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RESEARCH ARTICLE

COMPARATIVE STUDY BETWEEN THE ELECTRODE CU/ZN, CU AND FE AS CATHODE FOR ELECTROCHEMICAL REDUCTION OF AMMONIA

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Abstract

The comparative study between electrodes as cathode for electrochemical reduction of ammonia from artificial and real wastewater was carried out with Ti/Iro2 as anode and Cu, Fe and Cu/Zn as cathode. We studies effect of different electrodes as cathode, the presence and absence of NaCl and the effect of temperature such as 20^0C, 30^0C and 40^0C on ammonia reduction from wastewater. It was shown after 30min treatment under optimal condition which were Cu/Zn with current density 18.32mA/cm2, space between electrode of 1.1 cm, the temperature of 40^0C and amount of 0.5g/l of NaCl the COD concentration in municipal wastewater was 185mg/l a removal of 38% and the total of NH3-N con centration have been removed. The kinetic study showed that current density (current passed used during experience per unit volume) is an appropriate design.

Introduction:-

The ammonium in the water usually means a process of incomplete degradation of organic matter. Ammonia is from the reaction of iron-containing minerals with nitrates. This is an excellent indicator of water pollution by organic waste from agricultural, domestic or industrial. They can promote eutrophication, which is fatal to aquatic life and an obstacle to the disinfection of water sources [1]. Ammonium is itself not toxic but can cause several problems such a decrease in the efficiency of the chlorine treatment and the development of microorganisms responsible for flavors and odors. The oxidation of ammonia giving nitrite, which can in turn, gives nitrates by oxidation 'cause nitrites are unstable in water. Nitrate can cause serious health problems in humans such as the "blue baby syndrome" in infants, liver damage and cancer [2, 3]. The main reason for the increase of nitrate in groundwater was mainly attributed to the abusive use of nitrogen fertilizer [4]. Properties such as high solubility, less capacity for precipitation and adsorption makes nitrate removal a difficult task. Thus electrochemical methods have been evaluated for this purpose [5], Cu, Fe, Zn, Pt/Ir, Au [6]. However some electrodes such as Cu and Fe were recognized more promoters for the nitrate electro reduction. The aim of this work was to find the best conditions to reduce the concentration of ammonia and anodic oxidation of the produced of ammonia.

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Experiment

Electrode

Ti/Iro2-Pt anode (made in japan with Tohotech Company) with dimension of 61.5cm^2 (15cm × 4.1cm) was used in this work. Iro_2 was used as electrode coating material because of its high oxidability and long service life, and Pt because it is a great conductor of electricity and electrical catalytic ability. A Cu/Zn, Fe and Cu plates with the size of 67.5cm^2, 70cm^2 and 75cm^2 respectively was used as cathode.

Method:-

As shown in Fig 1 the electrolytic cell was designed in acryl plastic on the scale laboratory. The synthetic (NH4Cl) solution with a NH3-N ammonium concentration of 50 mg/l and volume of 300 ml was prepared. 0.7g/l of Na2SO4 was added into the solution used through the experiment in order to enhance the conductivity. The space between electrodes was kept constant (1.1 cm) and the electrode was cleaned with sandpaper to remove impurities and toxic layer and rinsed with water. To study effect of sodium chloride dosage on the complete ammonium reduction, NaCl concentration of 0 to 0.5g/l (w/v) was added to the synthetic ammonium solution .Thermostatic bath shaker was used to set the temperature. All experiment is realized with stabilized current power supply with an effective voltage 0-50 V. and effective current of 0-50A.

Mechanism and Reactions

In the electrolytic, ammonia is eliminated with anodic electro-oxidation. Electro-oxidation of ammonia occurs in two ways:

- ammonia is oxidized directly by the surface of the anode through the electrode such as Ti/Iro2-Pt
- Indirectly with the assistance of a mediator oxidation such active chlorine Cl2, HOCl, or OCl- which are produced at the anode [7, 8] .In indirect oxidation chloride is oxidized to chlorine in the solution at the anode and immediately reacts with water to form hypochlorite (HOCl) [9]

$$2Cl \rightarrow Cl2 + 2e \qquad (1)$$

$$Cl2 + H_20 \rightarrow HOCl + H^+ + Cl^- \qquad (2)$$

Finally, ammonia is oxidized to nitrogen gas or nitrate through the electrochemically oxidants as hypochlorus acid and hypochlorite ion in the vicinity of the anode [10, 11]:

$$3NH4 + 3HClO \rightarrow N2 + 3H_2O + 5H^+ + Cl^- \qquad (3)$$

$$NH4 + 4HOCl \rightarrow N0_3^- + 6H^+ + 4Cl^- + H_20 \qquad (4)$$

Analysis

The concentration of NH_3-N in the solution was determined with titrimetric method, nitrate was determined by standard colorimetric method using spectrophotometer (DR/4000 U spectrophotometer USA), the nitrate-nitrogen concentration with the spectrophotometric method with phenol disulfonic acid and the nitrite-nitrogen concentration with the N-(l-naphthyl)-ethylene diamine spectrophotometer method [12].

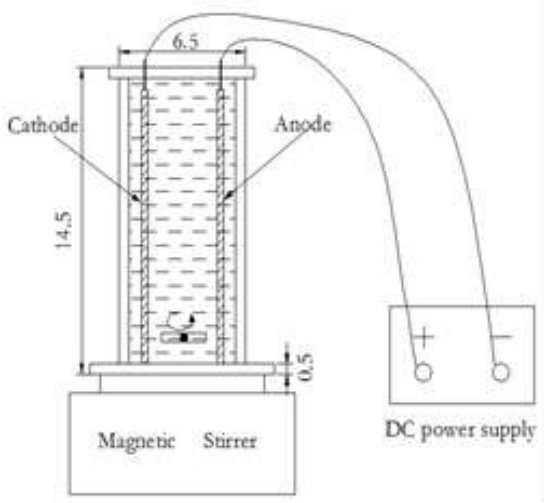

Figure 1:- Schematic of reactor system with two electrodes as anode and cathode all connected to Power supply.

Results and Discussion:-

Performance of removal of ammonia without NaCl

The reducing ammonia in the electrochemical cell is influenced by the electrode material.

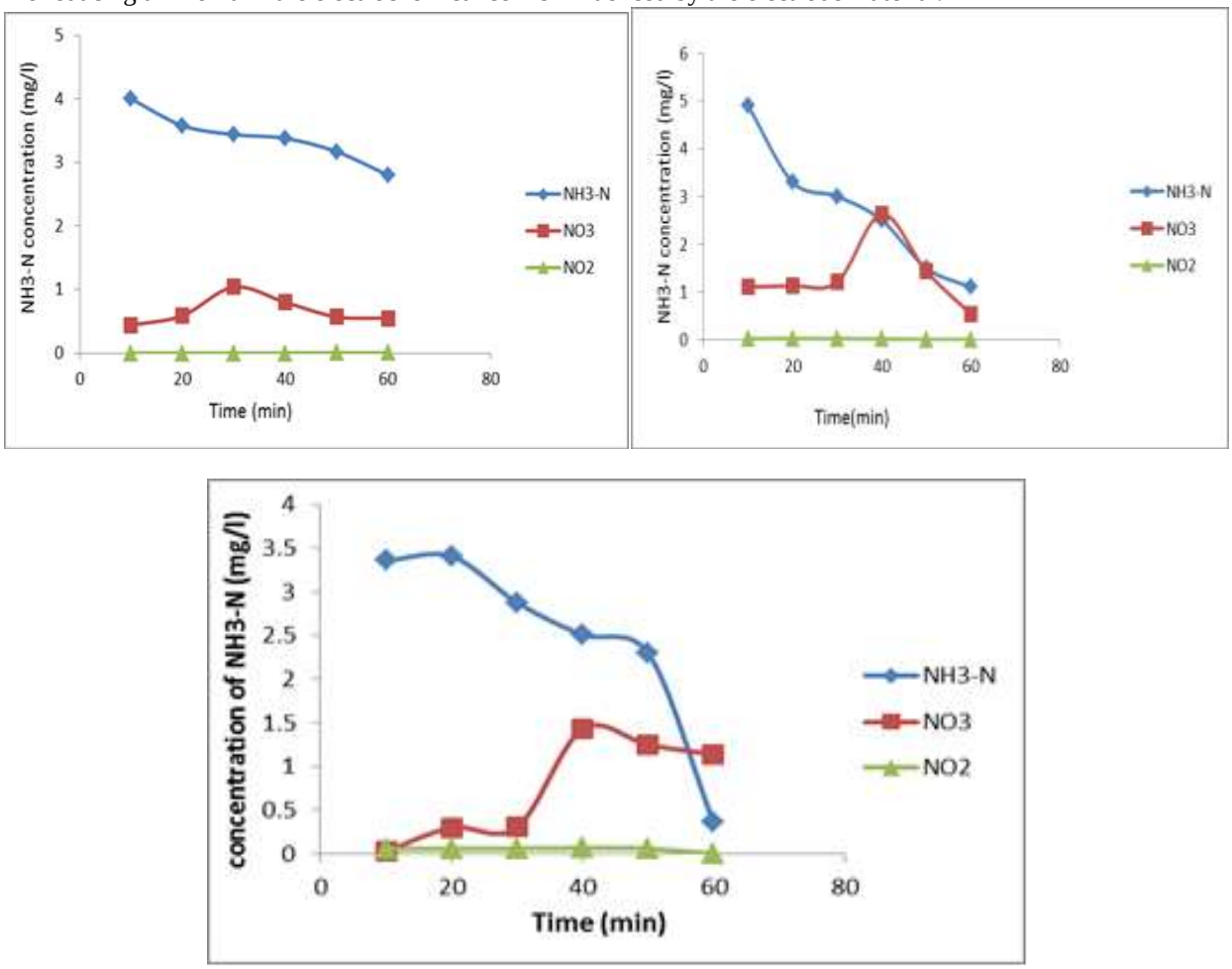

Figure 2:- Reduction of ammonia to nitrate without function of time NaCl (a, b, c) Cu, Fe and Cu/Zn Co=50 mg/l ; NaCl= 0 g/l ; pH= 5.1 ;18.38mA/cm2;D=1.1cm.

Cu cathode

[Fig.2 (a)] shows the removal of ammonia and formation of nitrite-N, nitrate-N during electrolysis by different cathode without NaCl. As seen in the figure the elimination of ammonium rate is 94.4% with the Cu electrode, whereas formation of nitrate as function of time was low, around 0.55mg/l. From previous studies indicate that copper generally has more negative potential, which inhibit the amount of hydrogen produced, and then disadvantage the removal of ammonium and formation of nitrate [13, 14]. The reason for this peak would be the oxidation/reduction Cu_2O to Cu [15]. That means less amount of evolution produce lead to the low selectivity of ammonia removal whereas has highest selectivity formation of nitrate than Fe.

Fe cathode

As seen in the [Fig.2 (b)] the removal of ammonia rate is 98.7% with the Fe electrode .The higher removal with iron electrode could be due to its greater ability to donate electrons. Nitrite - N is an intermediate product and can be oxidized to nitrate. The nitrite–N with Fe, Cu, detected was low. The reduction of ammonium to nitrate was relatively higher. At the beginning, the reaction evolved slowly during the first 30 minutes, due to the presence of ferrous ions which limits the reaction due to a low amount of oxygen dissolved in the solution .With the time precisely at 40 min ferrous compounds are oxidized at a rate higher enough to precipitate hydrated ferric hydroxide at high oxygen concentration as seen in figure1 (b) a sharply increased the formation of nitrate and favors removal of ammonia. The utilization of Ti/Iro2- Pt as anode considerably favors high removal rate of ammonium due to the

high oxidation ability. In the present experiment Fe cathode is more useful to the removal ammonium and reduction of nitrate than Cu electrode without NaCl.

Cu/Zn cathode

As shown in the [Fig. 2 (c)] the rate of ammonia removal increased significantly while the formation of nitrate increased too at the first time and finally decreased. The mechanism of electrolytic reduction of ammonia is complex. Without NaCl addition, the ammonia reduction and nitrate formation during electrolytic process can be attributed to the alloy Cu/Zn cathode which known for its good corrosion resistance, however Zinc has good electro activity while copper exhibit a good activity of electro reduction. As a result high efficiency for in the removal of ammonia is expected from the alloy Cu/Zn. As seen in the figure the removal rate of ammonia is 99.28%. According to the Yaning et al [16] the highest removal of ammonia was found to be better with Cu/Zn. The amount of nitrate obtained from ammonia reduction is 1.14 mg/l. From the result obtained, it can be concluded that Cu/Zn as cathode is more suitable than Fe, Cu in the absence of NaCl.

Performance removal of ammonia with NaCl

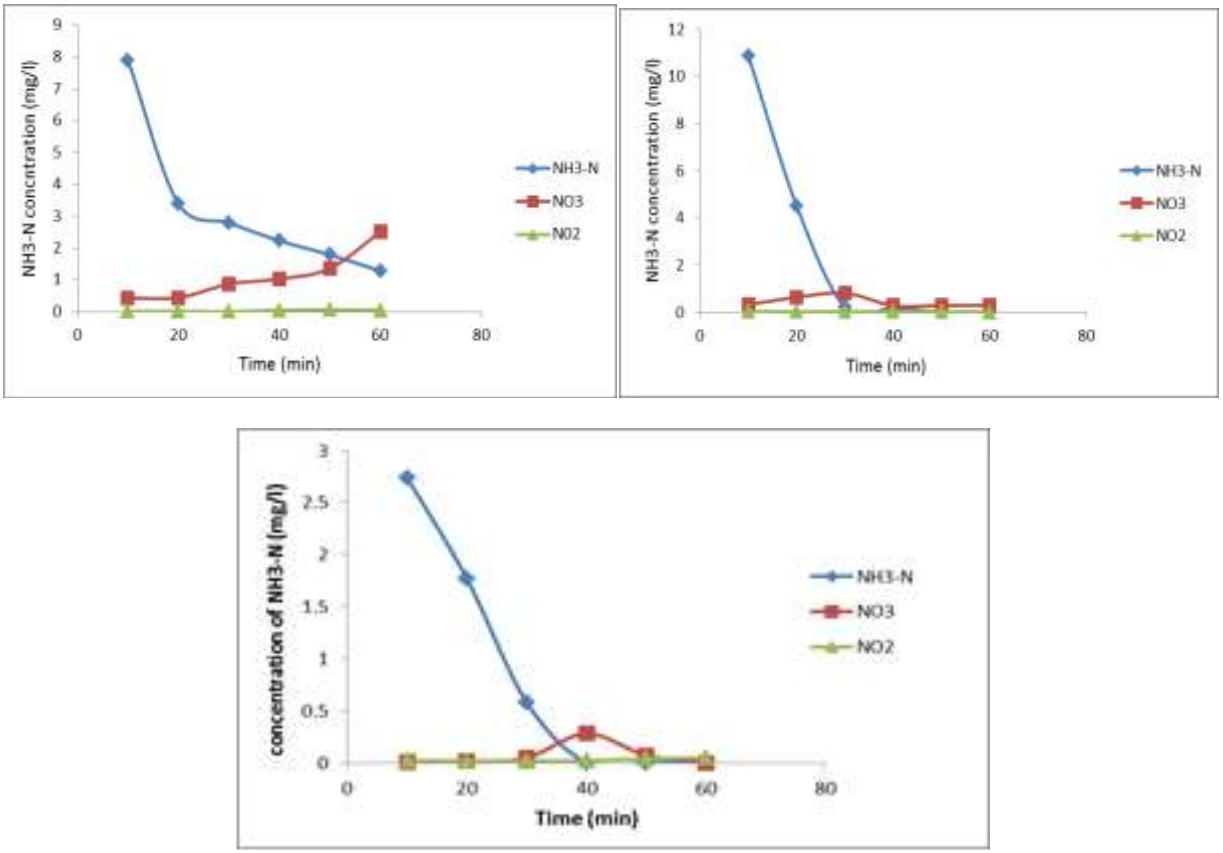

Figure 2:- Reduction of ammonia in the presence of NaCl (a, b, c) Cu, Fe and Cu/Zn Co=50 mg/l; NaCl= 0.5 g/l; pH= 5.1; 18.38mA/cm2; D=1.1cm.

Cu cathode

[Fig.3 (a)] shows the removal of the ammonia and formation of nitrite-N, nitrate-N during electrolysis with Cu as cathode in the presence of 0.5 g/l NaCl. Ammonia in the presence of 0.5g / l NaCl is removed to 97.44 percent in 60 min and a large amount of nitrate was formed 2.5mg/l. By comparing with results obtained by Fe cathode, the removal of ammonia is high than Cu cathode which was low whereas the quantity of nitrite and nitrate formed in presence of NaCl is higher with Cu electrode than Cu/Zn and Fe cathode. Probably, because Cu has good potential reduction. That is the reason why Miao Li et al [6] found the highest selectivity of nitrate reduction to nitrogen gas was better with Cu than Fe and Ti as cathode.

Fe cathode

[Fig.3 (b)] shows the removal of the ammonia and formation of nitrite-N, nitrate-N during electrolysis with a cathode of Fe in the presence of 0.5 g/l NaCl. Ammonium in the presence of 0.5g / l NaCl is totally removed in 50 min and nitrates up to 99.45% was observed. The electrolysis system that occurs is strong and fast. This is explained by the simultaneous attack of ammonia and the product of ammonium such as nitrite-N, nitrate-N with addition of NaCl. More ion hypochlorite was formed during electrolysis due to NaCl and the Ti/Iro2-Pt anode which has high oxidation ability. Also the fact that the iron is donating a large number of electrons which promotes the electrolysis system for removal of ammonia and nitrite-N, nitrate-N. [Fig.3 (a)] shows the removal of the ammonia and formation of nitrite-N, nitrate-N during electrolysis with Cu as cathode in the presence of 0.5 g/l NaCl. Ammonia in the presence of 0.5g / l NaCl is removed to 97.44 percent in 60 min and a large amount of nitrate was formed 2.5mg/l. By comparing with results obtained by Fe cathode, the removal of ammonia is high than Cu cathode which was low whereas the quantity of nitrite and nitrate formed in presence of NaCl is higher with Cu electrode than Cu/Zn and Fe cathode. Probably, because Cu has good potential reduction. That is the reason why (Miao Li et al, [6] found the highest selectivity of nitrate reduction to nitrogen gas was better with Cu than Fe and Ti as cathode.

Cu/Zn cathode

It is clear as shown in the fig3(c) that the ammonia removal rate greatly increased with the addition of NaCl. The removal of ammonia is 100% in 40 min. With the presence of chloride ion, the hypochlorite ion is formed and then faster oxide ammonia through presumed products such as nitrite and nitrate. Hence the important role played by the indirect oxidation during the electrochemical reduction of ammonia [17]

Performance removal with the effect of temperature

Cu cathode

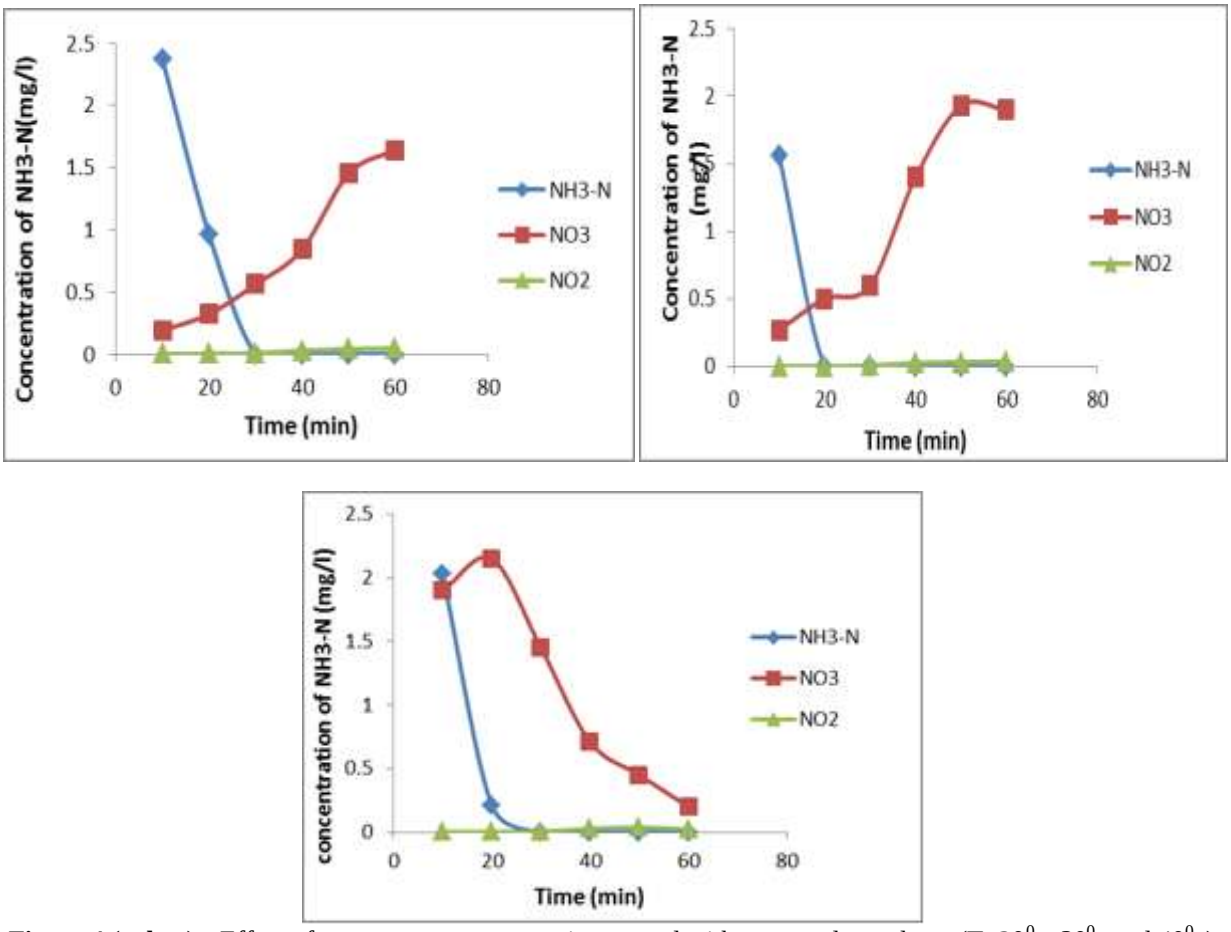

Figure 4 (a, b, c):- Effect of temperature on ammonia removal with copper electrode (T=20^0c, 30^0c and 40^0c) Co=50 mg/l; NaCl= 0.5 g/l; pH= 5.1; 18.38mA/cm^2

Cu cathode

It can be confirmed from [Fig.4 (a, b, c)] that increasing the temperature from 20^0C to 40^0C ammonia removal rate showed almost same results whereas the formation of nitrate increased as the temperature increased. The lowest ammonia removal rate was obtained with Cu, while that of Fe, and Cu/Zn cathode were the highest. This can be explained at the first by the fact the copper slowly dissolved in the ammonia solution containing oxygen. Secondly the previous studies have shown that the voltammetry study of cu would produce more negative potential and finally will make less evolution of hydrogen [13, 14]. That peak will be attributed to the oxidation/reduction of Cu2O to Cu species [15]. According to other results, Miao Li et al, [6] have also found that copper is less selective for the removal of ammonia. However a range of ammonia-products like nitrite and nitrate was formed during the electrolysis process. Nitrate formation from ammonia is 0.035, 2.05 and 1.27 with 200C, 300C and 400C respectively in 60 minutes. That why the low pH found. Low amount of nitrite was formed, that proved why they are intermediates products.

Fe cathode

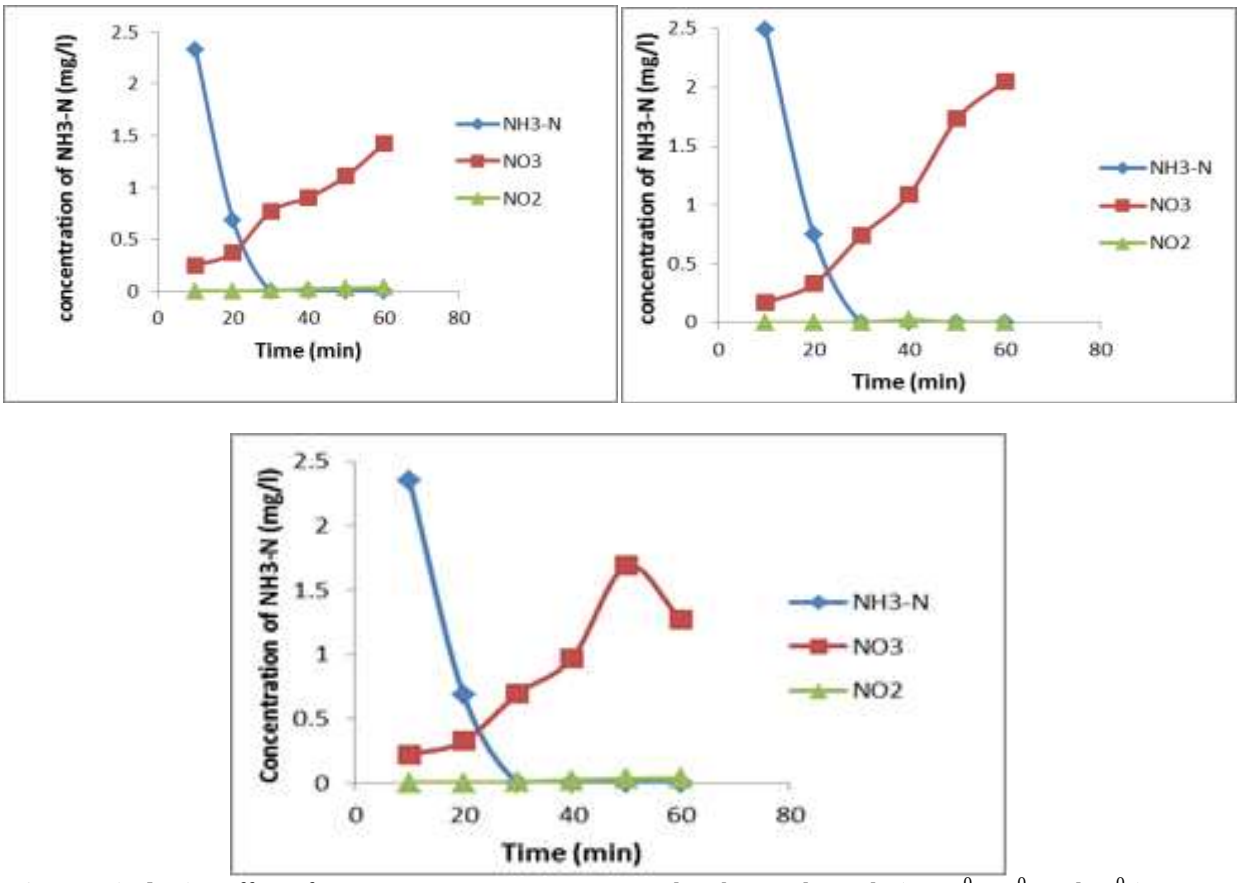

Figure 5 (a, b, c):- Effect of temperature on ammonia removal with iron electrode (T=20^0c,30^0c and 40^0c) Co=50 mg/l; NaCl= 0.5 g/l; pH= 5.1; 18.38mA/cm^2

The [Fig.5(a,b,c)] shows when temperature increased from 200C, 300C and 400C the percentage of ammonia removal is 98.8, 99.6 and 98.92 respectively in 20 min . The effect of 300C was found to be better than 200C and 400C because the formation of nitrate was significant during the 50 min and then decrease after that. This phenomenon can be explained by the fact Iron corrodes and produces hydrogen gas of hydrogen and ferrous hydroxides raising the pH of the solution which continues until entire solubility of ferrous hydroxide and a deposit of iron hydroxide on the surface of the metal as a film forms smothering the corrosion reaction. That's why Miehr et al, [18] found faster nitrate removal rate for oxide coated Fe0 .Where as in 30 min total amount of ammonia was removed. This can be explained by the fact the final pH is 6.0, 7.18 and 7.07 at temperature of 20^0C, 30^0C and 40^0C respectively. The reduction of ammonium to ammonia gas with iron electrode is due to the high pH. The amount of nitrate which is given out is 1.87 mg/l, 1.69mg/l and 1.84 mg/l. That means the amount of nitrate increased with

decreasing of the temperature. Increasing the temperature increased the rate of chloride ion. That means the presence of anions could inhibit the reduction of nitrate because that will decrease the active area of the surface of the electrode [19, 20]. The formation of nitrite is 0.040 mg/l, 0.046mg/l and 0.039 at 200C-300C and 400C respectively. Nitrite increases the cathodic current that means the nitrite reduction rate with iron electrode is faster than nitrate reduction rate.

Cu/Zn cathode

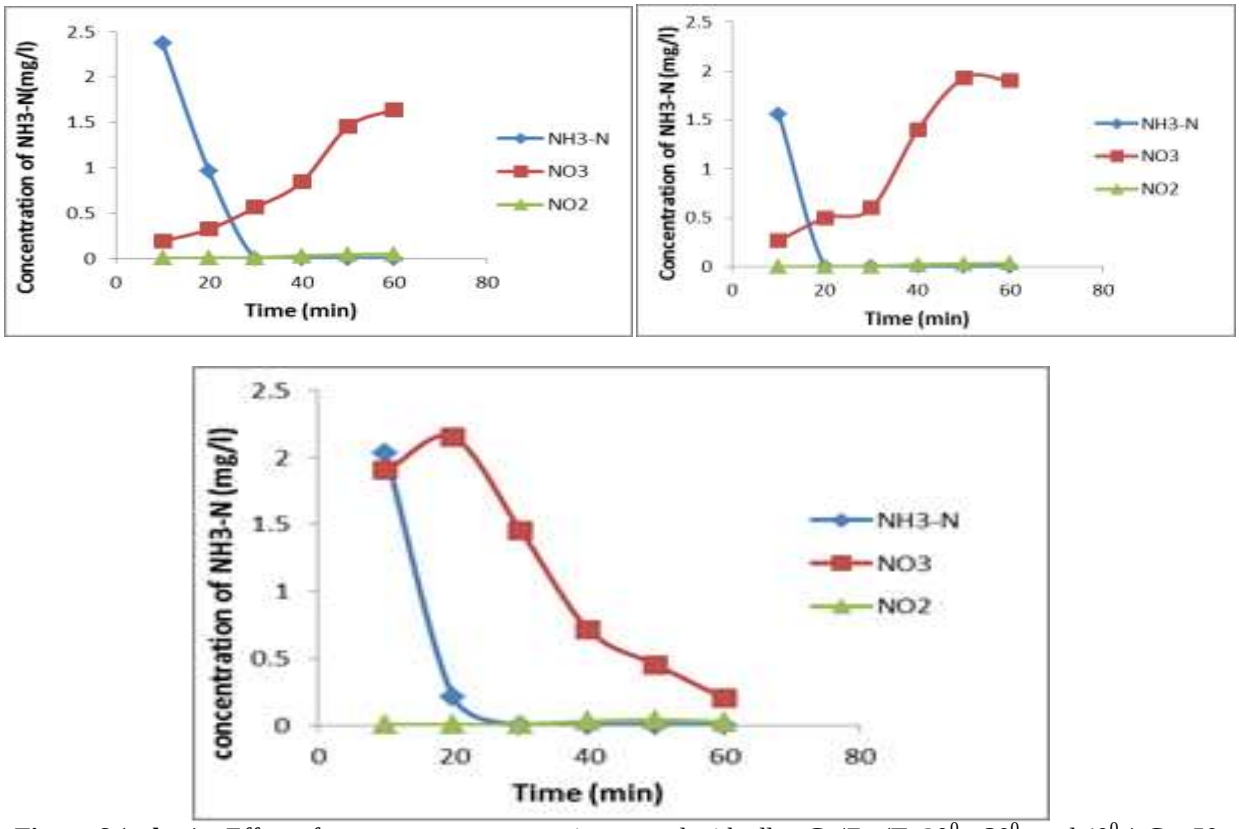

Figure 6 (a, b, c):- Effect of temperature on ammonia removal with alloy Cu/Zn (T=20^0c, 30^0c and 40^0c) Co=50 mg/l; NaCl= 0.5 g/l; pH= 5.1; 18.38mA/cm^2

From the [Fig. 6 (a,b,c)] ammonia was reduced by 98.08%, 100% and 99.5% in only 20 min with 20^0C 30^0C and 40^0C respectively. When temperature increased from 20^0C to 40^0C the percentage of ammonia decreased. This can be explained by the changes of pH in the different reactions during the oxidation of ammonia. The final pH is 7.13, 7.05 and 7.08 with the temperature around 20^0C 30^0C and 40^0C respectively. This result is in accordance with previous studies which reveal that optimum pH is between 7-9 [21, 22, 23]. It appears under alkaline conditions, strong oxidation of ammonia is due to ClO_3^- agent that has a low oxidability. This explains why at the temperature of 30^0C the elimination of ammonia is faster while the reaction occurs in low pH value which favors HOCl as agent oxidant. It has strong oxidation of ammonia removal. Nitrites detected throughout the experiment was in the order 0.045 mg/l, 0.037mg/land 0256mg/l with temperatures of 20^0, 30^0C and 40^0C respectively. Simultaneously nitrate ions may come from indirect oxidation of HOCl but also by the hydroxyl radical. So according to the results of research Cu / Zn is more suitable for the reduction of ammonia. The highest formation of nitrate was also found with Cu/Zn cathode and decreased finally with the time according to the standard discharge.

Degradation kinetic of NH3-N

Kinetic study plays a significant role in determining the retention time in any system of electrolysis seen to obtain desired removal. The disappearance of NH3-N is pseudo- first- order reaction based on analysis of the kinetic of electrochemical degradation with Iron electrode as cathode with current density 16mA/cm2, 0.5g/l of NaCl. Thus a first order reaction is characterized by a linear dependence of ln [NH3-N] versus time:

$$V = -d[NH3-N]/dt = K[NH3-N]/[NH3-N] = -kdt \quad (5)$$

Linear regression is calculated by follow way:

$$\int_{A_0}^{A_t} d[NH3-N]/[NH3-N] = -\int_0^t Kdt \quad (6)$$

$$\ln[NH3-N]_t - \ln[NH3-N]_0 = -Kt \quad (7)$$

$$[NH3-N/]_t / [NH3-N]_0 = e^{-5,6607t}$$

, K = - 5.6607 min^{-1} where $[NH3-N]_0$ is the initial concentration of dissolved contaminant measured with time equal t =0. The presence of soluble iron in the solution and a high area of the working electrode iron facilitate the removal of NH3-N and denitrification. The difference between the electrode copper and iron electrode for ammonium removal is due the number of electron giving.

Treatment effects on real wastewater under optimal condition

In this experiment we used the influent of Qinghua University Wastewater Treatment Plant, which consisted of domestic sewage wastewater from region of Beijing, without any pretreatment. The COD concentration of the raw sewage was 300 mg/L and the NH_3-N concentration was 90 mg/L. The alloy electrode of Cu/Zn with a current density of 18.32mA/cm^2, a space size between the two electrodes of 1.1 cm, temperature of 40^{0C} and an added amount of 0.5 g/L of NaCl, the raw sewage was electrolyzed, and the results are shown in Fig. 7. The electrodes have an excellent effect on the removal rates of COD and NH_3-N from the raw sewage. After 30 min of electrochemical reaction under the optimal conditions, the COD in raw sewage was 185 mg/L, a removal rate of 38%; and the total NH_3-N concentration have removed.

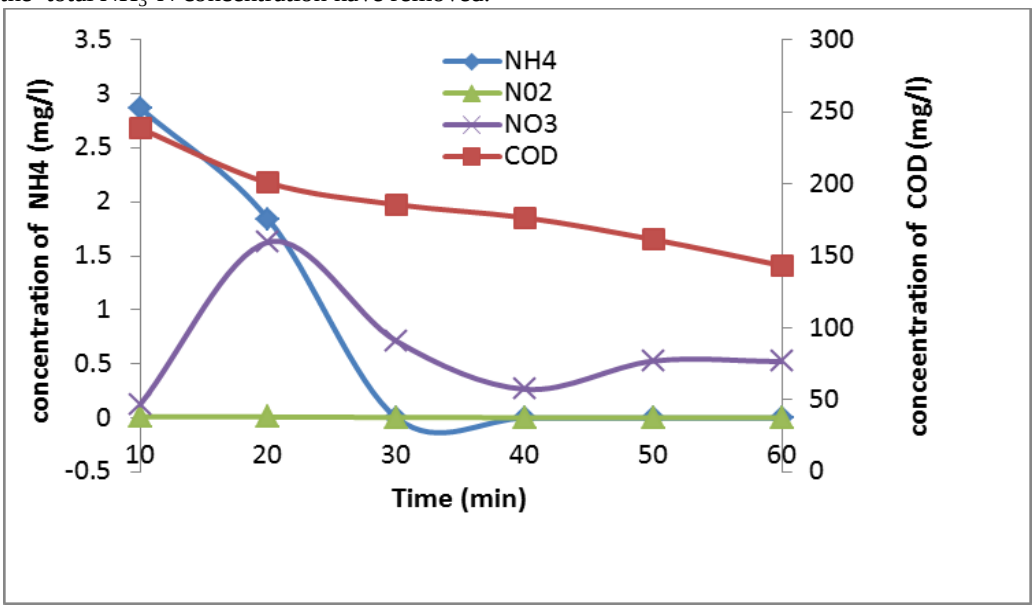

Figure 6:- Treatment of real wastewater under optimal condition.

Conclusions:-

Its concluded that Electrochemical for ammonia removal with Cu, Fe and Cu/Zn as cathode and Ti/Iro2 as anode is a good method. From the results of this experiment it appears that Cu/Zn electrode as cathode is better than Fe and Cu electrode for removal of ammonia with NaCl or without NaCl. The high formation rate of nitrate without NaCl was found with Cu/Zn and with NaCl addition it was Cu electrode as cathode .By increasing the temperature the removal rate of ammonia improved with relation to time, especially with Cu/Zn electrode around 40^0C whereas the highest formation of nitrate was found with Cu at around 30^0C. Electrochemical reduction of ammonia with ammonia concentration was studied follow first- order model law. The kinetic study showed that current density (current passed used during experience per unit volume) is an appropriate design.

Nomenclature

d	density mA/cm^2
T	temperature degree
D	space between electrode, cm
I	current , A
V	voltage , V
V	kinetic rate , en mol.L^{-1}.s^{-1}

Subscripts

NH3-N	ammonia
NO3	nitrate
NO2	nitrite
COD	chemical oxygen demand
Ti	titanium electrode
Fe	iron electrode
Cu	copper electrode
Cu/zn	alloy copper and zinc
Au	gold
Pt	lead

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