DYES AND PIGMENTS MANUFACTURING INDUSTRIAL WASTE WATER TREATMENT METHODOLOGY

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ABSTRACT - *Chemical coagulation- flocculation was used to remove the compounds present in wastewater from dye manufacturing industry. The character of wastewater was determined as its contained high ammonia (5712mg/L), COD (38000mg/L) and Total dissolved solids (56550mg/L) concentration. Most compounds found in the wastewater are ammonia, phenol derivatives, aniline derivatives, organic acid and benzene derivatives output from dyes and pigment manufacturing industries. Coagulants ferrous sulphate, ferric chloride, Polly-aluminium chloride, and hydrogen peroxide catalysed by ferrous sulphate and flocculants lime and NaOH were investigated. Results showed the combined Fe (III) chloride and Polly aluminium chloride with NaOH for flocculants was best suited for chemical oxygen demand (COD), NH3, and total dissolved solids (TDS) removal in dyes and pigment manufacturing waste water. The electrostatic interaction between flocks and organic contaminants played an important role in removal of organic contaminants, that chloride of Al (III) and Fe (III) were helpful for high flocculating effect for that COD, ammonia and TDS removal efficiency of dyes and pigment manufacturing industrial waste water. Combined PAC and FERRIC CHLORIDE coagulants with NaOH flocculants was superior to FERRPOUS SULPHATE, HYDROGEN PEROXIDE catalysed by FERROUS SULPHATE and single PAC and ferric chloride with NaOH or LIME coagulant. This efficiency differences is due to copolymerisation effect between flocks Thus, from the economic point of view, combined PAC and FERRIC CHLORIDE with NaOH is more suitable for treatment of wastewater effluent from dyes and pigments manufacturing. Also shows the possibility of ammonia recovery from waste water present in large amount (5712mg/L). Primary aeration of waste water results in 22.63% COD and 68.13% ammonia reduction than by chemical treatment by NaOH-PAC-FeCL3 results in 67% COD, 63.21% TDS and 95.38% of ammonia reduction. Further reduction of pollution parameters is carried out by tertiary treatment.*

KEY WORDS:- COD (chemical oxygen demands), TDS (total dissolved solids), coagulation-flocculation, ferric chloride, poly aluminium chloride, lime, NaOH, ferrous sulphate,hydrogen peroxide.

INTRODUCTION:

Substances which create the sensation of blackness or whiteness are also regarded as dyes or pigments. Colorants, not defined by this definition of dyes and pigments are called dyestuffs. Synthetic organic dyestuffs and pigments exhibit an extremely wide variety of physical, chemical and biological properties, making review of the Eco toxicological behaviour of the several thousand commercially available products difficult, production process are difficult to control the release of manufacturing material during dye manufacturing [1-13]. Industrial waste water is one of the important pollution sources in the pollution of water, soil and environment. It not only affects the ecosystem but also affects the human life .so it is necessary to treat the waste water before discharging it into the ecosystem by considering the financial aspects in mind. Sample analyses show high concentrations of ammonia, TDS, COD, aniline and large difference in COD to BOD ratio hence biological treatment is not possible. Then it requires some alternative methods to optimise the COD reduction by combination of different coagulant flocculants at different concentrations and conditions. A major environmental hazard present in dyes and pigment manufacturing industries is discharge of untreated waste water into the environment. Due to toxic nature of organic N-Based impurities present in water effect very badly to aquatic life cycle, plants and animals. Under the Water (Prevention and Control of Pollution) Act, 1974, every industry is required to provide adequate treatment of the effluents generated by it before their disposal, irrespective of whether the disposal is in a stream, on land, into sewerage system or into sea. However the small-scale industries, due to their limited size and scale of operations do not find it economically able to install integrated pollution control equipment. The common treatment methodology to enhanced effectiveness and economic stability required.

The Environment (Protection) Act, 1986 is also applicable for proper management of hazardous waste generated during treatment of effluent, as per the Hazardous Waste (Management, Handling & Trans boundary Movement) Rules, 2008 under this Act. Under these rules, “authorization” is required for generation, handling, collection, reception, treatment, storage, recycling, reprocessing, recovery, reuse and disposal of hazardous wastes.

This paper reviews the work on dyes and pigment manufacturing industrial waste water producing the following dyes products and row materials given in table 1 and table 2

TABLE NO 1

Sr no	Name of the dyes and pigment manufacturing industrial product	Qt. MT/month
A	Powder dyes (solid)	75
1	Basic dyes such as	
	Rhodamine	
	Malachite green/brilliant green	
	Methyl violet	
	Auramine	
2	Solvent dyes such as	
	Rhodamine base	
	Victoria blue base	
	Bismark brown base	
	Orange base	
	Solvent black	
B	Liquid dyes such as	120
	Rhodamine liquid	
	Malachite green liquid	
	Victoria blue liquid	
	Bismark brown /chrysiodine liquid	
	Methyl violet/ crystal violet liquid	
	Basic yellow liquid	
	Total	195
C	By product	6
	Aniline	
	Ammonia	
	N-Based organic compounds	
	Dyes and colour complex	
	Stripping solvent	
	Other	

TABLE NO 2

sr	Name of row material	Physical state	QT MT/month
1	Pthalic anhydride	Solid	10.00
2	Diethyl meta amino phenol	Solid	8.00
3	Dimethyl aniline/Mona methyl aniline	Liquid	20.00
4	Formaldehyde		5.00
5	Benzeldehyde	Solid	5.00
6	Meta phenyline diamine meta tolludine diamine	Solid	3.00
7	PANA	Solid	1.00
8	Sodium nitrite	Solid	1.00
9	Caustic soda	Solid	5.00
10	Hydro chloric acid	liquid	8.00
11	Sulphuric acid	Liquid	5.00
12	Acetic acid	Liquid	15.00
13	catalyst and surfactants	Solid	0.75

Here we seen above data (in table no 1&2) that shows highest per cent of aromatic amines, nitrogen based row material is used and there for highest amount of ammonia, aniline, phenol derivatives, aniline derivatives, organic acid and benzene derivatives output from dyes and pigment manufacturing industries based waste is generated during dyes and pigment manufacturing .where aniline, ammonia and N-based organic waste is very toxic and hazardous in nature .there also several other by product like dyes and dyes intermediates colour compound generated waste produced during manufacturing process.

Our treatment scheme must consider the approach to minimise the pollution parameters below the permissible limit decided by pollution control board and economic feasibility of process.

PROCESS APPROACH:

The purpose of this research has to reduce the COD, TDS, COLOUR and neutralization of waste to dispose it in a stable form. There are several methods available to treat waste water such as coagulation-flocculation, biological, tertiary by sand charcoal filter, adsorption methods, adsorption by charcoal, electrochemical treatment, electrocoagulation, o-zonation, evaporation followed by incineration process, photo catalysed hydrogen peroxide oxidation treatment process and some specific advanced treatment processes are available now these days. Evaporation followed by incineration is last option if none of the method works on toxic waste water. High COD disabled the evaporation and toxic behaviour disabled the biological treatment. So a treatability study is required here which also economic and environmentally feasible.

Selection criteria for treatment methodology based on BOD and COD level of waste water.

» Easily bio-degradable (COD/BOD < 2)

» Not-easily biodegradable (COD/BOD > 2)

» Not easily bio-degradable and toxic (high TDS, high COD, toxicants)

Main motive of our treatment methodology to:

» facilitates small scale industries and helps reduce the wastewater treatment cost for individual units.

» Help to achieve an economic treatment method in wastewater treatment.

»Help to optimize the cost of pollution abatement for each individual industry.

» Method is helpful for individual industries that have lack of manpower and technical expertise for the treatment of wastewater.

» Helpful for individual industries that lacks space for full-treatment facilities.

» Provide controlled way on treatment and disposal of wastewater.

» unit should be single and is able to treat, recycle, reuse and recovery option.

The characteristics of effluents use as main measurable and variable parameters of treatment scheme:

» Colour and odour – Indicates the colloidal portion of waste water they required specific treatment units.

» Total solids - Total solids include both the suspended solids and the dissolved solids, which are obtained by separating the solid and liquid phase by evaporation. Suspended solids are a combination of settleable solids and non-settleable solids, which are usually determined by filtering a wastewater sample through a filter paper. Settleable solids are those, which usually settle in sedimentation tanks during a normal detention period. This fraction is determined by conducting a test and measure volume of sludge in the bottom of an Imhoff cone after one hour of settling which solids remaining after evaporation or filtration are dried, weighed, and then ignited. The loss of weight by ignition at 500°C±50 °C is a measure of the volatile solids, which are classed as organic material. The remaining solids are the fixed solids, which are considered as inorganic (mineral) matter. The suspended solids associated with volatile fraction are termed volatile suspended solids (VSS), and the suspended solids associated with the mineral fraction are termed fixed suspended solids (FSS).

» pH: The biological treatment units at CETP are sensitive to pH of the effluent. Thus, this parameter is of high importance. Besides, acidic effluents cause corrosion related problems to the treatment scheme.

» Carbonaceous substrates: Carbonaceous constituents are measured by BOD, COD or TOC analysis. While BOD has been the common parameter to characterize carbonaceous material in wastewater, COD is becoming more common in most current comprehensive computer simulation design models.

» BOD test: The BOD test gives a measure of oxygen utilized by bacteria during the oxidation of organic material contained in a wastewater sample. The test is based on the premise that all the biodegradable organic material contained in the wastewater sample will be oxidized to CO_2 and H_2O, using molecular oxygen as the electron acceptor. Hence, it is a direct measure of oxygen requirements and an indirect measure of biodegradable organic matter.

» COD test: The COD test is based on the principle that strong oxidizing agents under acidic conditions oxidize most organic compounds to CO_2 and H_2O. COD will always be equal or higher than BOD, as the test is under strong oxidizing agent, which oxidizes to greater extent, including inorganics.

CONVENTIONAL METHODS AND SIMILAR WORKS:

»The conventional techniques adopted to treat the wastewater are physical, chemical and biological methods.

1. *Physical* – Sedimentation (Clarification), screening, aeration, Filtration, Flotation and skimming, degasification, Equalization.

2. *Chemica*l – Chlorination, Ozonation, Neutralization, Coagulation, Adsorption, Ion exchange.

3. *Biological*- a. Aerobic – Activated sludge treatment methods, Trickling filtration, oxidation, ponds, lagoons, aerobic digestion

b. Anaerobic – Anaerobic digestion, septic tanks, Lagoons The treatment process can be divided as:

I. Primary treatment process – Removal of suspended solids, oil, grit etc.

II. Secondary treatment process – Use of microorganisms in either aerobic or anaerobic condition for the reduction of the BOD and removal of colour and oil.

III. Tertiary treatment process is for the final removal and purification of the wastewater.

The dyes and textile industry effluents which are treated with various physical and chemical treatments such as coagulation, flocculation, o-zonation and biological treatment and nitrogen, phosphorous, organics and metal traces were removed and sludge is discharged. Then the main problem is of sludge disposal for which space is needed. According to A E Ghaly et al. [14], disadvantages of the biological processes are the presence of the toxic heavy metals which are harmful to the growth of microorganisms, most of the dye stuff used is non -biodegradable in nature and the time requirement for the treatment is more.

»PRIMARY TREATMENT PROCESS

By Das S 2000 [15] the first step is the removal of suspended solids, excessive quantities of oil, grease and gritty materials. The effluent is first screened for coarse suspended materials such as yarns, lint, pieces of fabrics and rags using bar screens and fine screens.

»COAGULATION

Neutralization of negative charge by higher valance cat-ion salt (Al+3, Fe+3) results in destabilisation of colloidal present in waste water. Coagulant dose are used to reduce the electrostatic repulsive forces by the addition of counter charged ions. Coagulants used are alum, Bentonite Clay, Poly aluminium Chloride (PAC), Poly aluminium Hydrochloride, Aluminium Chloride, aluminium Chlorohydrate, aluminium Sulphate, Ferric Chloride, Ferrous Sulphate Monohydrate, hypochlorite, H2 O2 /Fe2+ catalysed, ammonium sulphate, ammonium per sulphate, FeCl3, aluminium sulphates. According to literature "Coagulants for Optimal Waste water Treatment from bekart environmental" [16] sulphate and chlorides of iron and aluminium are some most commonly used chemical coagulants used for coagulation processes.

»FLUCCULATION

Flocculation is the agglomeration of destabilizing particles in to a large size particle known as flocks .which can be remove by sedimentation or floatation. Flocculation process enhance simply by adding neutral electrolytes like NACL and KCL in small amount that are able to reduce the zeta potential of suspended partials to zero and sufficient to induce flocculation of weakly charged, water insoluble, organic non-electrolytes such as steroids. In case of more highly charged, insoluble polymers and polyelectrolyte species, such as Ca-salts and alums or sulphates, citrates and phosphates are usually required to achieve flock formation depending on particle charge, positive or negative out of these we use Polly Electrolyte.

Mechanism: There are two major forces acting on colloids

1. Electrostatic repulsion
2. Intermolecular or van der Waals attraction force.

Some common Flocculants are NAOH, NAHCO3, CA(OH)3, lime, acryl amide, acrylic acid etc.

Harsha p. shrivastava et al. 2011[17] and Deepa chandran 2016 2229-5518 [18] studied and carried out various experimentation on master composite effluent neutralised with hydrated lime. Various types of flocculants and coagulants were tried on the effluent and separate out the sludge formed sludge formed % reduction of COD, TDS, EC and Colour was measured. Can-Zeng Liang et al. 2014 [19] performed experiments for the treatment of highly concentrated multiple dyes wastewater (MDW, 1000 ppm), poly aluminium chloride (PAC) and polydiallyldimethyl ammonium chloride (PDDA) were found to be the most effective coagulant and flocculent. The CF process can achieve about 90% of dye removal at the optimal dosage of PAC/PDDA=400/200 ppm, and the MDW with pH>3 is favourable for the coagulation flocculation treatment. Tak-Hyun Kim et al. 2003 [20] work on the artificial addition of electrolyte solution and to decrease the pollutant loading efficiently on the post electrochemical oxidation process in order to improve the performance of organics removal by PAC and FeCl3, Cl-based chemical coagulants, was found as successful step of electrochemical oxidation. And it seems that PAC and FeCl3 were able to achieve sufficient removal efficiency of organics as well as to exclude the artificial addition of a supporting electrolyte and chloride reactant. D. georjius et al. 2003 [21] and Sheng H. Lin 1996 [22] experimented on Coagulation/Flocculation by Ferrous Sulphate and lime. All the experiments were carried and simulated an actual industrial wastewater treatment plant. Treatment with lime alone proved to be very effective in removing the colour (70–90%) and part of the COD (50–60%) from the textile and dyes industrial wastewater. Moreover, the treatment with ferrous sulphate at maintained pH in the range 9.0±0.5 using lime was equally effective. S. Sadri Mmoghaddam et al. 2010 [23] analyse the results on experimentation that the decrease of initial pH was always beneficial for dye removal and no re-stabilization phenomenon was occurred even at the used maximum FCS (FERRIC CHLORIDE SLUGE) dosage. Also it seems that iron hydroxides of the FCS could neutralize the negative charges on dye molecules. Therefore, the sweep flocculation and/or the charge neutralization might play key roles in the enhancement of dye removal. The optimum initial pH, FCS dosage and initial dye concentration were found to be 3.5; 236.68 mg dried FCS/L and 65.91 mg/L, respectively. Dye removal of 96.53% is observed which confirms close to RSM (REFERENCE SURFACE METHODOLOGY) results.

»TERTIARY TTREATEMENT

The purpose of tertiary treatment is to provide a final treatment stage to raise the effluent quality before it is discharged to the receiving environment such as sea, river, lake, ground, etc., or to raise the treated water quality to such a level to make it suitable for intended reuse. This step removes different types of pollutants such as organic matter, SS, nutrients, pathogens, and heavy metals that secondary treatment is not able to remove. Wastewater effluent becomes even cleaner in this treatment process through the use of stronger and more advanced treatment systems. It includes sedimentation, coagulations, membrane processes, filtration, ion exchange, activated carbon adsorption, electro dialysis, nitrification and di-nitrification, etc. the membrane processes can be classified into sub-processes such as electro dialysis (ED) or electro dialysis reversal (EDR), microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO).

»ANILINE POLYMERISATION: Because the higher concentration of ammonia and aniline present in dyes and pigment manufacturing industrial waste water are responsible for their high COD and ELECTRICAL CONDUCTIVITY values. Aniline polymers are electrically conductive [24] and hence here higher EC value denotes their presence in waste water sample. And aniline best polymerised by Fe (iii) chloride in acidic conditions [25]. Aniline polymerisation using oxidative catalysed by acid is studied by R. L. hand et al. (1978) [16-27]

MATERIALS AND METHODS:

1. RESEARCH MAIN LINES AND ANALYTICAL METHODS:

a) Checking the concentrations of main pollution parameters of the waste water fed to the physical –chemical processes, analytical determination of all pollutants like COD, TDS , PH, COLOUR and Ammonia at each stage of experiment has to be done after coagulation -flocculation and filtration.

b) Checking the effects of operating conditions like PH, dosing quantity, and type of chemical we used. Check effectiveness of specific chemicals combination at specific treatment condition for pollution parameter reduction of waste water.

2. MATERIALS REQUIERED: (table 3)

Apparatus	Chemicals and materials
Eye protection (goggles)	Waste water sample
Fume cup board	NAOH
Gloves and laboratory safety cloths	Lime
Electrical conductivity meter	Ferrous sulphate
Magnetic stirrer	Polly aluminium chloride
PH meter	Iron iii chloride
Ammonical-N testing apparatus	Charcoal
COD testing apparatus	Poly electrolyte
Digesters	Sand
Weighing machine	Filter paper
Evaporator	Cod testing materials
Conical funnel	Ammonia testing materials
Burets and pipets	Cotton
Round bottom flask	
Beakers	

3. Initial Tastes:

The master composite sample was directly taken for studies all pollution parameters without the aid of any chemical oxidant. Highly coloured liquid with pungent odour were observed this odour shows the presence of high ammonia concentration and for that ammonia concentration tested.

Before aeration studies

NH3-N: Waste water sample taken from dyes and pigment manufacturing industries having high COD and ammonia in there waste water near Mumbai area TALOJA. The total effluent generation rate is 20 to 25 KLD.

Take 50ml waste water sample make up with 150 ml of double distilled water in round bottom flask, add 25ml Borate Buffer solution and adjust the PH to 9.5 using 6N NaOH using PH meter, heating the solution in distillation column at 85-90℃. Collect the distillate in a beaker dipped with 50ml boric acid indicator, collect up to 200ml then titrate the distillate with 0.1 N Sulphuric Acid. Note down burette reading and calculate the ammonia conc. by using formula; [APHA 4500-NH_3 C] [28]

NH_3 CONCENTRATION= BURETTE READING x NORMALITY x 14 x 1000 / ml OF SAMPLE mg/L

= 204x 0.1x14x1000/50 mg/L

= 5712 mg/L

COD test: The COD test is based on the principle that strong oxidizing agents under acidic conditions oxidize most organic compounds to CO2 and H2O. COD will always be equal or higher than BOD, as the test is under strong oxidizing agent, which oxidizes to greater extent, including inorganics.

Initial COD were measured by standard methods of APHA 5220 B [open reflux method] [29]

INITIAL COD =38000mg/L
INITIAL PH = 8.7 (MEASURED BY PH METER)

TDS: TDS by electrical conductivity measured by conductivity meter is calculated

ELECTRICAL CONDUTIVITY= 87 mS
TDS BY ELCRICAL CONDUCTIVTY=87 x 650 mg/L
=56550mg/L
COLOUR: Dark orange colour appears physically.
PH: By PH meter PH = 8.7

Experimental set up:

Waste water sample kept for primary aeration of 24 hour then take 1 Lt. of waste water sample in a beaker put into it a magnetic needle and keep on magnetic stirrer. Put PH meter rod into it and a burette for chemical solution dosing. A filter paper in conical funnel used for sludge separation by simply filtration. Tertiary filtration set up made by put a cotton plug into inner side out let of conical funnel then layer of sand and charcoal is made into it.

Treatment alternatives:

Flocculants taken are lime and NAOH, coagulants taken Ferrous Sulphate, PAC, Fecl3 and Fenton's reagent. The Sulphuric acid is taken for PH adjustment and Polly-electrolyte solution for flock's polymerisation. Out of these chemical make different combinations of coagulants and flocculants for treatment scheme. Select best combination which results in highest reduction of pollution parameters. Treatment procedure:

Coagulation –flocculation*:* After aeration of 24 hr. the sample volume of 1lt kept on magnetic stirrer and trying various flocculants up to PH 10.5 approx. and then neutralises to 7 by coagulants or first up to PH 4.5 by coagulants and then neutralises to 7. Give Retention time of 30 minute on stirrer then off the stirrer and wait for sludge settle down. Separate sludge by filter paper and pass through territory filter made up of sand and charcoal in conical funnel. Then again test the pollution parameters. This whole the procedure is trying for various combinations of stabilising chemicals. And analysing the data obtained for selection of best treatment scheme for given chemicals. Slower down the speed of stirrer at neutralisation step.

Fenton process: Hydrogen peroxide best stabilizes the waste between PH ranges 4-4.5 in presence of ferrous as a catalyst. After aeration solution after aeration PH become 7.4 neutralises to 7 by using concentrate H2SO4 then add H2O2 in the ratio H2O2: COD is 2 and ferrous in the ratio H2O2:Fe^{2+} is 4 now PH become 3 and then adjust PH up to 4.5 by using lime and watch clearly flocks are formed then continued on stirrer for 2 hour then again adjust PH up to flocks again starts to formed then finally neutralised and sludge out from waste water for further process. 30 ml of H2O2 and 16 gm of ferrous is required.

Tertiary treatment*:* After chemical treatment treated water is separated from sludge then it is passes through tertiary filter where remaining colour complex and some impurities adsorbed on charcoal and filtrate solution is clear then previous almost colourless.

RESULTS AND DISCUSSIONS:

»While much research has been performed to develop effective treatment technologies for waste water containing dyes and dyes manufacturing waste water and toxic materials no single solution has been satisfactory capable for treatment of dyes manufacturing waste water.

» High PH value was found 8.7 which is higher than the DOE standards. High PH of the waste water is due to presence of ammonia, basic dyes, phosphate and organic N-Based compounds. Excessive PH is harmful to aquatic life like fish and microorganism etc.

»The electrical conductivity is used for indicating the total dissolve solids and aniline polymers where TDS is concentration of the ionized constituents of the waste water. Initial value of electrical conductivity of waste water is found to be 87 mS which indicates that a large amount of ionic substances and electrically conductive aniline polymers releases from dyes and pigment manufacturing industrial waste water. The EC value is much higher than the DEO standards is very dangerous to aquatic life and irrigation. EC is indirect measuring parameter for charge carrying species concentration. Dyes and pigment manufacturing industrial waste water contains large amount of aniline and aniline derivative where polymerisation product of aniline has only the capacity of conducting polymers. And due to this conductivity of poly-aniline waste water sample shows high conductivity.

»High ammonia concentration is very dangerous to the environment. Here initial concentration of ammonia is 5712mg/L (molarity336mol/L) is 25 times more than the higher limit of corrosive and dangerous for the environment given below in table.

OSHA (Occupational Safety and Health Administration) has set 15 -minute's exposer limit for gaseous Ammonia of 35 ppm by volume in the environmental air and 8-hour for 25 ppm by volume [30].National Institute for Occupational Safety and Health recently in 1943 reduced the IDLH (Immediate Dangerous To Life and Health) from 500 to 300.

Conc. (w/w)	Molarity	Conc. (w/v)	Classification
5-10%	2.87-5.62 mol/L	48.9-95.7 g/L	Irritant
10-25%	5.62-13.29 mol/L	95.7-226.3 g/L	Corrosive
>25%	>13.29 mol/L	>226.3 g/L	Corrosive Dangerous for the environment

References for **TABLE NO 4** [31-34].

» COD 38000 mg/L such high value makes not feasible the treatment methods like evaporation, membrane separation, adsorption, electrocoagulation and advanced treatment methods by both economically and effectively. High deficiency of dissolved oxygen is very dangerous to the aquatic life even all the living bodes can't survive more on discharging the waste water to environment creates. Biological conversion into simple by product by using bioculture is not possible here because at high COD to BOD ratio biological treatment is not possible.so the only and economic way for this type of hazardous and toxic waste is to stabilised by chemically oxidants and sludge disposed underground so that there adverse effect on environment not imparts.

» Presence of aniline and aniline derivatives in dyes industries make the waste water toxic and difficult to treat. Dark red collared fumes are formed during aeration because of presence of aniline and its derivatives in waste water which was further best polymerised by Fe (iii) chloride.

» After aeration studies:

Aeration flow rate: 2 lpm/lt. given for 24 hour and analysed the sample every 4hour time duration.

Aeration is given for removal of dissolved gases and volatile organic material into the waste water sample. This step reduces some pollution parameters in significant amount. But it should be remember that the Environment (Protection) Act, 1986 is also applicable for proper management of hazardous waste generated during treatment of effluent, as per the Hazardous Waste (Management, Handling & Trans boundary Movement) Rules, 2008 under this Act. Under these rules, "authorization" is required for generation, handling, collection, reception, treatment, storage, recycling, reprocessing, recovery, reuse and disposal of hazardous wastes. And here high amount of ammonia is released during aeration this must be recovered as ammonium sulphate by absorbing it into the sulphuric acid solution or may be in another absorbent to recovering.

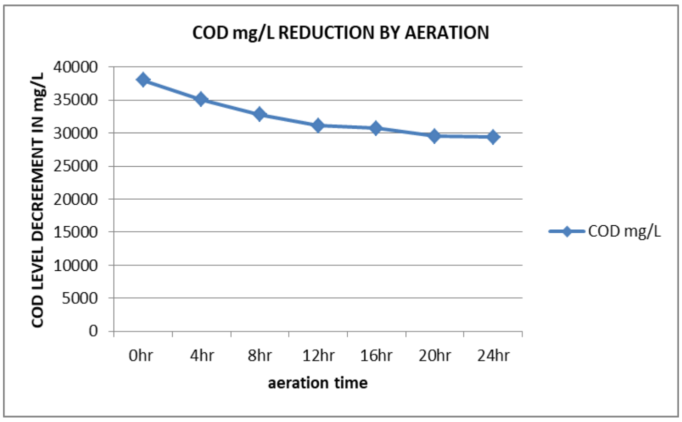
TABLE NO 5:

HOURS	COD mg/L	NH3-N mg/L	% COD REMOVAL	% NH3-N REMOVAL
0 hr.	38000	5712	---------	--------
4hr.	35100	4060	7.63%	28.92%
8hr.	32800	2940	13.68%	48.52%
12hr.	31100	2240	18.15%	60.78%
16hr.	30700	1960	19.21%	65.68%
20hr.	29500	1890	22.36%	66.91%
24hr.	29400	1820	22.63%	68.13%

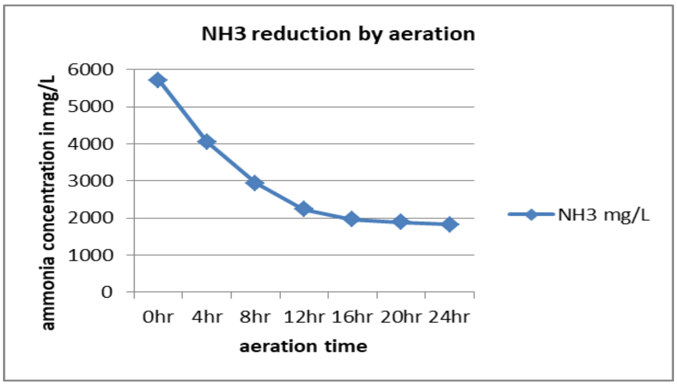
Analysing the data 68.13% of ammonia is reduced during aeration 3892 mg/L of ammonia get wasted with air and this implies the great opportunity of ammonia recovery as a base for fertilizer by absorption of ammonia in acid like hydrochloric or sulphuric from air. This is providing a great economic reduction of treatment cost due to recovery income. And 22.63% of COD reduction is observed and removal of large amount of ammonia and organic volatile matter is responsible for this much value of COD reduction. And final PH measured after aeration is 7.4 PH value decreases because of ammonia removal.

After observing the graph1 it concluded that COD continuously decreases up to a significant value of 22.63% COD reduction by pre-aeration has a significant decrement of COD in both the way by decreasing its pollution parameter and decreasing amount of chemical dose for stabilising the pollutants. This reduction is because removal of volatile organic pollutants and dissolved gases during. After all the reduction rate decreases with respect to time so the optimum aeration time is 12 to16 hour.

GRAPH 1:



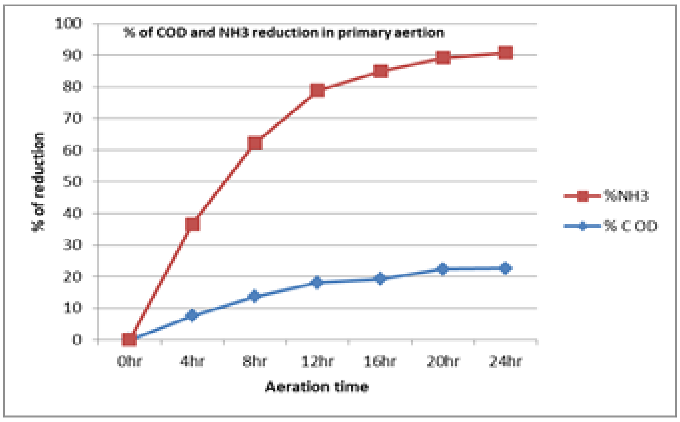
GRAPH 2:



Graph 2 shows the reduction in ammonia concentration with respect to time. Ammonia is stripped out by air and ammonia stripping rate is function of PH, Temp and Aeration rate so here aeration accelerate the ammonia removal by stripping with air. As ammonia decreases the PH value also decreases and hence the rate of ammonia stripping decreases because at lower PH value ammonia exists in ionic form (ammonium). Ammonia formed highly soluble ammonium ion with water in acidic and neutral condition that's by its rate of removal decreases. But after all in 24 hours aeration 68.13% of ammonia stripped out.

Graph 3 shows the decrement in COD value as well as ammonia concentration by aeration. Here volatile organic matter and dissolved gases stripped out with aeration and this was the main reason for COD reduction both the rate decreases after 12 hours of aeration so this time value may take as optimised aeration time. This COD and ammonia reduction is very helpful for chemical treatment process by process cost reduction because chemical consumption for chemical treatment as well as for processes treatment efficiency. Large amount of ammonia reduction concentrate our mind towards the great opportunity of ammonia recovery from dyes and pigment manufacturing waste water during the process. And that can again optimised the treatment process cost by recovery.

GRAPH 3:



» POLUTION PARAMETRS ANALYSE AFTER CHEMICAL REATMENT:

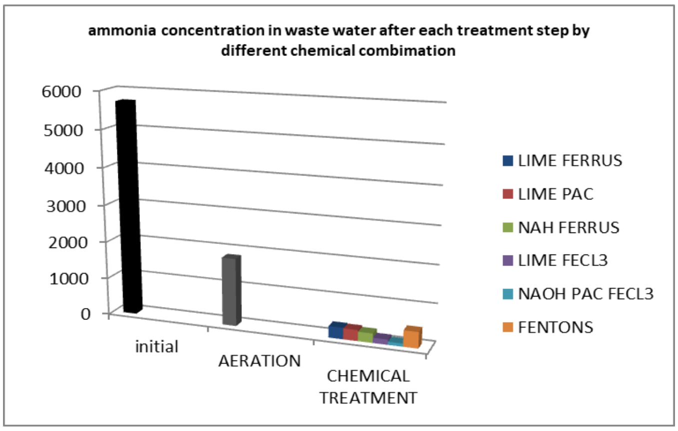
Waste water sample treated by various coagulants. Most compounds found in the wastewater are ammonia, phenol derivatives, aniline derivatives, organic acid and benzene derivatives output from dyes and pigment manufacturing industries. Coagulants ferrous sulphate, ferric chloride, Polly-aluminium chloride, and hydrogen peroxide catalysed by ferrous sulphate and flocculants lime and NaOH were investigated.

TABLE NO 6:

METHODS	DATA AFTER CHEMICAL TREAMENT				% REDUCTION OF POLLUTION PARAMETERS AFTER AERATION in chemical treatment		
Coagulants and Flocculants	CODmg/L	ECmS	TDS by (EC)mg/L	NH3 mg/L	COD	TDS	NH3
INITIAL	38000	87	56550	5712	-------	------	------
After aeration	29400	81	52650	1820	22.63	6.89	68.13
Lime-ferrous	17000	52	33800	308	42.17	40.22	83.07
Lime-PAC	18300	47	30550	294	37.75	45.97	83.84
NAOH-FERROUS	16400	56	36400	252	44.21	35.63	86.15
LIME-FECL3	15400	37	24050	140	47.40	57.47	92.30
Naoh PAC-fecl3	9700	32	20800	84	67.00	63.21	95.38
FENTONS TRT.	12600	28	18200	434	57.14	67.81	76.15

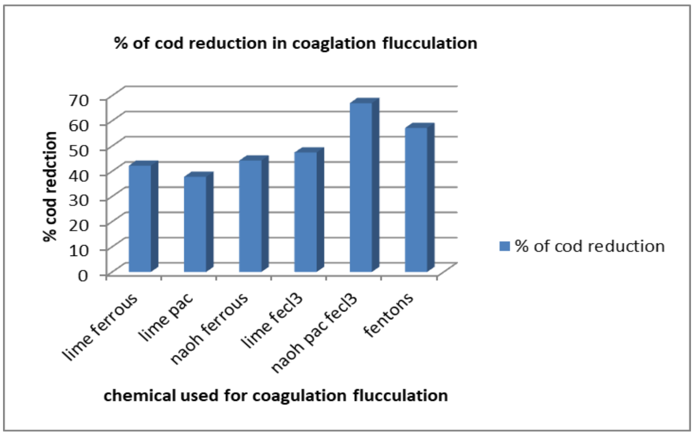
Coagulation is destabilisation of colloidal by addition of chemical that neutralizes the negative charge by higher valence coagulants (counter charged ions) to reduce the repulsive forces. And flocculation is the agglomeration of destabilizing particles in to a large size particle known as flocks which are further remove by sludge separation in settling and filter by filtering media. Analysis of data given in table6 shows that the COD concentration now reduced to 17000: 18300: 16400: 15400: 9700: 12600mg/L TDS concentration to 33800: 30550: 36400: 24050: 20800: 18200 mg/L and ammonia concentration to 308: 294: 252: 140: 84: 434: mg/L respectively by treatment by lime ferrous: lime PAC: NaOH PAC: NaOH ferrous: lime fecl3: NaOH PAC fecl3: Fenton's.

GRAPH 4:



Ammonia removal by chemical treatments method were analysed and it is found that it results in reduction of concentration up to a permissible value to the environment. Only treatment by Fenton's and lime-ferrous resulted the concentration value exceed the permissible limit to the environment which was decided 300 mg/L for recycle and reuse of waste water in the process. Highest ammonia reduction by chemical treatment is obtained by NaOH-PAC-FeCL3 (shown in graph 4).

GRAPH 5:



After destabilisation of colloidal and agglomeration of flocks, pollutants removed from waste water in the form of sludge. NaOH-PAC-FeCL3 gives highest % of COD reduction up to 67% of COD reduction. Fe (iii) chloride is responsible for aniline polymerisation and using PAC plus FeCL3 together is responsible for copolymerisation pollutants. This copolymerisation is responsible for higher % of COD reduction by NAOH-PAC-FECL3 then by other single chloride and sulphate of Fe and AL. it is also seems that NAOH having higher flocculation power then lime and same anion gives better treatability results with NAOH than lime. In Fenton treatment Fe(ii) is converted into Fe(iii) in presence of highly oxidative oxidants like hydrogen peroxide and then iron iii trivalent ion catalysed the polymerisation and stabilisation of charge by producing high hydroxyl ion. Fenton's treatment gives 57.14 % of COD reduction.

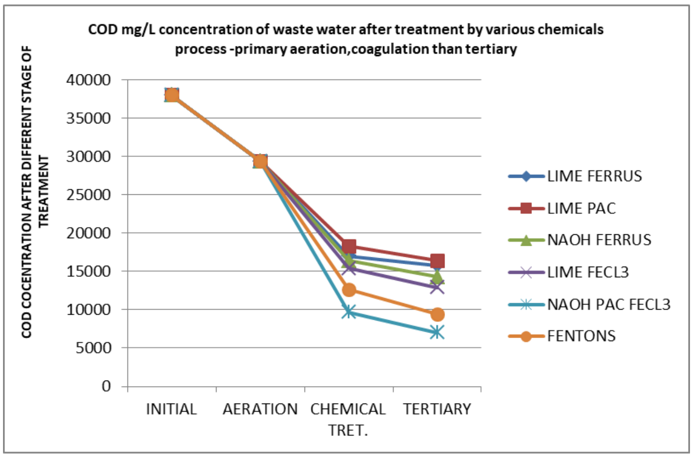
TABLE NO 7:

POLLUTION PARAMETER AFTER TERTIARY FILTERATION BY SAND-CHARCOAL FILTER				
Tertiary after treated by	COD	TDS(EC)	% reduction in tertiary COD	TDS
Lime-ferrous	15800	22100	7.05	34.61
Lime –PAC	16400	20800	10.38	31.91
NAOH-ferrous	14300	26650	12.80	26.78
Lime –fecl3	12900	15600	16.23	35.13
NAOH-pac-fecl3	7000	13650	27.83	34.37
Fenton's method	9400	11700	25.39	35.71

Charcoal is suited best adsorbent for colour removal. Even after chemical treatment complete removal of colour is not possible. Adsorption methods best suited for colour reduction it results in highest % of colour reduction, almost it makes colourless the waste water after passing through sand charcoal filter.

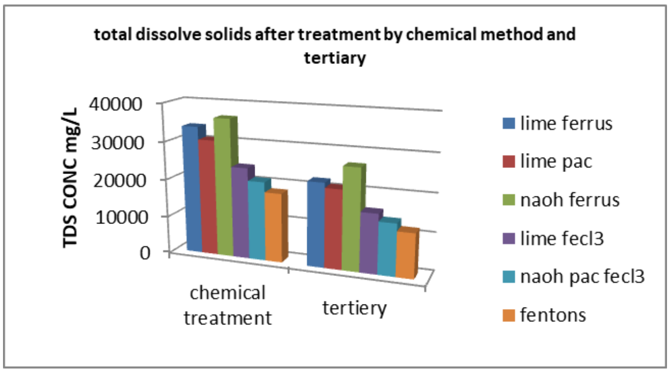
Charcoal adsorption method is also used for COD reduction by filtering and adsorbing coloured complex and organic matter from waste and results in 10-25% of COD reduction by tertiary tretment after the chemical treatment. Aniline polymer, phenolic derivatives and organic acids dissolved in dyes manufacturing waste water has great affinity to adsorbed by charcoal. Tertiary treatment gives up to 35% of TDS reduction after chemical treatment.

GRAPH 6:



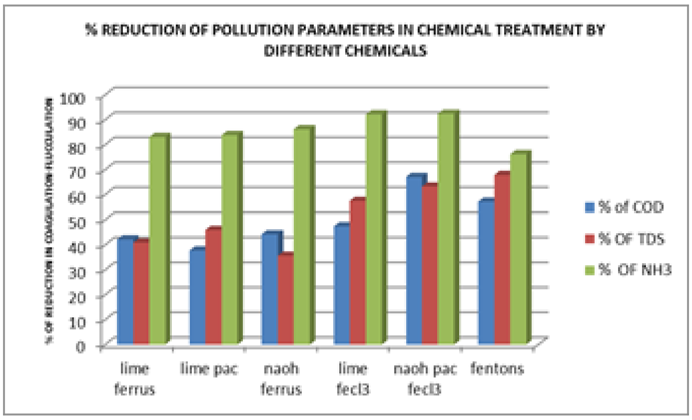
Graph6 shows total COD reduction throughout the process and the effectiveness of various chemicals are as follows NAOH-PAC-FECL3>FENTON>LIME-FECL3>NAOH-FERROUS>LIME-PAC>LIME-FERROUS. And the order of highest COD reduction by process are as follows CHEMICAL TRATMENT>AERTION>TERTIARY. And overall highest COD reduction was obtained by NAOH-PAC-FECL3 FOLLOWED BY AERATION AND TERTIARY TREATMENT in which the total 81.57% of COD reduction was resulted.

GRAPH7:



Total dissolve solid by conductivity is measure of total charged particles present in waste water sometimes conductivity increases due to the dosing of ionic electrolytes using for chemical treatment and simultaneously decreasing as the destabilisation effect of coagulants on colloidal particles and finally combined effect of both resulted in electrical conductivity value of waste water. Also one another measure region for high TDS value is the electrically conducting behaviour of conductive aniline polymerisation products are formed during chemical treatment. But they are sludge out after chemical treatment and then tertiary treatment is given for further reduction. Graph7 shows the highest TDS reduction was obtained by Fenton (79.31%) and then by NAOH-PAC-FECL3 (75.86%) by whole the process aeration chemical treatment and then tertiary. Here small rise in conductivity by naoh-pac-fecl3 treatment is because of the electrolytic nature of chemicals and high amount of chloride dosing.

GRAPH 8:



Comparison in removal efficiency of all pollution parameters by chemical treatment is shown in graph8. Naoh-pac-fecl3 treatment gives best result overall for all parameters and out of which mainly for COD reduction and COD was our main pollution parameter. Then Fenton's treatment method was found to be second most effective chemical method selection for dyes manufacturing waste water treatment.

» SCOPE:

Now the COD value of waste water is reduces to a level so that secondary or biological treatment is possible for further treatment plan.

Treated water now can be reused or recycled in the process. Research shows the ammonia recovery option for treatment plan.

CONCLUSIONS:

Our research shows the reduction in pollution parameter by different coagulants used for treatment of dyes and pigment manufacturing industrial waste water.

Aeration reduced the COD up to 22.63% and NH3 up to 68.13% then by chemical treatment followed by tertiary filtration through sand charcoal filter. Chemical treatment results by different coagulants are as follows:

By Lime- Ferrous COD 42.17%, TDS 40.22%, NH3 83.07%
By Lime –PAC COD 37.75%, TDS 45.97%, NH3 83.84%
By NAOH-Ferrous COD 44.21%, TDS 35.69%, NH3 86.15%
BY Lime-$Fecl_3$ COD 47.40% TDS 57.47%, NH3 92.30%
BY NAOH-PAC-$Fecl_3$COD 67.00% TDS 63.21%, NH3 95.38%
By FENTON COD 57.14% TDS 67.81%, NH3 76.15%

Chemical treatment by naoh-pac-fecl3 gives best treatment efficiency. Overall process aeration chemical treatment by naoh-pac-fecl3 and tertiary gives total 81.57% COD, 98.52% NH3 and 75.86% TDS reduction efficiency and almost completely colourless treated water. Total COD reduction throughout the process and the effectiveness of various chemicals are as follows NAOH-PAC-FECL3>FENTON>LIME-FECL3>NAOH-FERROUS>LIME-PAC>LIME-FERROUS. And the order of highest COD reduction by process are as follows CHEMICAL TRATMENT>AERTION>TERTIARY. And overall highest COD reduction was obtained by NAOH-PAC-FECL3 FOLLOWED BY AERATION AND TERTIARY TREATMENT in which the total 81.57% of COD reduction was resulted. Research also shows the ammonia recovery option with treatment scheme by air ammonia stripping with air.

REFRENCES:

1. Swett, L., A. Twhigg, and Kirtland E. McCaleb. The Organic Dyes and Pigments Data Base. US Environmental Protection Agency, Industrial Environmental Research Laboratory, 1984.

2. Gardiner, Deirdre K., and B. J. Borne. "Textile waste waters: treatment and environmental effects." Coloration Technology 94.8 (1978): 339-348.

3. Reife, Abraham. "Dyes, environmental chemistry." Kirk-Othmer encyclopedia of chemical technology (1993).

4. United States Tariff Commission. Synthetic Organic Chemicals, US Production and Sales, 1971. US Government Printing Office, 1973.

5. US Tariff Commission. "Synthetic Organic Chemicals, US Production and Sales, 1970." USTC Publication 479 (1973).

6. Moore, James W., and Subramaniam Ramamoorthy. Organic chemicals in natural waters: applied monitoring and impact assessment. Springer Science & Business Media, 2012.

7. Clarke, E. A., and R. Anliker. "Organic dyes and pigments." Anthropogenic compounds. Springer Berlin Heidelberg, 1980. 181-215.

8. Anliker, R. "Colour chemistry and the environment." Coloration Technology 8.1 (1977): 60-72.

9. Anliker, R. "Color chemistry and the environment." Ecotoxicology and environmental safety 1.2 (1977): 211-237.

10. Anliker, Rudolf, and G. Muller. "Fluorescent whitening agents." Fluorescent whitening agents. Georg Thieme, 1975.

11. Compton, Steve J., and Clive G. Jones. "Mechanism of dye response and interference in the Bradford protein assay." Analytical biochemistry 151.2 (1985): 369-374.

12. Zollinger, Heinrich. Color chemistry: syntheses, properties, and applications of organic dyes and pigments. John Wiley & Sons, 2003.

13. Brown, D., H. R. Hitz, and L. Schäfer. "The assessment of the possible inhibitory effect of dyestuffs on aerobic waste-water bacteria experience with a screening test." Chemosphere 10.3 (1981): 245-261.

14. Ghaly, A. E., et al. "Production, characterization and treatment of textile effluents: a critical review." J Chem Eng Process Technol5.1 (2014): 1-18.

15. Das, Subrata. "Textile effluent treatment-A Solution to the Environmental Pollution." (2000).

16. Coagulants for Optimal Wastewater Treatment from Beckart Environmental

17. Srivastava, Harsha P., et al. "Performance of modified poly (vinylidene fluoride) membrane for textile wastewater ultrafiltration." Desalination 282 (2011): 87-94.

18. Chandran, Deepa. "A review of the textile industries waste water treatment methodologies." Int. J. Sci. Eng. Res 7 (2016): 392-403.

19. Liang, Can-Zeng, et al. "Treatment of highly concentrated wastewater containing multiple synthetic dyes by a combined process of coagulation/flocculation and nanofiltration." Journal of Membrane Science 469 (2014): 306-315.

20. Kim, Tak-Hyun, et al. "Effects of Cl-based chemical coagulants on electrochemical oxidation of textile wastewater." Desalination155.1 (2003): 59-65.

21. D. georjius, A. Aivazidis, J.Hatiras.K.Gimouhopoulos Water Research Volume 37, Issue 9, May 2003, Pages 2248-2250

22. Lin, Sheng H., and Chi F. Peng. "Treatment of textile wastewater by electrochemical method." Water research 28.2 (1994): 277-282.

23. Mac, A. G. "Diarmid, J, C. Chiang, M. Halpern, WS Huang, SL Mu, NDL Somasiri, W. Wu and SI Yaniger." Mol. Cryst. Liq. Cryst 121 (1985): 173.

24. Nestorović, Gordana D., Katarina B. Jeremić, and Slobodan M. Jovanović. "Kinetics of aniline polymerization initiated with iron (III) chloride." Journal of the Serbian Chemical Society71.8-9 (2006): 895-904.

25. Hand, Rodney L., and Robert F. Nelson. "The Anodic Decomposition Pathways of Ortho-and Meta-substituted Anilines." Journal of The Electrochemical Society 125.7 (1978): 1059-1069.

26. Hand, Rodney L., and Robert F. Nelson. "Anodic oxidation pathways of N-alkylanilines." Journal of the American Chemical society 96.3 (1974): 850-860.

27. Moghaddam, S. Sadri, MR Alavi Moghaddam, and M. Arami. "Coagulation/flocculation process for dye removal using sludge from water treatment plant: optimization through response surface methodology." Journal of hazardous materials 175.1 (2010): 651-657.

28. STANDARD METHOD FOR AMMONIA CONCENTRATION. APHA-4500 NH3 C.

29. STANDARD METHOD FOR COD TEST. APHA 5220 B(OPEN REFLUX METHOD).

30. Illinoisattorneygeneral.gov. Retrieved 21 May (2011).

31. Haq, Syed Nomanul (28 February 1995) Name, Nature and things, ISBN 978-0-7923-3254-1. Retrieved 22 June (2010).

32. FR. Basilini VA-Lentini , pp-80-81.,(1625)

33. Crosland, Maurice P. Historical studies in the language of chemistry. Courier Corporation, 2004.

34. Rideal, Samuel. "Disinfection and Disinfectants (an introduction to the study of)." (1895).