Removal of Ammoniacal Nitrogen by using Albite, Activated Carbon and Resin

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Abstract— Ammonical Nitrogen in waste waters promote Eutrophication of receiving waters and are potentially toxic to the aquatic life. Albite, Sodium Cation Exchange Resin and Activated Carbons have shown an affinity for Ammonium ions (NH4+) and were, potentially used for the removal of NH4+ ions.The major objective of this study was to evaluate the capacity of albite, Sodium Cation Exchange Resin and Activated Carbon to remove Ammonical nitrogen from waste waters using Batch Studies. Several operating variables such as pH, Temperature, Initial Ammonium ion Concentration on the exchange capacity were explored. Batch Studies were conducted using different concentrations of ammonical nitrogen and different amounts of Zeolite, Sodium Cation Exchange Resin and Activated Carbons. This experimental approach of removing Ammonia from Synthetic Waste waters using Resin, natural Zeolite and Activated Carbon has been simulated for the study of Ammonia Removal from synthetic waste waters.

Index Terms— Ammonical nitrogen, air stripping,ion exchange,Zeolites, ammonium removal ,albite,activated carbon,resin

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1 INTRODUCTION

Water is generally known as an important necessity for all activities such as living consumption, industries agricultural and routinely human activities of drinking washing and bathing. Clean drinking water is essential to human and other living things. However, the sources of the clean drinking water are contaminated by chemical constituents (organics, inorganics and gases) and physical contaminants (colour, odour and solid).Inorganic pollutants such as ammonia-nitrogen are the main problems water treatment plants (WTPs).

The Presence of ammoniacal nitrogen in municipal, industrial and agricultural wastewaters   promotes eutrophication of receiving waters and is potentially toxic to fish and other aquatic life [1] [2]. When ammonia accumulates to toxic levels, fish cannot extract energy from feed efficiently. If the ammonia concentration becomes high enough, the fish will become lethargic and eventually fall into a coma and die. In properly managed fishponds, ammonia seldom accumulates to lethal concentrations. Of particular concern are the deleterious effects that inorganic forms of nitrogen (nitrate, ammonia, and nitrite) exert on human health. If nitrate is reduced to nitrite and ammonia by natural or artificial processes, it poses a serious public health threat, especially for very young infants [3]

For drinking water, the USEPA has set the maximum contaminant level (MCL) at 1 mg NO_2–N/L. However, Indian current regulation shows the MCL at 1.5 mg NH_3-N/L. Nitrate and ammonia stimulates the excessive growth of algae and other unwanted aquatic plants. They also have harmful effects on aquatic wildlife directly through toxic effects or indirectly by oxygen depletion. Ammonia in water is either unionized ammonia (NH3) or the ammonium ion (NH4+). The relative proportion of the two forms in aqueous solutions is mainly affected by pH. Un-ionized ammonia is the more toxic form and predominates when pH is high [4]. Ammonium ion is relatively nontoxic and predominates when pH is low. In general, less than 10% of ammonia consists the toxic form when pH is <8. However, this proportion increases dramatically as pH increases

General chemical methods of ammonical nitrogen removal from waste water includes the following:

Air Stripping:

Air stripping is a full-scale technology in which volatile organics are partitioned from ground water by greatly increasing the surface area of the contaminated water exposed to air.Air stripping involves the mass transfer of volatile contaminants from water to air. For ground water remediation, this process is typically conducted in a packed tower or an aeration tank. The typical packed tower air stripper includes a spray nozzle at the top of the tower to distribute contaminated water over the packing in the column, a fan to force air countercurrent to the water flow, and a sump at the bottom of the tower to collect decontaminated water.

In waste water, either ammonium ions, NH_4^+, dissolved ammonia, or both may be present. The pH dependency unfurls that at pH = 7 only ammonium ions may be present in true solution. At pH = 12 only dissolved ammonia gas is present, and this gas can be liberated from waste water under proper conditions. The equilibrium is represented by the equation shown here below. As the pH is increased above 7.0, the reaction proceeds to the right.
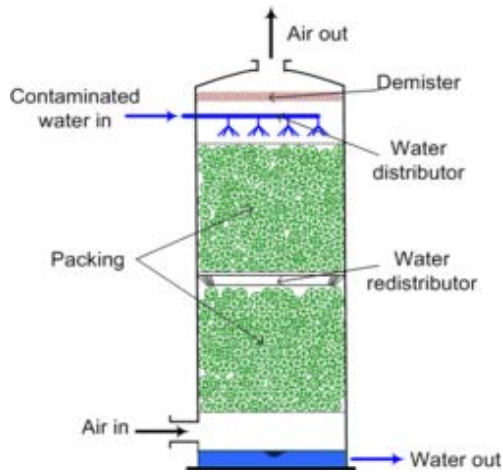
Fig 1.1: Air Stripping Process

Two major factors affect the rate of transfer of ammonia gas from water to the atmosphere are the surface tension at the air water interface, and Difference in concentration of ammonia in the water and the air. The ammonia stripping process then consists of (1) raising the pH of the water to the values in the range of 10.8 – 11.5 (2) formation and reformation of water droplets in a stripping tower, and (3) using air water contact and droplet agitation by circulation of large quantities of air through the tower.

Break Point Chlorination:

Breakpoint chlorination is the point where the demand for chlorine has been fully satisfied in terms of chlorine addition to water. Breakpoint chlorination consists of a continual addition of chlorine to the water upto the point where the chlorine enquiry is met and all present ammonia is oxidized, so that only free chlorine remains. This is usually applied for disinfection, but it also has other benefits, such as smell and taste control. In order to reach the breakpoint, a super chlorination is applied. To achieve this, one uses chlorine concentrations which largely exceed the 1 mg/L concentration required for disinfection." All Chlorine reacts with any organic materials present until they are destroyed. Chlorine then reacts with amino acids or urea. These compounds come from proteins or from urine in pool water. The products of this reaction are called chloramines.

If more chlorine is added the chloramines are themselves broken down until there is nothing left to react. At this point chlorine begins to appear as 'free chlorine residual'. This point is termed 'breakpoint.Waters containing nitrogenous material, such as milk wastes or sewage effluents, yielded pronounced "break-point" curves, whereas waters deficient in these forms of pollution and substantially free of ammonia-nitrogen, seldom produced a typical "break-point" curve upon chlorination.
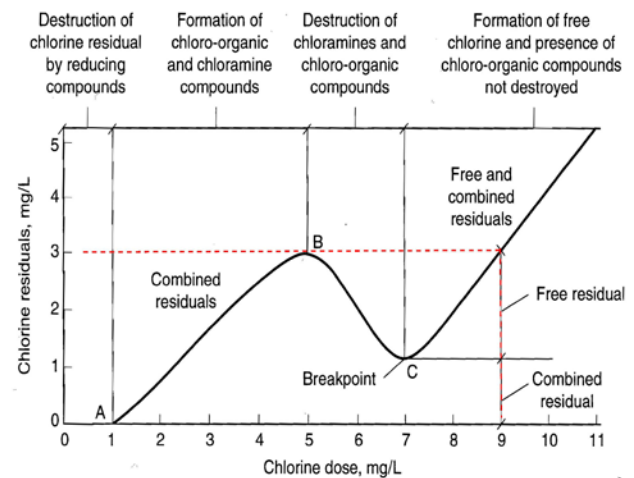

Fig 1.2: Break Point Chlorination

Chemical Precipitation:

In Chemical Precipitation, supernatant of an aerobically digested activated sludge was used as the substrate with the aim of phosphorous and nitrogen removal. During the precipitation process of ammonium and phosphate ions with magnesium sulfate usually results the magnesium ammonium phosphate (MAP). MAP is a white inorganic crystalline compound which can be used as fertilizer. The crystallization process depends on multiple parameters such as: concentrations of phosphate, ammonium and magnesium, pH value, ionic strength of solutions, N/P ratio

Steam Stripping:

Wastewater is fed in to the Stripper and heated up by the steam. The NH_3-rich steam was discharged from this stripper and transferred to the Steam Compressor. The steam generated was reheated by the compressor and used as the heat source for the wastewater at the re-boiler.After heat exchange at the re-boiler, NH_3-rich steam was fed to NH_3 Catalytic Converter and decomposed into nitrogen and steam. NOx is produced in NH_3 catalytic reaction as by-product and decomposed in De-NOx Reactor. Gas after the catalytic reactions contained the small amount of the leak NH_3 which was cooled and scrubbed before the release to the atmosphere .

Ion Exchange with Zeolite:

The traditional method for removal of ammonia and organic pollutants from wastewater is biological treatment, but ion exchange offers a number of advantages including the ability to handle shock loadings and the ability to operate over a wider range of temperatures. The ion exchange method usually employs organic resins, which are very selective. However, they are very expensive.

The discovery of natural Zeolite deposits has lead to an increasing use of these minerals for the purpose of eliminating, or at least reducing, many long standing pollution problems. Both natural and synthetic Zeolites have shown their ability for removing several cations from solutions concerning adsorption and ion

exchange features In order to comply with the increasingly strict limits being placed on ammonia levels in sewage discharged into receiving waters, a high-rate ammonia removal process was needed.

Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents .They are known to have an affinity for ammonium (NH_4^+) and other cations and possess a unique framework[14].. Overseas studies have established that zeolites have the potential to remove NH_4^+ from municipal, industrial, and aqua cultural wastewaters. The capacity of zeolites to remove NH_4^+ from wastewaters has been found to vary, depending on the type of zeolite used, zeolite particle size, and wastewater anion-cation composition .

The main features of Zeolites are high level of ion exchange capacity, adsorption, porous structure, molecular sieve, dehydration and rehydration, low density and silica compounds. However, the structural characteristics (e.g., porosity, density, and channel length) and the composition and exchangeability of Ca, Na, K, and Mg cations in Zeolites, amongst other factors (e.g., zeolite particle size and zeolite concentration in the host rocks) are also known to influence zeolite capacity to remove NH_4 from wastewaters. Clearly, the NH_4 removal capacities and performance of Zeolites cannot be predicted by a single zeolite chemical-physical parameter.

Natural zeolites have a strong capacity to remove NH_4^+ from pond discharges; they may be used at the end of a two-pond system or within an oxidation pond-constructed wetland sequence as a filtering bed. Even in farms where land application is a preferred alternative to a two pond system, zeolites play a useful role as an absorbing medium for NH_4. In these farms, wastewaters are initially passed through zeolite beds before being applied to soils (particularly soils with a low nitrate retention capacity) to minimize the risk of groundwater nitrate pollution (by absorption of applied ammonical N in Zeolites, thus minimizing its nitrification to nitrate for leaching and to reduce the agricultural area required for land application of wastewaters.

For Zeolites, the pore diameters vary from around 0.45 to 0.6 nm, and these pores dictate the size of ions that enter the Zeolite pores and undergo ion exchange. The effective pore size of the crystal lattice comprises channels of two different sizes, and each type may display a different selectivity behavior for certain cations. Barrer et al. claimed that the separate ion sieve effects of the two kinds of channel or pore size in the Zeolite, and the free dimensions of these channels, allow a cation of a particular size to access none, one, or both of the channels for exchange. Hence the degree of exchange is specific for each Zeolite with each cation in solution [5]The present work considers the Ammonia removal from Synthetic Waste waters using Resin, natural Zeolite and Activated Carbon.

2.0 MATERIALS
All the glassware used in the present study was Pyrex Quality, Manufactured by borosil Glassware Ltd, Mumbai. Distilled water was used throughout experiments in the laboratory, with pH 7.0-7.2.Analytical Reagent grade chemicals were used in the present study.Reagents were prepared from Analytical Grade Chemicals, using double Distilled Water.
Albite ($NaAlSi_3O_8$) which is a natural zeolite, activated carbon and resin are the three adsorbents of ammoniacal nitrogen on

which the batch experiments are conducted to evaluate the maximum ammonia uptake by the adsorbent.

2.1EQUIPMENTS
The instruments used for carrying out the present study included digital pH meters (HACH) for pH measurements and conductivity meters (HACH), UV-VISIBLE spectrophotometer (Analytic JENA SPEKOL 2000), Shaker (LSI-2005RLN), Kjeldahl Instrument (KPS 020).

2.2 Water Source:
Ammonia Stock Solution: Dissolve 2.969gms of NH_4Cl(ammonical nitrogen) in 1000ml of distilled water to give 1000mg/l stock solution. From the Stock Solution, 100 mg/l and 200 mg/l of Standard concentrations are prepared for the batch experiments

Synthetic waste water:
The synthetic source of water for Ammonia Removal was prepared in the Waste Water Treatment Laboratory. Synthetic waste water was prepared by adding the below mentioned chemicals in required amounts (table 2.2) and was diluted to 1000ml with distilled water. Synthetic waste water samples were prepared by diluting appropriate amounts of ammonium chloride stock solution to distilled water.

The composition of synthetic waste water is peptone - 0.1225, Beef Extract - 0.0805, Urea - 0.1475, Sodium Chloride - 0.059, Calcium Chloride - 0.059, Potassium chloride - 0.12, Magnesium sulphate heptahydrate - 0.035, Dipotassium hydrogen phosphate - 0.09.

3.0 METHODOLOGY

Analytical Methods

Monitoring of pH:
During the adsorption batch studies of Ammonia Removal, the pH of the Synthetic Sample was adjusted by adding HCL or NAOH.

Monitoring of Temperature:
Temperature was monitored between 28-35^{0}C for the adsorption of Ammonia onto the albite ,activated carbon and resin

Monitoring of RPM (Rotations Per Minute):
In order to provide proper mixing of the known concentrations of ammonia with the albite,activated carbon and resin, the samples were placed in a shaker and the RPM was maintained between 145-150.All these monitoring processes were done by following by using standard methods for the Examination of water and Wastewater[6]

Adsorption studies
Adsorption of ammonia was calculated by titrating it against 0.02 N H_2SO_4.The instruments used for measuring different parameters are magnetic stirrer, electric balance, pH meter, stopwatch, electric furnace, thermometer and sieves. Adsorption measurements were carried out via a batch technique at room temperature (30 ± 3 °C), Accordingly 100 ml of ammonia solution of 100 mg/l and 200 mg/l concentrations were shaken on orbital shaker with 0.5 g and1.0g of dry albite zeolite ,dry activated carbon and resin at 150 rpm in 250 ml conical flask for a given time period of 60 min (range-0min, 10min, 20min,30min, 40min,50min, 60min). The solution was then filtered through Whatman filter paper No. 42 (circular, 14.0 cm). The first 2-3 ml portions of the filtrate were rejected because of adsorption of ammonia on the

filter paper. The concentration of ammonia was determined by using the kjeldahl method. The percentage adsorption was calculated also calculated simultaneously.

4.0 RESULTS
Effect of pH
Apparent Ammonium ions removal was positively increased with increasing pH from 8.9 to10.8, while no further significant removal rate was increased at pH 11.9. This result explains the fact that a small fraction of Ammonia also has an effect for a change in the pH.Waste water solutions containing Ammonia with pH 9.5 described in the experimental section has shown best results for Ammonia Removal.

Effect of contact time
The removal rate of Ammonium in the sample was high in the initial 5minutes, but thereafter the rate significantly levels off after 1 hour. This change in the rate of removal was due to the fact that initially all adsorbent sites were vacant and the Ammonia uptake was high. Afterwards, the Ammonium uptake rate by the Albite, Resin and Activated Carbon decreased significantly, due to the decrease in the adsorbent sites.

Effect of Temperature
Initially, the temperature was $27^{o}C$ and with increase in temperature there was an apparent increase in the Ammonia removal rate. This apparent increase in the thermal activation enhances the selectivity of Resin, Albite and Activated Carbon for the Ammonium Ions.

Effect of quantity of the adsorbent:
It has been observed from the results that percent removal of ammonia increases with increasing amount of the adsorbent. This is due the greater availability of the active sites or surface area, when the adsorbent quantity is increased. Although 0.5gm,1.0 gm dose of adsorbent shows ammonia removal more than 89% but it may be concluded that by increasing the adsorbent dose, the removal efficiency (%) beyond a dose of one gram adsorbent is not striking. Therefore, the value of 1.0 g of albite dose appears to be optimal, It is also evident that below a dose of one gram, the removal rate is exceptionally high. Beyond that, the percentage removal reaches almost a constant value. Very slow increase in removal of ammonia beyond an optimum dose may be attributed to the attainment of equilibrium between adsorbate and adsorbent at the operating conditions; giving it a distinct mark over other adsorbate.

Influence of Selectivity of Ammonium Ions for Adsorbents
The selectivity of Ammonium ions for adsorbents was purely based on the availability of vacant adsorption sites on its surface. This reason explains the total ion exchange capacity of Resin and Activated Carbon to that of Albite

3.6 Graphs showing the concentration of Ammonia versus time intervals by using 0.5gms, 1 gm of Resin, Zeolite and Activated Carbon by the adsorption studies conducted in three batches.
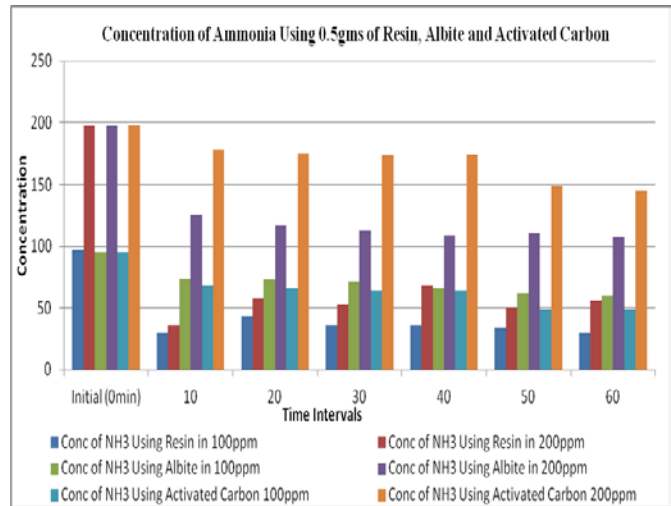**Batch-1**

Fig 3.6a indicates adsorption of Ammonia versus time intervals when 0.5gms of adsorbents are used
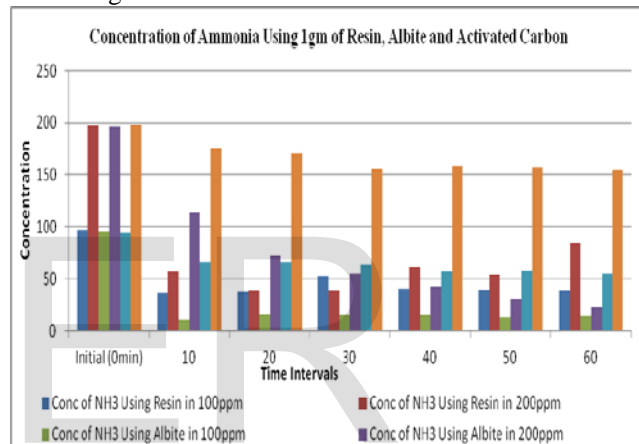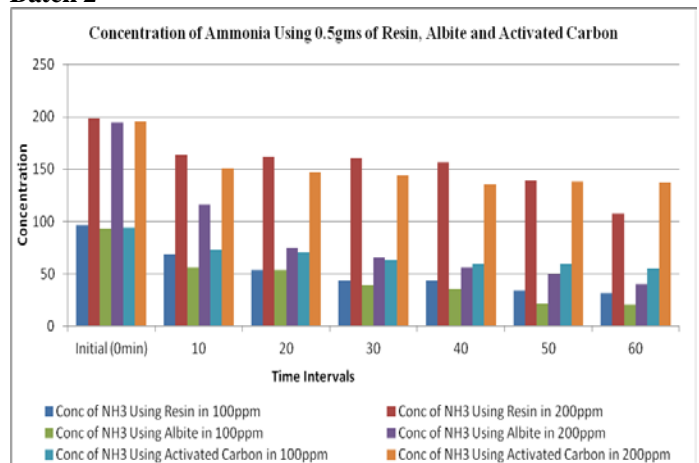

Fig 3.6b indicates adsorption of Ammonia versus time intervals when 1.0gm of adsorbents are used

Batch 2

Fig 3.6c indicates adsorption of Ammonia versus time intervals when 0.5gms of adsorbents are used
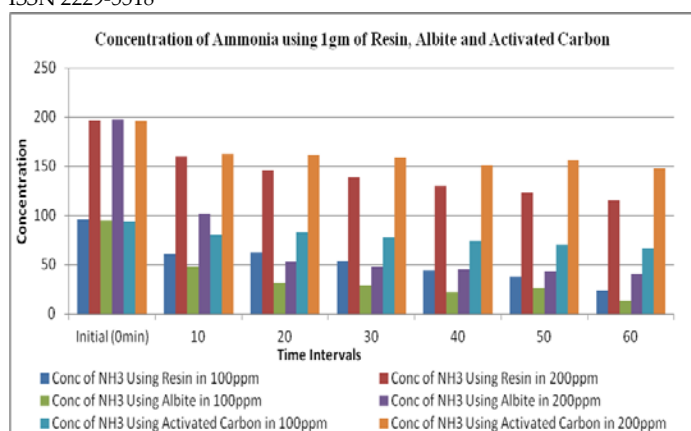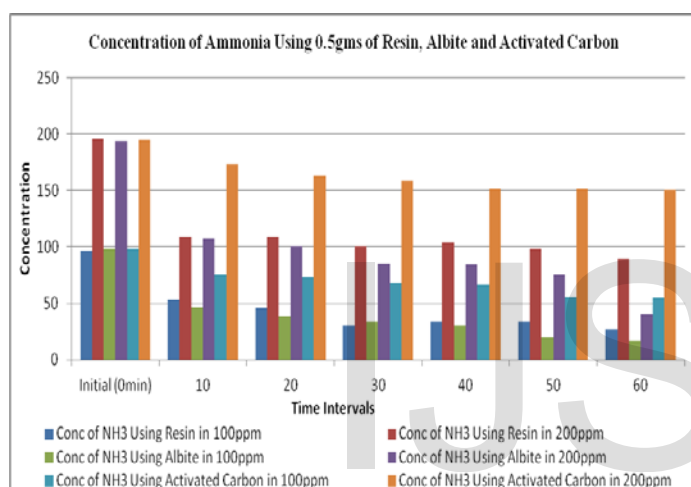
Fig 3.6d indicates adsorption of Ammonia versus time intervals when 1.0 gm of adsorbents are used

Batch 3

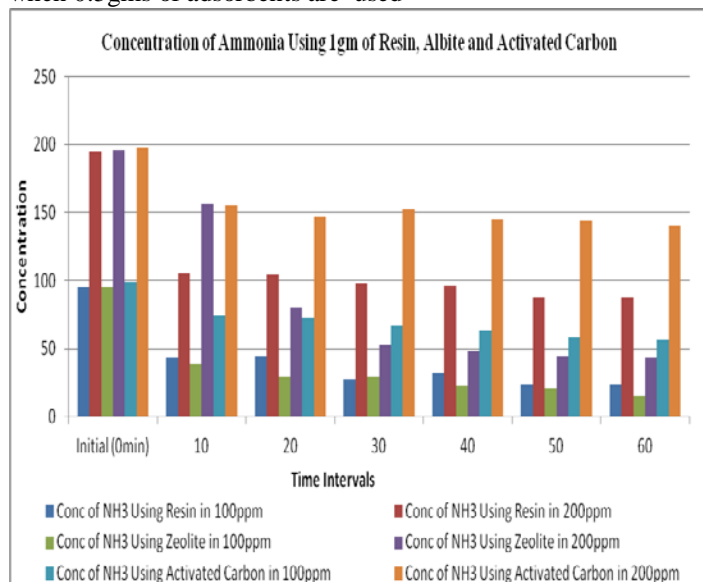Fig 3.6e indicates adsorption of Ammonia versus time intervals when 0.5gms of adsorbents are used

Fig 3.6f indicates adsorption of Ammonia versus time Intervals 1.0gm of adsorbents are used.

Effects of Adsorbate concentrations:

Fig.3.8a and 3.8b presents the effects of ammonia concentrations such as 100mg/l and 200 mg/l on the removal efficiency (%) of albite.activated carbon and resin.It is seen from the figure 3.8a and 3.8b that the removal of ammonia increases with the increase ammonia concentration. The removal efficiency of size fraction appears to be 89 % at ammonia concentration of 100 mg/l. It can be concluded that adsorption process is highly dependent on initial concentration of ammonia because at lower concentration, the ratio of the initial concentration of ammonia to the available surface area is low (concentration / surface area) and subsequently the fraction adsorption of ammonia increases. However, at higher concentration the availability of active sites for adsorption becomes less and hence the percentage removal of ammonia decreases.

Percentage of Ammonia Removal by adsorption studies:

Graph 3.8 a and 3.8 b shows that of the three adsorbents studied here, Albite (natural zeolite) has the highest capacity for ammonium ion. Resin shows the next to highest capacity. The lowest capacity is exhibited by
 activated carbon. Overall, Ammonia percentage removal ranged between the following levels for Resin it is 41-75%, Albite 77-88% and for Activated Carbon it is 21-46%.On the basis of these results, Albite (natural resin) was found to be an efficient adsorbent in the removal of ammonium ions from the synthetic waste water systems in batch adsorption studies.
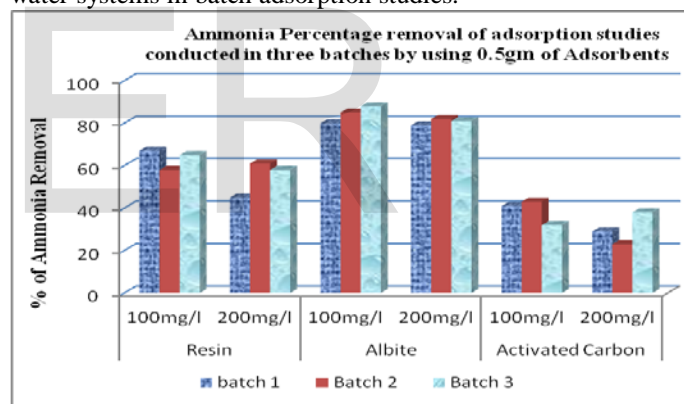

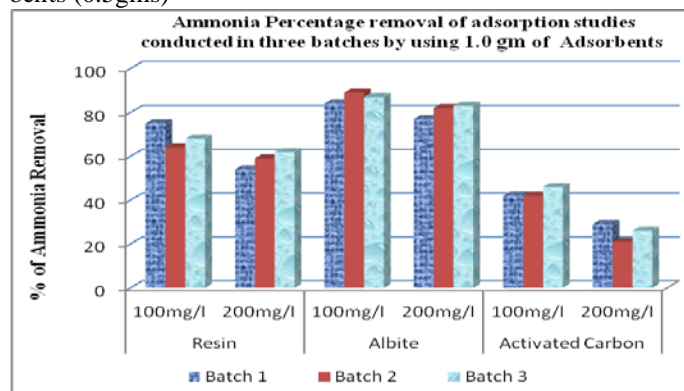Fig 3.8a graph showing the overall percentages of three adsorbents (0.5gms)

Fig 3.8b graph showing the overall percentages of three adsorbents (1.0gms)

5.0 CONCLUSION

The adsorption studies of Ammoniacal nitrogen from Synthetic Water were performed successfully with selective Ion-Exchange Process using Resin, Zeolites (Albite) and Activated Carbon. The Albite, activated carbon and resin were found to be equally effective at removing Ammonium ions from Ammonium Chloride Solutions containing 100mg/l and 200mg/l. However, in solutions containing higher Ammonium Concentrations, Albite was more effective than Resin and Activated Carbon. Batch studies of Ammonia Removal were found to be essential for the description of how Ammonium concentration interacts with the adsorbents. Adsorption of Ammonia by adsorbents (Resin, Albite and Activated carbon) was initially fast during 5-10 minutes depending upon the Initial Ammonium Concentration and then gradually decreased with increase in time.Vigorous shaking and a contact time of 60 minutes between Ammonium ions and Adsorbents in the batch experiments reduced the effect of particle size on Ammonia removal.The percentage of Ammonia Removal varied between different adsorbents depending upon the mass, chemical composition and surface area. The maximum ammonium ion concentration achieved in this study was 10.2 mg/lit corresponding to the removal efficiency of 88% using 1gm of Albite .

6.0ACKNOWLEDGMENTS

7.0REFERENCES

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