2800	0.216	84.8	1.40	54
5	5	3.414	12.41	11.31	10.034	1.620	2700	0.192	82.8	2.9	48
6	6	3.121	11.68	11.21	10.887	1.675	2900	0.397	49.3	12.8	48

Graphical representation of flocculation study:

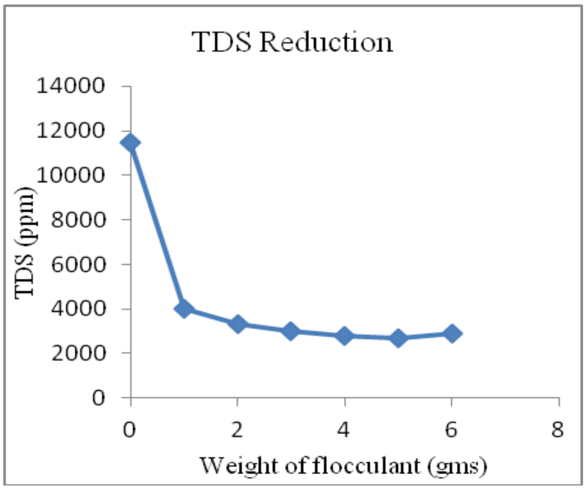

Fig.-3: TDS vs. weight of flocculant

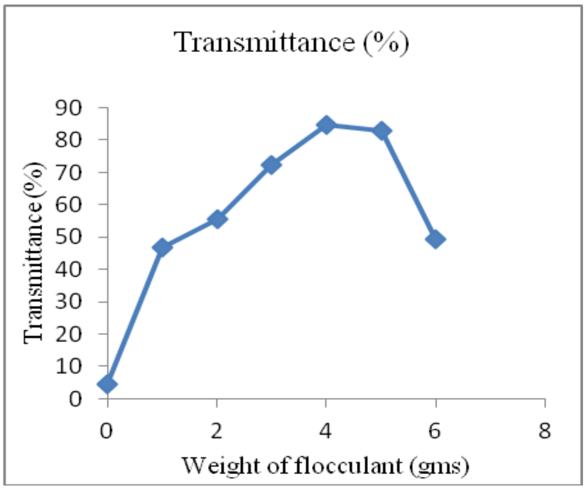

Fig.-4: Transmittance vs. weight of flocculant

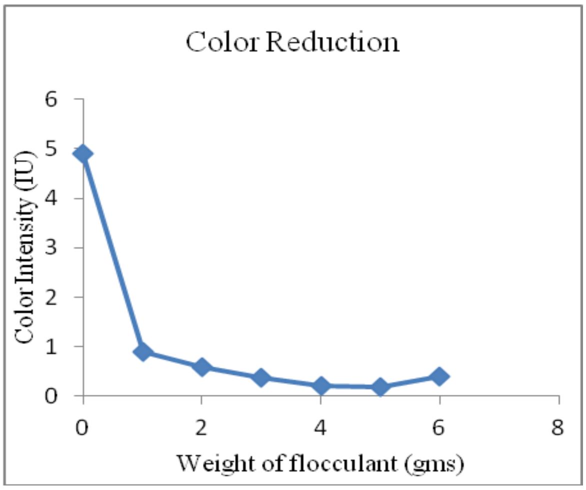

Fig.-5: Color intensity vs. weight of flocculant

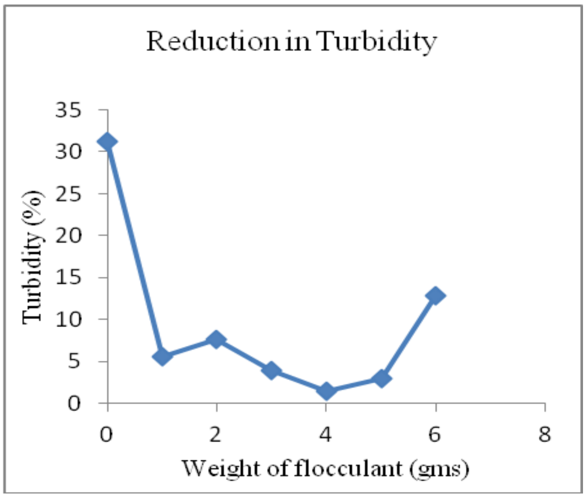

Fig.-6: Turbidity vs. weight of flocculant

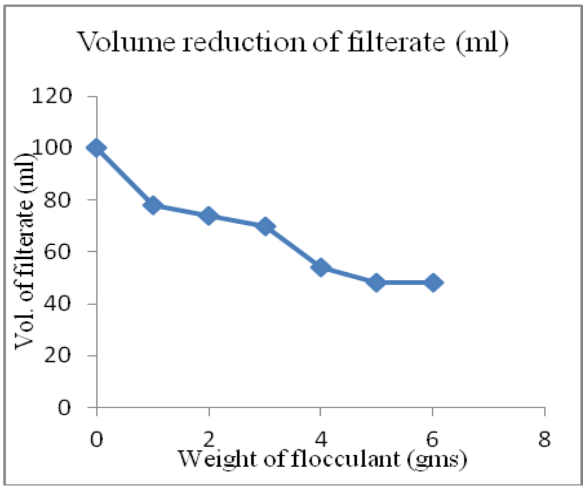

Fig.-7: Vol. of filtrate vs. weight of flocculant

From above graphical data and tabulated data optimum dosage of flocculant is found to be 4% (40g/L) of spent wash. This dose is higher because of higher organic and inorganic matter present in the spent wash. At this dose, effective color removal, turbidity, TDS and improvement in transmittance is observed.

3.5 Combination of coagulants and flocculants:

In this study the dosage of coagulant is optimized for optimum color and COD reduction, which included 2% calcium hydroxide and 1% alum. Later it was observed that the dosage of PAA is reduced from 4% to 1%. The detailed study for different parameters is mentioned below in Table-5.

Table-5: Coagulation and flocculation combine study

Sr. No.	Dosage of Coagulant & Flocculant (gm)	TDS (ppm)	Color Intensity (IU)	Transmittance (%)	Turbidity (%)
Control	0	11500	4.9	2.9	49.5
1	0.3	5200	2.951	6.2	31.2
2	0.5	3500	0.652	45.2	6.5
3	1	2400	0.253	75.7	3.8
4	1.5	2400	0.211	75.3	3.5
5	2	2500	0.152	80.5	3.8

**Weight of coagulant (gm) consists of 2% Calcium hydroxide and 1% Alum*

Graphical representation for combination of coagulants and flocculants study:

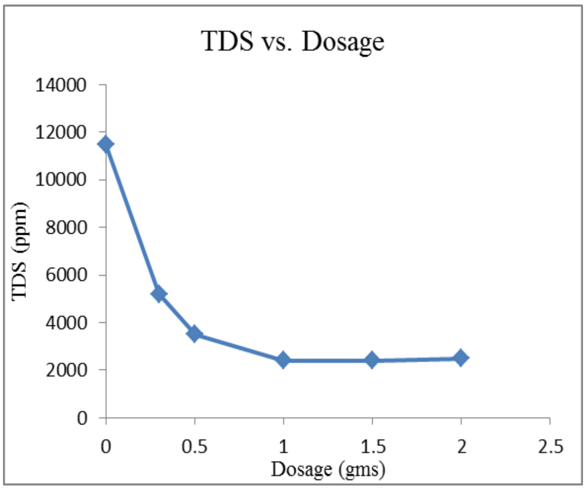

Fig.-8: TDS vs. Dosage

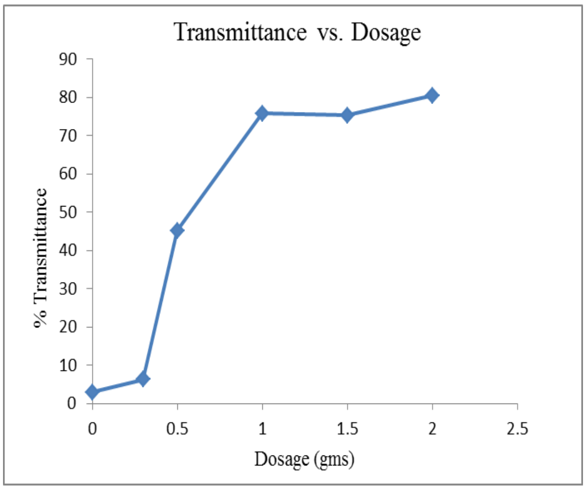

Fig.-9: Transmittance vs. Dosage

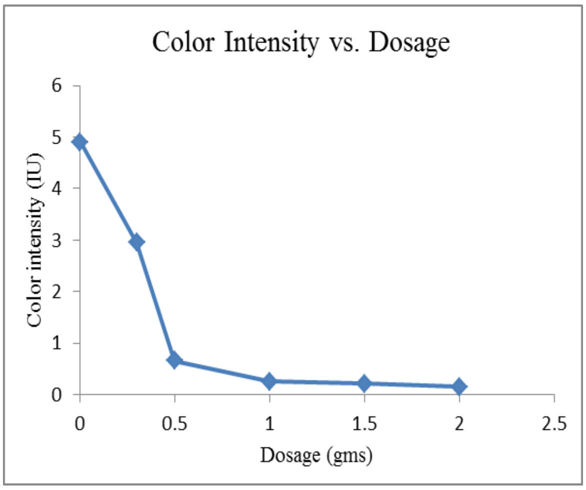

Fig.-10: Color Intensity vs. Dosage

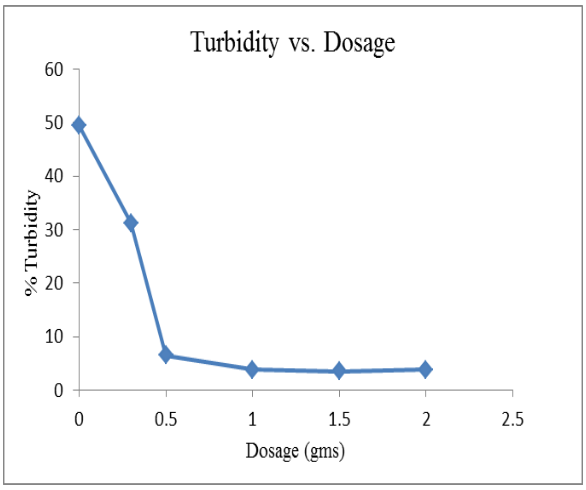

Fig.-11: Turbidity vs. Dosage

Dose optimization of polyacrylamide was determined along with combination of alum and lime. From above observation Table-5, after primary treatment of lime and alum at 2 % and 1% dosage, the flocculant dosage was reduced from 4% to 1%. Primary treatment was found to be beneficial for reduction in dosage of PAA.

3.6 OPTIMIZATION OF VARIOUS PARAMETERS:

3.6.1 Optimization of temperature:

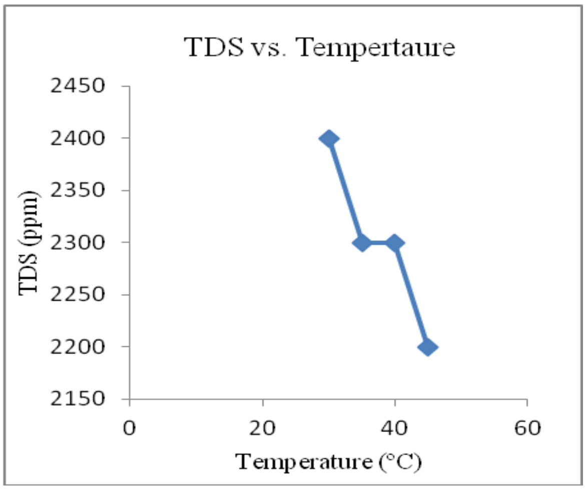

Fig.-12: TDS vs. Temperature

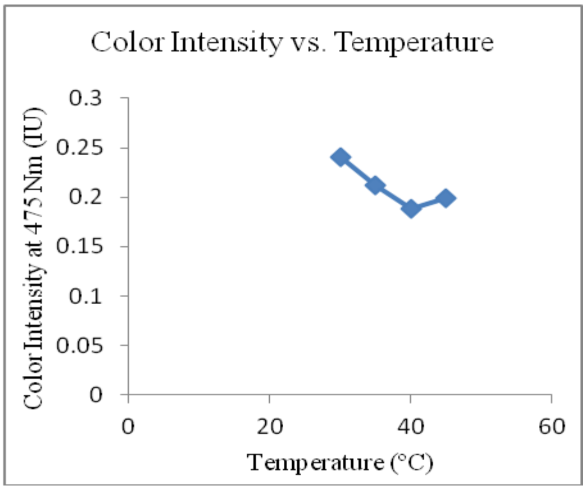

Fig.-13: Color Intensity vs. Temperature

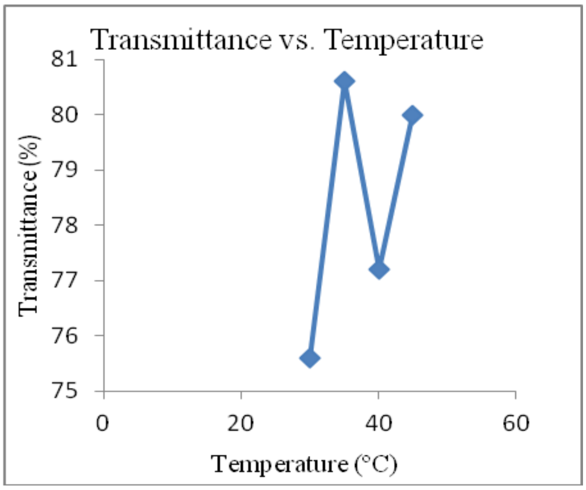

Fig.-14: Transmittance vs. Temperature

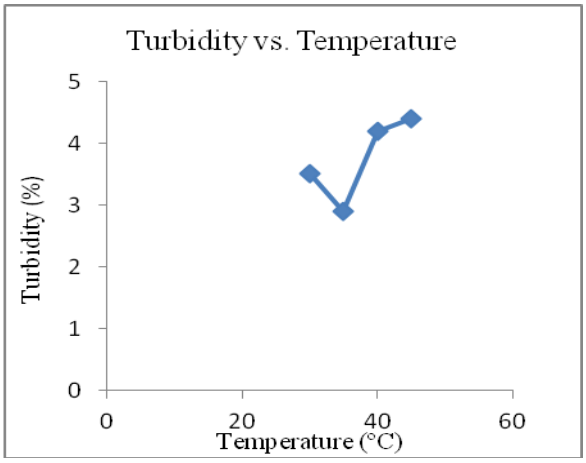

Fig.-15: Turbidity vs. Temperature

From above study the optimum temperature is observed to be 35ºC showing maximum reduction in turbidity and color and value for transmittance is maximum as compared to the other temperature values.

3.6.2. Optimization of pH:

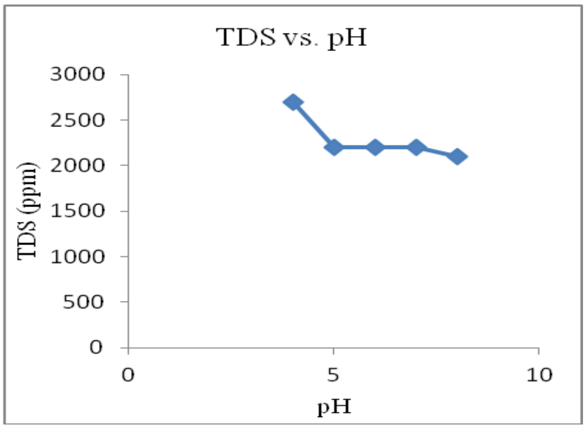

Fig.-16: TDS vs. pH

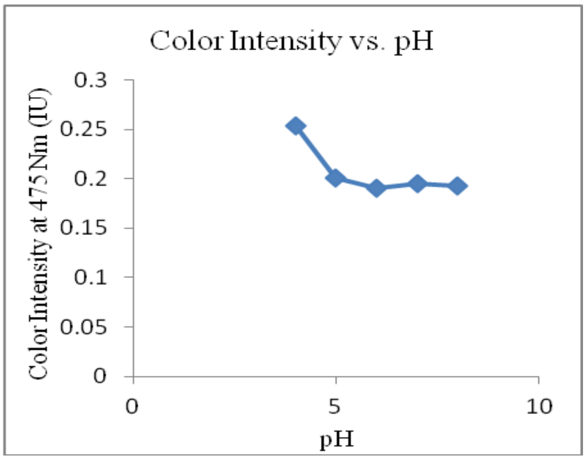

Fig.-17: Color Intensity vs. pH

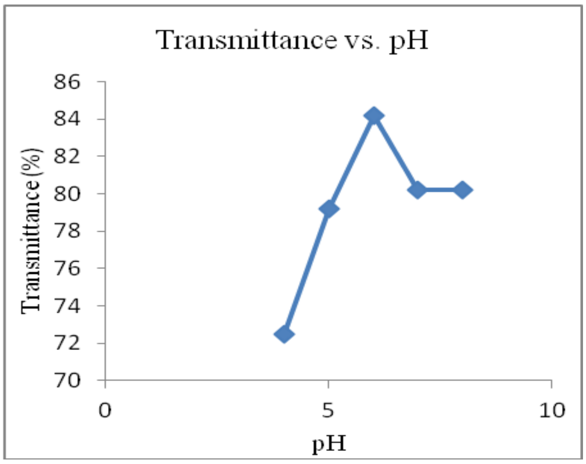

Fig.-18: Transmittance vs. pH

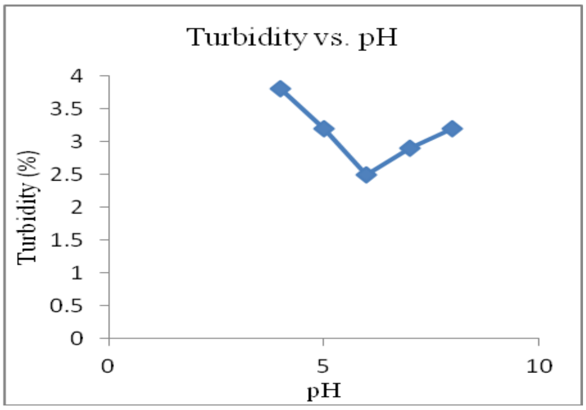

Fig.-19: Turbidity vs. pH

From the above study for pH optimization, the reduction is found to be highest for 6 pH value where turbidity and color intensity are reduced and also the value for transmittance is maximum as compared to the other pH values.

3.6.3 Optimization of agitation speed:

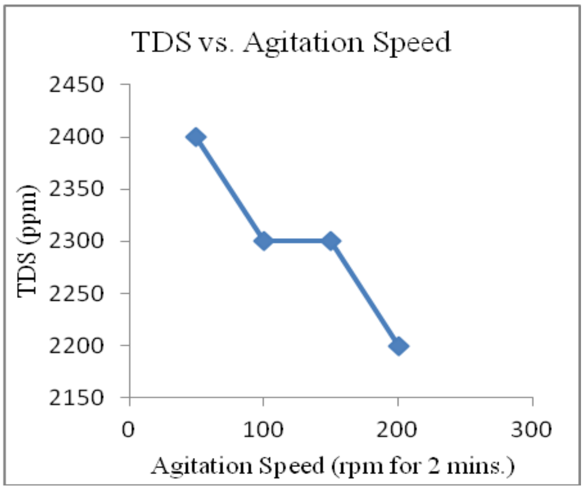

Fig.-20: TDS vs. Agitation Speed

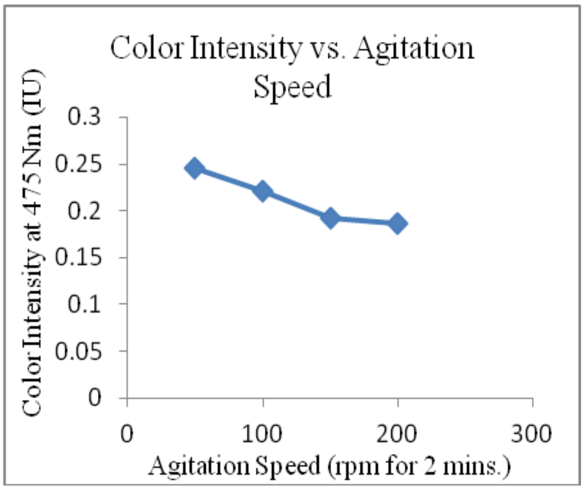

Fig.-21: Color intensity vs. Agitation speed

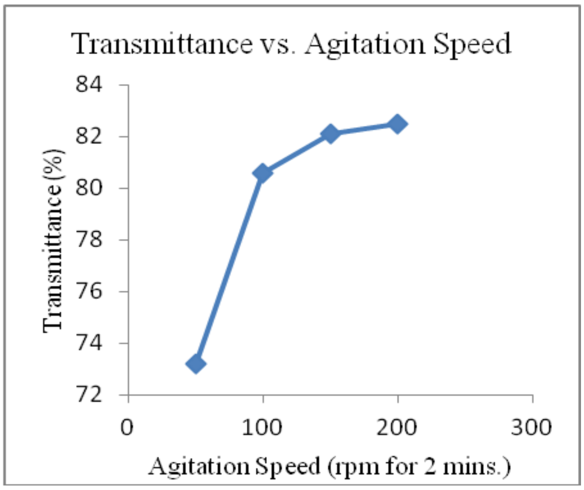

Fig.-22: Transmittance vs. Agitation Speed

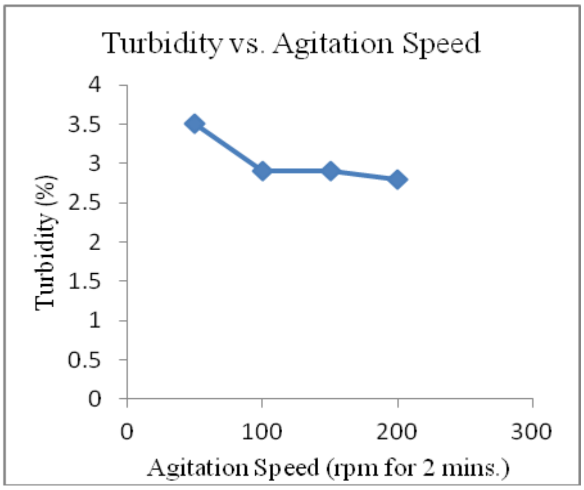

Fig.-23: Turbidity vs. Agitation Speed

From the above study for agitation speed, the optimum is observed at 150 rpm showing maximum reduction in turbidity and color and the value for transmittance is maximum as compared to other rpm values.

Thus from observation the optimum dosing is done form various parameters for effective removal of color at 6 pH value, optimum agitation speed of 150 rpm and optimum temperature as 35ºC.

4. CONCLUSIONS:

Coagulation and flocculation are found to be effective methods for decolorization of spent wash. Dose of coagulant (lime and alum) are optimized at 2% and 1% on basis of effective color and COD reduction. At optimized coagulant dosage the color and COD reduction is observed as 46% and 30% respectively.

Use of flocculant at 4% dosage showed good results in terms of 95% color reduction, 93% turbidity removal, 75% TDS removal and transmittance was improved by 80%. After primary treatment of lime and alum at 2% and 1% respectively the dosage of flocculant is reduced to 1% and showed the same results.

Optimum parameter study is carried out to determine the optimum pH, temperature and agitation speed on basis of color reduction, transmittance, turbidity and TDS. Thus from the experimental study optimum pH is found to be 6, temperature at 35ºC and agitation speed as 150 rpm.

Treatment cost per m^3 is determined to know effectiveness or feasibility of treatment and treatment cost required is found to be 0.40 INR per litre. Cost recovery can be attained effectively by using spent wash for the production of biogas, sludge as fertilizer and yeast cell mass for single cell proteins (SCP) production which would help to generate economy from the spent wash.

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