

Ammonia Recovery from Dyes and Pigment Manufacturing Industrial Waste Water in Physio-Chemical Treatment Subsequent with Air Stripping at High pH

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Abstract - Conventional primary- secondary and biological treatment of paint and pigments manufacturing industrial waste water has limited capacity of removing nitrogenous compound. Because of high COD and toxic nature of n based waste does not have possibility of biological conversion/Bio-degradation. But there has a great opportunity of removing/recovery of ammonia which is present in highest concentration formed (by several reactions and side reactions during manufacturing processes) from waste water during treatment process and process is feasible by both economically and environmental health aspect point of view. These are desorption of molecular ammonia at liquid-air interface in an alkaline medium during flocculation using NaOH in primary treatment by slow rate ammonia stripping by air because of ammonia is a weak base and replaced by a strong base like NaOH and become in free molecular form in aq. solution. 95% off ammonia has been removed and then recovered by adsorption of stripped molecular ammonia in concentrate acid H₂SO₄ at gas -liquid interface and obtained as ammonium sulphate formed by reaction of strong acid and weak base and has great importance in agriculture sector as a fertilizer. Then further treatment of coagulation and tertiary treatment is done on this waste water for COD reduction.

Key Words: COD (chemical oxygen demand), Ammonia recovery, stripping, absorption, pH, flocculation, NaOH, ammonium Sulphate, fertilizer.

1. INTRODUCTION

The disposal of paints and pigment manufacturing waste water is a major problem from global viewpoint. Paints and pigment manufacturing industries produces a lot of waste water which contains several contaminants, including dyes and acidic and caustic dissolved solids, toxic aromatic and N-based compounds. According to Allen et al. 1971 and Reife et al. 1996 dyes and pigments are substances which when applied to substrate lead to selective reflection or transmission of incident day light [1-2]. 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 and research work on the Eco toxicological behaviour of the several thousand

commercially available products and their production process which are difficult to control the release of manufacturing material during dye manufacturing and the treatment methodology of generated waste [3 - 5]. David C. Bomberger et al in 1984 identified and studied the sources of pollution and their effects in dyes manufacturing industries and in their Wiedhaup, K.: Acta Pharm. Technol. Suppl. 8, 67 (1979) they describe the physical, chemical and biological treatment of waste from dyes industries and process efficiency to remove colour and N- Based waste [6]. Resource Conservation and Recovery Act (RCRA) requires that hazardous solid wastes produced by manufacturing operations be identified and disposed in a manner that limits the release of hazardous materials to the environment. Untreated effluent from dye stuff production and dyeing industries contains highly coloured and toxic components which are objectionable to discharge into open water. They required extensive testing of discharged waste parameters 40-80% of coloured components are easily adsorbed on bio mass so that this would be mixed with municipal waste but it is seen that after all it is not decomposable so that some advance treatment must be required. In general, the most losses of material during manufacturing process are intermediates that do not react and by-products such as incomplete dye or pigment molecules. The intermediates and by-products from the dye manufacture are present either in the product or in the solid waste streams regulated under RCRA (Conservation and Recovery Act), which include wastewater, solid residue, and the vapour and dust emissions. The losses products discharged in the plant effluent and some is discharged on any waste water treatment solids. The dyes and pigment present in water is undesirable. So a very small amount of these colouring agents are very highly visible and may be toxic to the aquatic environment. It is well known that dye effluents be toxic and/or carcinogenic to mammalian animals [7-16]. The toxic behaviour waste streams are also described by many author's that it effects the ecosystem but also affects the human life that's by it necessary to treat before discharging or not to be re-used in process due to high COD, TDS, TSS, NH₃-N and complex mixtures of by products and intermediates have undesirable effects. So be needed a practical solution which is compatible environmentally as well as economic aspects. This paper reviews the work on dyes and pigment manufacturing industrial waste water producing the following dyes product.

TABLE1 Product and by Products

sr no	Product name	total Qt. MT/month
A.	POWDER DYES (SOLID)	
1	Basic dyes such as	
	a. rhodamine	
	b. malachite green /brilliant green	
	c. methyl violet	
	d. auramine	
2	solvent dyes such as	
	a. rhodamine base	
	b. victoria blue base	
	c. bismark brown base	
	d. orange base	
	e. solvent black	75
B	liquid dyes such as	
	a. rhodamine liqued	
	b. malachite green liquid	
	c. brilliant green liquid	
	d. victoria blue liqued	
	e. bismark brown/chrysioidine liquid	
	f. methyle violet/ crystal violet liquid	
	g. basic yellow liquid	120
	toal	195
C	By Product	
	amonia	
	organic amines	
	organic n-based compounds	
	aromatic polymer complexes	
	sulfur based impurities	
	dyes as impurities	6

Table 2 row materials

sr no.	Name of Row material	physical state	Qt. mt/month
1	pthalic anhydried	solid	10
2	dimethyle meta aminophenol	solid	8
3	dimethyl aniline/mona methylaniline	liquid	20
4	formaldihyde		5
5	benzaldehyde	solid	5
6	meta phenyl diamene/meta tolludine	solid	
	diamine	solid	3
7	PANA	solid	1
8	dodium nitrite	solid	1
9	caustic soda	solid	5
10	hydrochloric acid	liquid	8
11	sulphuric acid	liquid	5
12	acetic acid	liquid	15
13	catalyst and surfactants	solid	0.75

Here we seen above data that shows highest per cent of aromatic amines, aromatic amines, nitrogen based row material is used and there for highest amount of ammonical nitrogen and aniline 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. John Pearision and George R. Stewart in October 1993 analysed the effect of ammonia on plants Ammonia taken up by plants is directly assimilated and this uptake can have a strong effect on the nutrient imbalances of the plant [17]. Ammonia or azane is a compound of nitrogen and hydrogen with the formula NH₃. The simplest pnictogen hydride, ammonia is a colourless gas with a characteristic pungent smell and ubiquitous in nature. It is significantly used as nutritional needs to terrestrial

organisms by serving as a precursor to food and fertilizers. Ammonia also a building block for synthesis of many pharmaceutical products and is used in many commercial cleaning products. Ammonia has been recognised as a labile form of nitrogen in agricultural system. Evolution oh NH₃ as a fertiliser application made its great importance and presented a pathway of recovery as a fertiliser like ammonium chloride and ammonium sulphate. India uses 7.6% of total world-wide ammonia and out of them 88% of the ammonia used for agricultural purpose as fertilisers [18], in precursor to nitrogenous compounds [19], in cleaner, (ammonium hydroxide) used as a cleaner for many surfaces, in fermentation to adjust PH, as antimicrobial agent for food products[20], as refrigerant[21-23], for remediation of gaseous emissions[24-25], energy density of ammonia is 11.5MJ/L so it is used as fuel in ammonia engine and high octane rating fuel [26-30], as a stimulant in respiration[31], in textile industries for treatment of cotton material[32], as lifting gas, as darkener in wood working[33]. Ammonia also has many other uses like laboratory use of anhydrous ammonia (classified as toxic and dangerous for the environment). The hazardous nature is depending on conc. of ammonia: "Dilute" ammonia solutions are usually 5-10% by weight "Concentrated" solutions are grater then 25% by weight. Ammonia solutions should not be mixed with halogens (must not be comes in contact with iodine), as toxic or explosive products are formed so that ammonia containing solutions should not be directly treated with halogens and its compounds. This has required to treating waste water by removing/recover ammonia before it is fed to the water or environment directly because of toxic nature and to other chemical treatment processes because of explosive and toxic products formation. Many similar work has been done on ammonia removal from varies sources of generation. Y. Folk man and A.M. Waschs in 1973 studied and experiments the process of release of ammonia through holding ponds and effect of PH on ammonia stripping in nitrogen removal through ammonia release from holding ponds [34]. According to D. L. N. RaoLalita Batra in his research "Ammonia volatilization from applied nitrogen in alkali soils" June 1983, this is seen that ammonia is volatilised due to highly alkali soil and losses from applied nitrogenous fertilisers and largely governed by PH/alkalinity of the system. Volatilisation obeys first order kinetics [35]. The physical and chemical processes commonly used for ammonia recovery from dyes and pigment manufacturing industrial waste water are: Struvite (magnesium ammonium sulphate) formation, photo-chemical and electrochemical processes, ion exchange and membrane processes, chemical oxidation and adsorption [73-74].

2. EXISTING TECHNIQUES

Some familiar methods of ammonia recovery from different type of waste are discussed below.

Steam and air stripping Recovery of ammonia: desorption of ammonia from industrial, municipal waste water streams

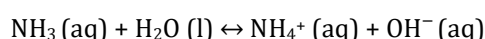
and biogas plant contains high conc. of ammonium nitrogen is stripped with air by providing alkaline medium.

Absorption of ammonia from waste gases: from waste gases ammonia gas is absorbed because of its high solubility at low PH and efficiency enhanced by lowering the saturation temp. Biological conversion: biological conversion by some nitrifying plant and bacterial conversion into direct nitrogen and nitrogen based bio fertilisers is possible at low concentration because at high conc. ammonia shows toxic behaviour and it is impossible condition for bacterial growth. In case of dyes manufacturing industries there also many other toxic compounds like aniline are present.

Some previous research works on ammonia recovery are: by I. Çelen & M. Türker "Recovery of Ammonia as Struvite from Anaerobic Digester Effluents" in 2010 [36]. By Lorenzo Liberti et al 1979 ammonia recovered from secondary effluents using selective ion exchange method with production of a slow-release fertilizer as $MgNH_4PO_4 \cdot 6H_2O$ [37]. Precipitation by magnesium ammonium phosphate is done by M. Altinbas et al 2002 [38]. Zeng L et al 2008 recovered ammonia from anaerobically digested cattle manure by steam stripping and evolution is performed at different PH [39]. H. W. H. Menkveld et al. 2017 Recovered ammonium from digestate as fertilizer by stripping of ammonia and formed ammonium sulphate [40]. Wendong Tao and Anayo T. Ukwuani 2015 recovered ammonia through thermal stripping at PH 9 & 11 and acid absorption of ammonia to form ammonium sulphate fertilizers [41]. Sibel Başakçılardan-Kabakci et al. 2007 study on Recovery of Ammonia from Human Urine by Stripping with air and Absorption sulphuric acid [42]. Now these days control of nitrogen is of increasing importance. Many of waste water contain ammonia and untreated wasted in stabilisation processes.

3. THEORETICAL BACKGROUND:

In dyes and pigment manufacturing industrial waste water usually found soluble ammonia and organic nitrogen based compounds. Due to toxic behaviour at high concentration biological conversion of waste is not possible. And dissolve ammonia is also a main reason of high COD level of waste water. The ammonia released in various streams during process as a by-product is stripped with water is present as waste in effluent water. Ammonia is presence in equilibrium between the molecular; gaseous form (NH_3) and the ionic form (NH_4^+), and reaction given as



Reaction equilibrium highly depends on PH and temperature. Ammonia exist in basic medium as free molecular ammonia whereas in acidic and neutral medium as ammonium ion. Because of the conversion of ionic ammonium ion to free molecular ammonia favoured by high PH is convert to gaseous form and it is stripped with air in

alkaline medium. At NTP ammonia exist in ionic form at PH 7 and less and at PH greater than 11.5 all the ammonia is found in gaseous form [43-45].

The transfer of ammonia from water to air occurs when the partial pressure of dissolved gas in water is greater than that of the gas in air at liquid air interface because this transfer rate is a function of relative partial pressure and whole the mass transfer operation is well described by Henry's Low [46-48]. According to Henry's Low the mass transfer rate is directly proportional to concentration gradient at interface and follows the first order kinetics [49]. Given by equation

$$\frac{dm}{dt} = -KC$$

Where

m= mass of ammonia transferred

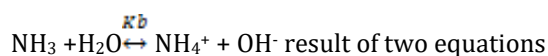
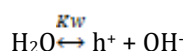
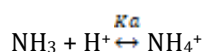
t= time

C= ammonia concentration

K= ammonia transfer rate from waste water to air and is a function of pH, Temperature, Turbulence, surface area and air velocity.

Folkman and Wachs developed formulas for ammonia losses in alkaline medium when effluent treated with lime at PH 11 and determine the coefficient of ammonia release rates [34]. Also Stratton carried out work on ammonia losses from alkaline water under natural mixing and turbulent conditions [50].

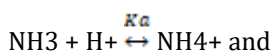
The uptake of gaseous ammonia from waste is a function of temperature, gas-liquid interaction time, and PH in the range 0-13 [51]. When uptake measurement at low PH is taken the rate changing parameter generally used is temperature and at high PH parameter mainly used is PH.



Here ammonia is Lewis base, and hydroxide is a stronger Lewis base. However, both are stronger Lewis bases than water is. Pure water always has some amount of "free" H^+ and OH^- due to self- ionisation ($Pk_w=14$) and $pk_b NH_3$ is 4.8 and pk_a of NH_4^+ is 9.2 so NH_3 is stronger base than NH_4^+ is basic. When ammonia is added to water some of those hydronium ions react with the ammonia to form ammonium. Since conc. of hydronium ion is decreases, the conc. of hydroxide ion must be increases to maintain equilibrium. But this equilibrium reverse when some strong base attack. NaOH is strong base then ammonia it produces hydroxide ion which replaces the ammonium ion and ammonium ion converted to free molecular ammonia.

Where $K_b = [NH_4^+][OH^-] / [NH_3]$

Ammonia is very soluble in water the Henrys constant for ammonia in water $57.5 \frac{mol}{l - atm}$ at $25^{\circ}C$. Ammonia is weak base which combines with proton to form ammonium ion in water as



$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

The value of K_a is 5.5×10^{-10} at $25^{\circ}C$ and the concentrations of NH_3 and NH_4^+ vary with PH [52].

At acidic and neutral conditions it exists as ammonium ion and at PH greater than 11.2 highly basic conditions it exists as free ammonia molecule at NTP [53]. Ammonia absorbed and mix as impurities during several process steps manufacturing, washing, leakage, stripping and in by-products formed it arises into effluent water. But for mix-waste type effluent water the values of Henry low constant, k_a and k_b is some different or deviated from standard values. Here NH_3 is toxic no NH_4^+ than also treatment of waste water is required because if waste water is discharged freely in the environment this ammonium ion containing waste water react with clay having zeolite and releases ammonia which is toxic and harmful to the environment. NH_3 already is of basic nature and increases the PH up to 10 of waste water and small amount Na present in clay is sufficient to rises the PH up to 11.2 of waste water where NH_3 releases as free molecular ammonia so that it is harmful to Fishes, plants, animals and other aquatic species by discharging in environment [54, 55].

Desorption of molecular ammonia in alkaline medium at liquid air interface known as ammonia stripping. Additional advance waste water treatment process recurred where other chemical and biological treatments are ether not possible or not feasible. The purpose of this paper is to investigate the ammonia recovery in chemical treatment of dyes manufacturing industrial waste water. Removal of ammonia by stripping from waste water into the air has been developed as a process that can be used in conjunction with flocculation treatment with NAOH. NAOH spent for flocculation rises the PH to high values is used to convert most of the ammonium ion to free ammonia in molecular form dissolve gas in appropriate condition desorbed from waste water and transferred to the air. NAOH treatment is investigated as a part of whole treatment scheme that's by ammonia recovery during process step is very beneficial and also COD reduction step of process scheme.

4. MATERIALS AND METHODS:

4.1. 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, Ammonia and Aniline at each stage of experiment has to be done after stripping, coagulation -flocculation and filtration.

b) Checking the effects of operating conditions like PH, dosing quantity, rate of aeration and detention time. Effect of close loop aeration, single time dosing and continues dosing to maintain high PH on ammonia recovery and effect of CO_2 washing on dosing.

4.2. Materials Required: (table 3)

Apparatus	Chemicals
Eye protection (goggles)	Waste water
Fume cup board	NAOH
Gloves and laboratory safety cloths	HCL or H_2SO_4
Long 2 beaker so that fumes not come out with bottom outlet valve	KOH for CO_2 washing
2 Aeration pump with air stone	Boric acid for ammonia absorption from air
PH meter	Round bottom flask
Air tubes	
Heaters for regeneration and evaporation	
Freezer for crystallization	
Heating apparatus	
4 small beaker of 250ml for absorber and regenerator	
2 beaker of 500ml for evaporation and crystallization	
Silver foil for covering the beakers to make close system	
Ammonical-N testing apparatus	
COD testing apparatus	

4.3. Initial Tests:

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 $85-90^{\circ}C$. 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] [56]

$$\frac{NH_3}{\text{BURETTE READING} \times \text{NORMALITY} \times 14 \times 1000} = \frac{\text{CONCENTRATION}}{\text{ML OF SAMPLE}} \text{mg/L}$$

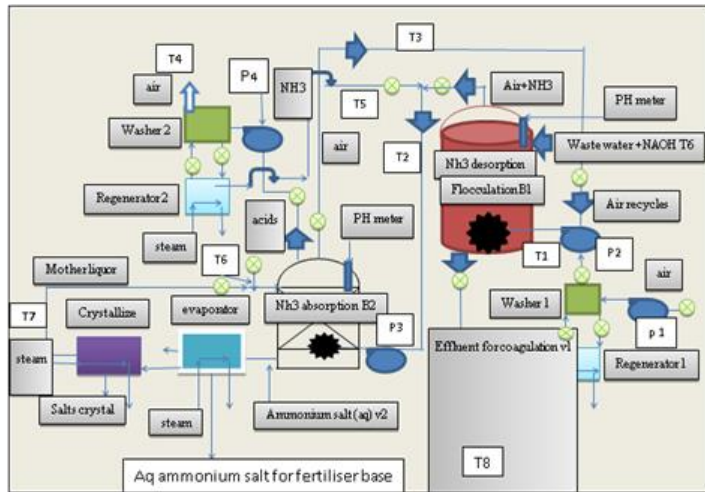
$$= \frac{204 \text{ ml} \times 0.1 \times 14 \times 1000}{50} \text{mg/L}$$




$$= 5712 \text{ mg/L}$$

Initial COD were measured by standard methods of APHA 5220 B [open reflux method] [57]

INITIAL COD =42000mg/L
INITIAL PH =8.7 (MEASURED BY PH METER)

4.4. Block Diagram for Ammonia Recovery as Ammonium Salt During Flocculation Process by Desorption (Ammonia Stripping with Air) at High pH (Fig. 1)



-  Pump p 1 to 4
-  Valve
-  Tubes T 1 to 8
- V1 Out let valve of beaker 1 (stripping beaker)
- V2 out let valve of beaker 2 (absorption beaker)
- B1 desorption or stripping beaker
- B2 absorption beaker
- Washer 1 and 2
- Regenerator 1 and 2

4.5. Experimental Setup:

Take 1 Lt. Solution of waste water in beaker1 and Dip into it the air stone connected with pump1, A PH meter and tube6 for NaOH dosing. Beaker1 connected with tube1 for aeration by air stone, tube2 for air out let and tube 8 at bottom for out let of flocculated effluent for further processing of treatment process. Beaker1 have enough volume so that it occupies volume (expanded during aeration) of waste water plus sufficient space for stripping air then closed the beaker from top in such a way that inlet-out streams can passes material. Tube2 connected from top of desorption beaker to inlet of pump2 for aeration of stripped ammonia and air mixture into beaker2 for absorption of ammonia into acid solution. Beaker2 contain 500ml of H₂SO₄ aqueous solution for absorption of NH₃ and this beaker is also closed. Tube3 connected from top of absorption beaker to inlet of aeration pump1, now the whole system is closed so that air can recalcultates between striper and absorber. Beaker2 volume should be enough occupied acid space for air recycled into

the system. Out let of ammonium sulphate solution from beaker2 by valve2 is send to the evaporator and crystalliser assembly, tube 6 is provided at beaker2 for acid inlet and also used for recycle mother liquor from crystalliser (optional) or the ammonium sulphate solution may be take out directly from evaporator and used as base for fertilizer production. Inlet pump provided with two way inlet valve so that it can inlet the air from atmosphere at starting stage and then from tube3 provided for air recycling, similarly at beaker2 air outlet provided with two way outlet valve so that air can recycled as well as discharged to the atmosphere. And two washers and regenerators assembled for air washing before and after use to remove atmospheric CO₂ to minimize re-carbonisation and NH₃ to minimize air pollution. Ammonia through washer2 is recycled to absorption beaker2 and both the washer solution is regenerated. Inlet air from atmosphere is washed with KOH for CO₂ separation and regenerated at 70°C and out let air washed with boric acid and regenerated at 90°C.

4.6. Stripping System:

Ammonia stripping rate is function of PH, Temperature, surface turbulence and aeration rate [58]. There are three type of aeration processes generally used;

Air stripping tower: The process is design in such a manner so that large quantity of air is fed into the tower and the formation of small water droplets to increase contact surface between air and water. The efficiency and other parameters were optimised.

Forced stripping: To reduce detention period of high PH effluent the equipment is equipped with agitator that agitate or break the gas film formed at water air interface, increases the water air surface contact and create turbulence.

Free stripping: ammonia is freely released from waste water in long size equipment by natural free aeration even without a mechanical device.

But be can use only slow rate aeration for stripping and free stripping is done at slow rate because there are two process parallel running one is ammonia stripping and another is flocculation of waste water. And flocks are formed in flocculation process can broke by turbulence created by fast aeration. So we have to use only slow aeration or free stripping.

4.7. Treatment Plan:

Waste water first treated by flocculation dosing solution of NaOH in varying amount and ways, respectively PH increases to >11 to convert the ammonium ion into free ammonia, in keeping with subsequent stripping process. Dosing amount and aeration time is analysed during the experimentations as further procedure proceeded.

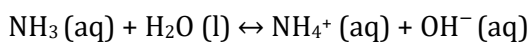
Air leaving the stripping beakers enriched with ammonia fed to the absorption beaker filled with sulphuric acid. A counter current air is fed to the sulphuric acid solution flow.

This absorption beaker contains ammonium sulphate at bottom which is used as base fertilizer.

The air is used in a closed circuit between the stripping and absorption beakers. Air is recirculated between the two beakers without emission into the atmosphere until it is highly contaminated with organic volatile component of dyes waste. And after all air is passes through boric acid or phosphoric acid (Ammonia Absorbing Solution) so that its concentration of emission in the environment is never exceed to a permissible value whenever it is discharged.

4.8. pH as Driving Parameter:

Here in throughout the experiment PH was main driving parameter because ammonium ion concentration is inversely proportion with PH and free molecular ammonia concentration is directly proportional to the PH. value. D. L. N. Rao et al. in 1983 studied the volatilisation of ammonia is governed highly by high PH/alkali [35]. Nitrogen Losses from Alkaline Water Impoundments by Frank E. Stratton in 1969, investigated the gaseous ammonia volatilisation from alkaline water in coagulation-flocculation pre-treatment at $\text{pH} > 11$, and subsequent ammonia stripping and the stripped ammonia was recovered by absorption with sulphuric acid to producing ammonium sulphate, which was reused as a base fertilize [81].



Reaction equilibrium highly depends on PH and temperature. Ammonia exist in basic medium as free ammonia molecule whereas in acidic and neutral medium as ammonium ion. Because the conversion of ionic ammonia to molecular ammonia favours high PH and gaseous form is the prerequisite of ammonia stripping an alkaline medium is required. At NTP ammonia exist in ionic form at PH 7 and less and at PH greater than 11.5 all the ammonia is found in gaseous form [59-61].

So that as PH increases the free ammonia concentration increase for stripping with air and ammonia is Lewis base, and hydroxide is a stronger Lewis base than water and pK_b of NH_3 is 4.8. and if free molecular ammonia concentration increases then also its stripping rate increases but ammonia is also a base and contribute its PH value in waste water with stripping as free molecular ammonia desorbing from waste water its concentration decrees in waste water and hence the PH value due to ammonia basicity is also decreases, again this decrement in PH value lowers the concentration of free molecular ammonia (free molecular ammonia concentration is favoured by high PH value) concentration and due to this the rate of ammonia stripping also decreases. So we use PH as a rate the stripping rate determining parameter.

4.9. Methods of NaOH Dosing for Coagulation process:

Initially research work is concentrated on ammonia removal by ammonia stripping in flocculation process. During experimental procedure we have to find out the variations in resulting parameter with respect to driving parameters and driving parameters variations with respect to dosing and time. For this purpose we have to observe every minute change in each parameter and it effect on the process.

METHOD 1: Rising the PH from 8.7 to 11.3 of the waste water sample in beaker1 by using NaOH solution and give aeration for ammonia stripping (free stripping), as ammonia stripped its concentration in the waste water decreases and hence the PH value also decreases, note down the PH after every 1 hour period till its PH decrement goes slower down.

METHOD 2: Rising the PH from 8.7 to 11.3 of the waste water using NaOH solution and give aeration (free stripping) for one hour, note down the PH value and again rises the PH up to 11.3. Repeat the same procedure every hour until the PH decrement of each hour goes to slower down.

METHOD 3: Maintain the PH of waste water at the value of 11.3 by adding NaOH drop wise continuously in every 10 minute time duration and this was very short duration with respect to total aeration time in previous methods so we can assume it to be a continuous variation with time scale. Give aeration in same as in previous. It must remember that the dosing period is less than the aeration time for purpose of NaOH amount optimisation.

4.10. Ammonia Stripping:

NAOH spent for flocculation rises the PH to high values convert the ammonium ion to free ammonia in molecular form dissolve gas in appropriate condition desorbed from waste water and transferred to the air. Free molecular ammonia is transferred from liquid film to gas film at liquid air interface because of concentration gradient that is partial pressure difference between liquid film and gas film of ammonia.

In a waste stream, ammonium ions exist in equilibrium with ammonia.

1. Below pH 7, virtually all the ammonia will be soluble ammonia ions.
2. Above pH 12, virtually all the ammonia will be present as a dissolved gas.
3. The range between 7 and 12, both ammonium ions and dissolve gas exist together.
4. Percentage of dissolved gas increases with temperature and PH.

The parameter temperature, PH, aeration rate and surface turbulence favour removal of ammonia from solution.

After ammonia removed from the wastewater there are three possible methods of disposal.

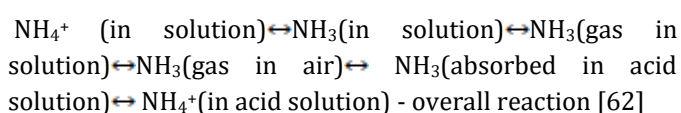
1. Air dispersal.
2. Concentration as ammonium sulphate or equal.
3. Thermal destruction.

The process of ammonia stripping is easier and less expensive to conduct when removing nitrogen from wastewater in the form of ammonia than converting the same to nitrate-nitrogen before removing it.

4.11. Ammonia Absorption:

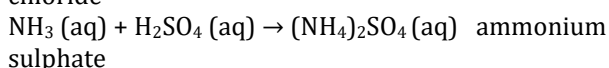
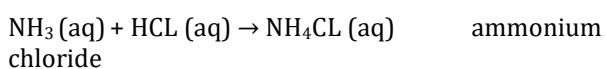
After that stripped ammonia with air is sent to the absorption beaker filled with aqueous H_2SO_4 for ammonia absorption. Stripped ammonia with air is freely aerated in aqueous sulphuric acid solution where ammonia reacts with sulphuric acid to form ammonium sulphate in beaker2. After absorption the outlet air is recycled again for stripping so that this is sent to the inlet of aeration pump1 of stripping beaker1. PH of beaker2 increases because of consumption of sulphuric acid in ammonium sulphate formation this increasing PH value retard the ammonia absorption so we have to send after an optimal increased value of PH the aqueous ammonium sulphate solution discharged through beaker2 and send to the evaporator for concentrating the aqueous ammonium sulphate. Then there are many possible ways out of them it used directly as base for fertiliser production or it may be crystallises to solid ammonium sulphate and the mother liquor is recycled to the absorption column.

Through the process of ammonia stripping and absorption the overall equilibrium reaction is given as



4.12 Ammonium Sulphates as N- Based Fertilizers:

Basicity is most important characteristic property of ammonia, ammonia considered as weak base. Ammonia reacts with acid to form salts; thus with HCL (Hydrochloric acid) it forms ammonium chloride, with nitric acid ammonium nitrate and with sulphuric acid it form ammonium sulphate [63]. Moisture present with ammonia gas is necessary for salt formation [64-65]. Reaction with HCL gives white precipitate which can observe easily. All salt produced with ammonia contain ammonium ion and known as ammonium salts. Reaction takes place with HCL and H_2SO_4



Detection of ammonia and ammonium salt is done by addition of Nesler's reagent which gives yellow colouration in the presence of even small amount of ammonia or ammonium salt [64]. According to U.S. Geological Survey, Reston, Virginia (2016) approximately 88% (as of 2014) of ammonia is used as fertilisers as its salts, solution and anhydrously [66]. N- Based fertilisers are used to improve yield of crop such as maize and wheat, 30% of nitrogen used as agricultural nitrogen in USA. Soil nutrient's required mainly three minerals which are NPK (Nitrogen, Phosphorus and Potassium) and out of them maximum N- based fertilizers production is done by using ammonia as raw material.

4.13. Safety, Precautions and Air Pollution Aspects:

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 [67]. 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

Table no 4 ammonia discharge limit

References for table no 4, [68-71].

Sulphur sticks are burnt to detect ammonia even for concentration and larger quantities can be detected by warming the salts with a caustic alkali or with quicklime characteristics smell of ammonia appears [65]. Ammonia gas is so much toxic in nature and creates noise pollution also due to its pungent smell. Air releases after complete stripping and absorption process contains some minimum amount of ammonia and this is the major concern of environmental health, hazardous and safety aspects. Previous studies and data were shown the maximum allowable limit of ammonia concentration in discharged air of process is $25mg/m^3$ [67]. This may cause adverse effect on eyes, nose and throat irritations (300 to $500 mg/m^3$) [45, 74] and nearby environment effected badly by air pollution so it must be treated or washout with highly absorbing solvent like boric acid or phosphoric acid before discharging to environment. Use mask, gloves, eye glass and other safety equipment's during experimental performance.

4.14. Uses of Washer and Regenerator:

Generally they are not performed at laboratory scale but they highly influenced the process efficiency and environment pollution. Atmospheric air contains CO₂ absorbed in waste water at high PH and reacts with hydroxide to form carbonates and this reaction favours by high PH. also ammonia is base and reacts with CO₂ to form ammonium carbonate this re-carbonisation process of effluents running parallel with ammonia stripping process and competed with ammonia stripping process and slowing the stripping rate by gradually reducing the PH by converting the hydroxide and ammonia to carbonates. The re-carbonisation rate increases in winter due to low temperature during winter which favours the CO₂ absorption. So intake air must be washed with KOH solution before inlet to the process. And KOH solution re-generated by application of heat and recycled to the washer. Similarly after stripping air contain some unabsorbed ammonia which is major concern of air pollution. This outlet air wash with some highly ammonia absorbing solution like boric acid or phosphoric acid to purify the air discharged to atmosphere. This acid solution re-generated by application of heat and the absorbed ammonia recycled to ammonia absorption beaker.

5 RESULTS AND DISCUSSIONS:

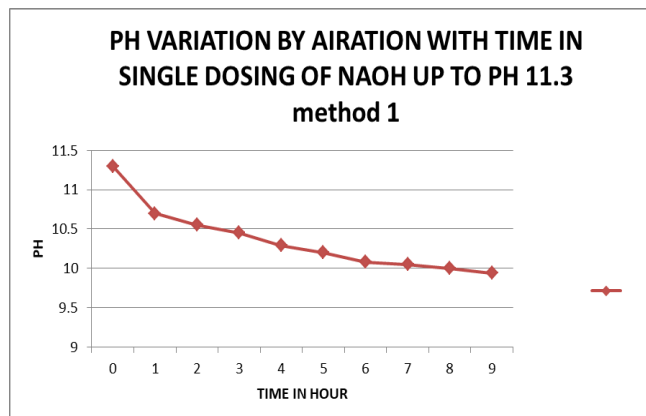
5.1» PH (A DRIVING PARAMETER) VARIATION IN DIFFERENT METHODS:

Table no 5: (PH data obtained by method 1 and method 2)

Solution PH made 11.3 once only by NaOH dosing method 1			Solution maintained at PH 11.3 each hour by adding 6N NaOH solution dosing method 2		
Time in hour	PH measured per hr.	PH Decrement	PH measured per hr.	PH increases to 11.3	PH decrement each hour
0 hr	11.3		11.3	-	
1 hr.	10.75	0.55	10.75	11.3	0.55
2 hr.	10.55	0.20	11.10	11.3	0.20
3 hr.	10.38	0.17	10.93	11.3	0.37
4 hr.	10.29	0.09	11.02	11.3	0.28
5 hr.	10.20	0.09	10.90	11.3	0.40
6 hr.	10.08	0.12	10.97	11.3	0.33
7 hr.	10.05	0.03	10.99	11.3	0.31
8 hr.	10.00	0.05	11.16	11.3	0.23
9 hr.	9.94	0.06	11.20	11.3	0.10

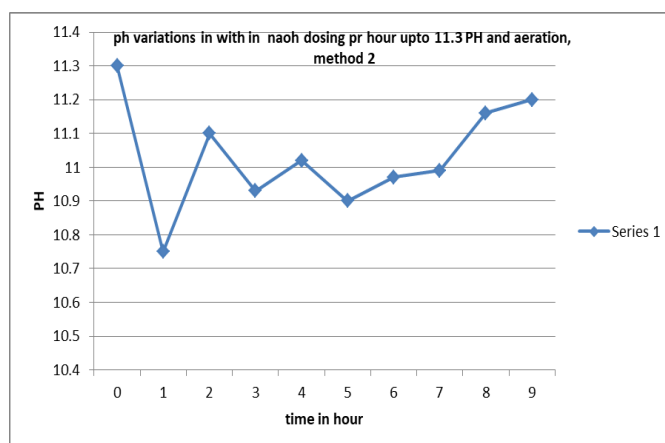
On analysing the PH data from table 5 it of method2 it is clear that after maintaining PH at 11.3 each hr. stripping rate get accelerated by high PH value. And for same % of ammonia reduction as of method1 it requires less aeration time then method one.

Graph 1: Graphical representation of PH vs time data obtained in method1.



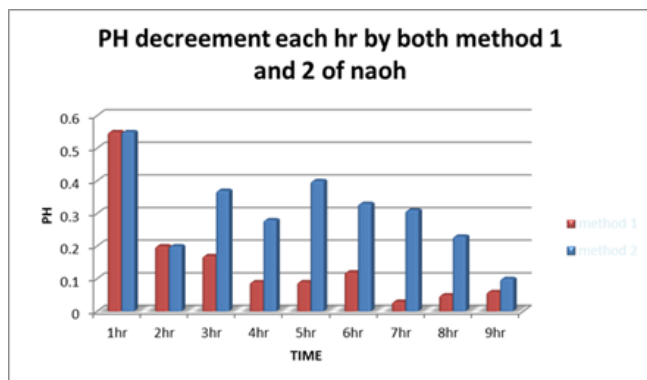
On analysing the above data given in table 5 in method 1 the PH decreases sharply in first hour and then PH decrement of each hour is slower down. Basically it shows the PH dependency of ammonia stripping. Initially stripping rate is faster because of high PH step by step as ammonia releases from waste water its PH value decreases and hence the stripping rate decreases. Graph 1 show that the PH changing rate is slower down and it is directly proportional to stripping rate so the stripping rate also decreases. Then the aeration time of 6 hr for method1 is taken as optimum time.

Graph 2 graphical representations of pH vs. time data obtained in method2.

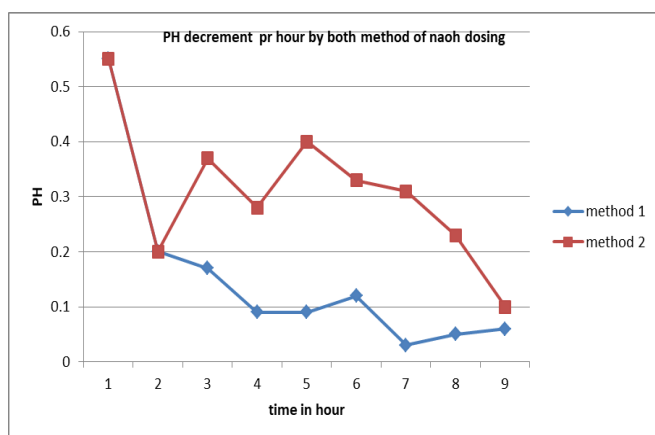


Graph 2 shows much decrement observed in first three hour from reference value of 11.3. And after 5 hour decrement slows down that means stripping rate slows down. But for comparison with method 1 we take 6 hr as aeration time.

Graph 3:pH decrement per hour by both methods



Graph 4 pH decrement



On observing graph 3 & 4 the variations of PH decrement by both methods get slows down after 6 hour of aeration period so it was taken as aeration time of stripping for method1 and method2.

After all it concluded that stripping rate is mainly influenced by PH value so it must be maintained at 11.3 so as to driving force for ammonia stripping (PH) is not decreases and stripping rate continues till to equilibrium value of ammonia concentration in waste water. And also much less time of aeration is required for same % of ammonia stripping. For comparison we take 4 hr as aeration time for method1. After that final tests for ammonia concentration were taken.

5.2» FINAL TESTS FOR AMMONIA:

Finally after stripping at many stage tests for COD and ammonia concentration are taken by using standard method APHA 4500-NH₃ C [56] for ammonia and standard method APHA 5220 B (open reflux method) for COD. Initial ammonia concentration is 5712 mg/L [57].

Final COD measured is 27000mg/L.

TABLE 6: Ammonia reduction by various aeration methods

Aeration condition/aeration time	Ammonia concentration Mg/L	% reduction
At PH 9.7/6hr	2925	48.79
At PH 10.7/6hr	1111	80.54
At PH 11.3 method1/6hr	602	89.46
At PH 11.3 method2/6hr	406	92.89
At PH 11.3 method3 /6hr	308	94.60

5.3» PROCESS KINETICS:

Process follows first order kinetics and its equation for first order plug –flow type if aeration beaker chosen is cylindrical in shape is given as

$$\ln \frac{C}{C_0} = -kt$$

Where C₀=initial concentration

C= concentration at time t

K= reaction rate constant (function of temp, PH, and aeration rate)

Here different PH conditions provided in 3 different methods and calculating reaction rate constants for all three methods. Rate of displacement of weak base ammonia by strong base NaOH is equal to rate of mass transfer of ammonia from beaker by stripping so that we are using reaction term.

C₀= 5712 mg/L

C₁ = 602 mg/L by method 1 and t₁ = 6 hr.

K₁= 0.375011 hr.⁻¹

C₂=406 mg/L by method 2 and t₂ = 6 hr.

K₂= 0.44066 hr.⁻¹

C₃= 308 by method 3 and t₃ = 4 hr.

K₃ = 0.730056 hr.⁻¹

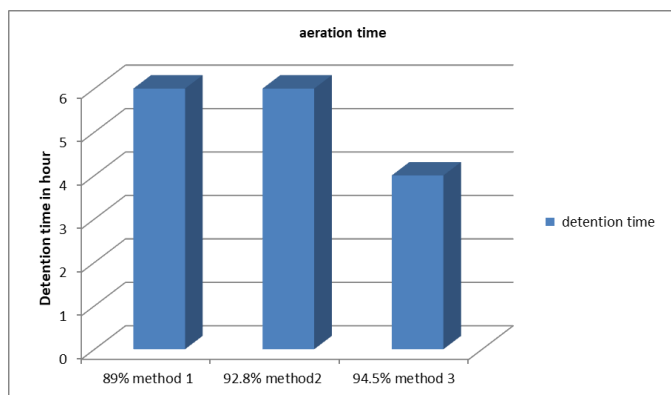
Method3 have highest reaction rate constant.

5.4» EFFECT OF pH ON AERATION TIME:

As PH increase ammonium ion decreases whereas free molecular ammonia increases so ammonia stripping increases. As PH increases rate of stripping increases and hence the aeration time decreases in table no. 7 we observe that ammonia concentration decreases as PH increases. At same PH 11.3 method3 take least time of aeration and give highest ammonia reduction in waste water. Graph 5 shows

the detention time comparison of all three methods with % of ammonia reduction.

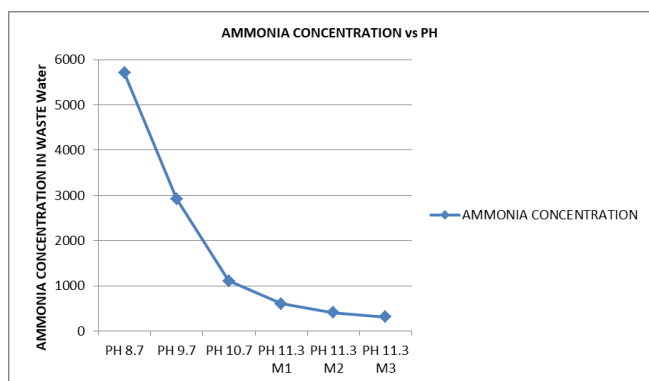
GRAPH 5: detention time vs. methods



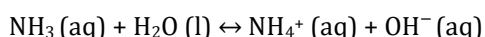
5.5» EFFECT OF PH ON AMMONIA CONCENTRATION WASTE WATER SOLUTION:

$NH_3(aq) + H_2O(l) \leftrightarrow NH_4^+(aq) + OH^-(aq)$
 Reaction equilibrium highly depends on PH and temperature. Ammonia exists in basic medium as free ammonia molecule which was stripped with air. Because the conversion of ionic ammonia to molecular ammonia favours high PH and gaseous form is the prerequisite of ammonia stripping an alkaline medium is required. Graph 6 shows how fast ammonia concentration decreases on increasing PH value at 8.7 it was 5712 mg/L and reduces to 2925mg/L at PH 9.7, 1111mg/L at PH 10.7 and directly to 602mg/L.

GRAPH 6: ammonia concentration vs pH



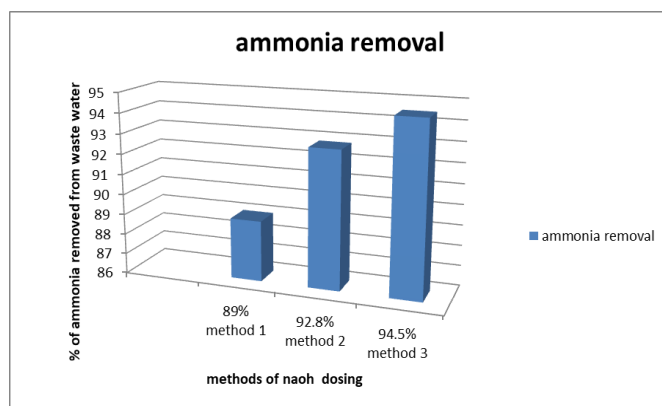
5.6» EFFECT OF NaOH DOSING ON AMMONIA CONCENTRATION:



As ammonia dosing increases reaction equilibrium shifted in backward direction. NaOH is strong base and ammonia is weak base so displacement reaction take place, NaOH produces hydroxide ion in its equivalent concentration and this hydroxide ion shifted back the above reaction. Now the

free molecular ammonia concentration increases hence the stripping rate increases in method1 the stripping rate decreases because but in case of method3 due to continuous dosing stripping rate is higher than both 2 method also method3 required large amount of NaOH for that the continuous dosing period is taken to be less than aeration period. Graph 7 compare the % of ammonia removal ammonia by all three methods.

GRAPH 7:Ammonia Removal in Methods



5.7» AMMONIA AND COD REMOVAL EFFICIENCY:

After analysing the whole procedure method3 results the best ammonia reduction of 94.5% ammonia reduction in 4hr aeration and 35.7% of COD reduction. At different PH give different efficiency at PH 9.7 give 48.79%, at PH 10.7 give 80.54%, at PH 11.3 m1 give 89.46%, at PH 11.3 m2 give 92.89 and at PH m3 give 94.60% of ammonia reduction

5.8» SCALING PROBLEM:

The ammonia stripping process required high PH value and for that much amount of NaOH is needed and this NaOH combined with CO₂ to form sodium carbonate causing scaling problem. Also paint and pigment industrial waste water having Organic-N based impurities which also causes scaling problems.

5.9» FOAMING PROBLEM:

presence of aniline during aeration much amount of aniline fumes of dark red colour are formed causing foaming problem so anti foaming agent is required.

5.10»ACIDIC CHARACTER OF RECYCLED AIR FROM ABSORBER:

Air recycled between absorber and stripper. Here air comes from sulphuric acid solution after absorption is of acidic character and cause small decreases in PH of stripping beaker but it does not affect the treatment efficiency because ammonia combines with sulphuric acid to form ammonium

sulphate and ammonium sulphate used in chemical treatment of waste water so it is helpful in coagulation of waste water.

6. CONCLUSIONS:

Free stripping of ammonia from paint and pigment manufacturing industrial waste water during chemical stabilisation process at high PH is low cost ammonia recovery and waste water treatment step. Ammonia recovery process reduces the cost of waste water treatment by sales of recovered ammonia based fertiliser as well as it reduces the chemical consumption in COD reduction step of waste water treatment. The treatment process cost reduced by both reduction in chemical consumptions and recovered ammonia. PH was the main measurable stripping rate driving parameter.

Initial measurements shows the value of COD was 42000 mg/L and the value of ammonia was 5712 mg/L, after stripping the value of COD become 27000 mg/L and the value of ammonia by method 3 which results highest ammonia reduction in lowest aeration period become 308 mg/L in waste water were measured. Treatment method 3 results in 35.7 % COD reduction and 94.6 % of ammonia reduction in 4 hour aeration period. And % of ammonia reduction by method 1 is 89% in 6 hour and by method 2 is 92.8% in 6 hour aeration period. Finally method 3 in which PH continuously maintained (but less than aeration period for NaOH amount optimisation) at 11.3 was found best way of stripping process. No air pollution problems occurred from ammonia stripping by air in closed air recycling system. And more than this the ammonia washing before it releases to the environment make the process free from air pollutant. Absorption of CO₂ in KOH from air before it is feed to the process reduced the re-carbonisation of hydroxide and hence reduced the extra consumption of NAOH required to maintain high PH value. KOH and BORRIC ACID/ PHOSPHORIC ACID are re-generated and cost of re-generation is very low because of low re-generation temperature in the range 70 to 90°C. COD decreases to 27000 and this deficiency remains because of presence of other dyes industrial waste composition which was further stabilised by Coagulation by Iron iii chloride and tertiary filtration. Also remaining ammonia was stabilised in this chemical stabilisation process and purified water reused in further plant operations but most significant ammonia reduction is done in stripping step and hence it is recovered. Ammonia and some organic compounds present in waste was removed in stripping step decreases the value of chemical oxygen demand for further stabilisation process and it was the most beneficial step in chemical consumption because low COD require less chemical amount in stabilisation process. Air recycled between absorber and stripper. Here air comes from sulphuric acid solution after absorption is of acidic character and cause small decrees in PH of stripping beaker but it does not affect the treatment efficiency because ammonia combines with sulphuric acid to

form ammonium sulphate and ammonium sulphate used in chemical treatment of waste water so it is helpful in coagulation of waste water.

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