CATALYTIC REDUCTION OF NITRATES IN SURFACE WATER USING ACTIVATED CARBON-SUPPORTED Fe–Cu CATALYST

A. G. Hakke[1] , Dr. V. D. Salkar[2]

[1]M.Tech. Student, (Civil-Environmental Engineering), [2]Professor,

Dept. of Civil Engineering, Walchand College of Engineering Sangli, Maharashtra, (India)

ABSTRACT

The activity and selectivity of bimetallic catalysts (Fe–Cu) supported on granular activated carbon are studied in order to optimize the metal composition for the reduction of nitrate in surface water using formic acid as reducing agent. Catalytic tests are carried out in a batch reactor at room temperature. The activity of catalyst is found to depend onthe iron and copper content as well as dose of reducing agent – formic acid. Different proportions of Fe and Cu were tried in order to determine the best proportion of the elements for sake of maximizing nitrate removal.The maximum removal of nitrate was obtained for 100 ppm Nitrate solution using 100 mg/lit catalyst with Fe: Cu ratio as 6:1, and 0.3 ml/lit of formic acid. The Carbon-supported Fe–Cu Catalyst is observed to be significantly effective in the transformation of nitrate to nitrogen gas.

Keywords: Nitrate Reduction, Bimetallic Catalysts, Activated Carbon, Formic Acid.

I INTRODUCTION

Nitrate contamination of ground water resources is increasing more or less ubiquitously. This trend has raised concern as nitrates cause methemoglobinemia and cancer. Several treatment processes can remove nitrates from water with varying degrees of efficiency, cost, and ease of operation.Nitrates have general formula as NO_3^-,and are normally used to manufacture the fertilizers and pesticides. Though a fertilizer increases agricultural production,the agricultural run-off containing remnants of fertilizers degrades water quality. Nitrates are also naturally occurring compounds that are metabolic products of microbial digestion of wastes containing nitrogen such as animal feces or fertilizers. The use of nitrogen fertilizers, manure of animals and wastewaters are the major causes for surface and ground water pollution with nitrate ions[1][2][3].Nitrate contamination of surface water is of special concern as the surface water is the prime source of drinking water. Nitrates are in various forms, on drying typically a white or crystalline powder is obtained.

Nitrates are potentially very harmful and toxic, if consumed. They react with iron in blood and cause lack of O_2 to tissues of organs[4]. According to the permissible limit given by World Health Organization and Indian drinking water standards (IS 10500:2012) the acceptable limit of nitrate for drinking and discharge water is 45 ppm and 100 ppm respectively[5]. Conventional methods for nitrate removal can be divided into two categories as physicochemical and biological. Physicochemical treatment methods, such as ion exchange, electro dialysis,

and reverse osmosis, are effective, but only serve to transfer NO_3^- from water into a concentrate phase which requires further treatment or disposal. Biological de-nitrification is commonly used for wastewater treatment, but rarely for drinking water due to challenges associated with the variability of incoming water quality and operational control, the production of unwanted sideproducts, high turbidity in finished water, and concerns for pathogen exposure[6].The catalytic reduction is one of the most promising alternatives for nitrates removal without drawbacks of the conventional methods. Hence catalytic hydrogenation method is in use for reduction of nitrate to nitrogen[7].The monometallic catalysts are practically inactive for the reduction of nitrate. Bimetallic catalysts are more active catalysts for nitrate reduction. The activity of the catalysts is quite different depending on the noble metal. The maximum activity of catalysts is depending on an atomic ratio of noble metal and promoter atoms to obtain a very active catalyst for reaction. The presence of a second metal, namely copper, is necessary forthe reduction of nitrates[8][9][10][11]. The nitrate reduction activity and selectivity depends on different pH values for different bimetallic catalysts. At high pH, strongly adsorbing oxygenated species block bimetallic nitrate adsorption sites. The faster nitrate reduction at lower pH was attributed to the greater production of H_2, which in turn refreshed the surface reactivity of the nanoparticles [12][13][14]. The method of preparing catalyst, pH of solution and metal loading affect the reactivity and selectivity of bimetallic catalyst for nitrate removal. Monometallic Fe/C catalyst was reported to be effective for reduction of nitrate using hydrogen gas as a reducing agent[15].

Formic acid can be used as a source of H_2.It decomposes into H_2 and CO_2 on the surface of diverse noble metals (Eq. (1)). H_2 gas evolved,then serves as a reducing agent whereas CO_2 can effectively neutralize hydroxide ions, which are produced during the nitrate reduction (Eq. (2) and (3)).Formic acid produces CO_2 which becomes HCO_3^- and CO_2 and effectively consumes OH^- ion and buffers the reaction solution.Besides of acting as a reducing agent, formic acid effectively suppresses the solution pH without using additional buffers. Further, earlier studies have reported no formation ofnitrite or ammonia consequent to use of formic acid[15].
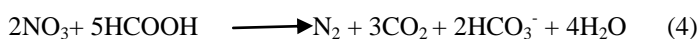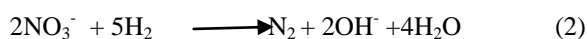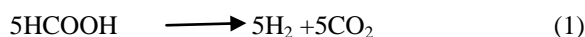
$$5HCOOH \longrightarrow 5H_2 + 5CO_2 \qquad (1)$$

$$2NO_3^- + 5H_2 \longrightarrow N_2 + 2OH^- + 4H_2O \qquad (2)$$

$$2CO_2 + 2OH^- \longrightarrow 2HCO_3^- \qquad (3)$$

$$2NO_3 + 5HCOOH \longrightarrow N_2 + 3CO_2 + 2HCO_3^- + 4H_2O \qquad (4)$$

Fig. 1 Mechanism of Nitrate Reduction by Formic acid as a reducing agent.

The objective of the present work is to study catalytic nitrate reduction in batch process at room temperature over bimetallic catalyst (Fe–Cu) supported on granular activated carbon. The attempts are made to determine optimal proportion ofFe and Cu, as well as optimal dose of formic acid as the reducing agent, in order to enhance nitrate removal from artificial solution prepared with deionized water and sodium nitrate.

II MATERIALS AND METHODS

2.1   Materials and Chemicals

All chemical reagents were used as received without further purification. Charcoal activated granular extra pure carbon (LOBA Chemie, Mumbai, particle size between 0.1 to 0.3 mm) is used as support. Ferric chloride (Thermo Fisher Scientific India Pvt. Ltd., Mumbai), Cupric chloride (LOBA Chemie Mumbai), Formic acid (LOBA Chemie Mumbai, HCOOH 85%), Sodium nitrate (NaNO$_3$, Thermo Fisher Scientific India Pvt. Ltd.,Mumbai), Acetone (Fisher Scientifics, Mumbai),and Sodium hydroxide flakes (Fisher Scientifics 98%, Mumbai) were procured from Chemine enterprises, Sangli. Orbital shaker (Spectra lab Instruments Pvt. Ltd., Mumbai) and Magnetic Stirrer (Spectra lab Instruments Pvt. Ltd., Mumbai) were used for mixing the reagentsfully.All aqueous solutions were made in deionized (DI) water obtained by usingLaboratory Water Still system (Lab Hosp instrument and Equipment mfg. Co. Mumbai).

2.2   Preparation of catalyst

Fe-Cu/C catalyst was prepared by adsorption method. Charcoal activated granular extra pure carbon was used as support. Ferric chloride was used for Fe metal loading on the granular activated carbon knowing that 162.206 gram of FeCl$_3$contains 55.847 grams of Fe$_2^+$. The activated carbon granules were stirred with solution of ferric chloride (FeCl$_3$) in acetone for 24 h and air dried. Cupric chloride was used for Cu metal loading on the monometallic catalyst knowing that 170.04 gram of CuCl$_2$ contain 63.54 gram of Cu.The monometallic catalyst was stirred with solution of Cupric Chloride (CuCl$_2$) in acetone for 24 h and air dried.The bimetallic catalyst was filled in the glass column and connected to the nitrogen gas supply. The whole system was kept in a furnace and heated at 450ºC in nitrogen flow for 8 hr. in order to activate the bimetallic catalyst by decomposition of metal salt.

2.3   Batch Experiments

Catalysts were tested in batch reactorat room temperature. Details of batch reactor are shown in Fig. 2. Batch experiments were performed using a three neck glass reactor equipped with a magnetic stirrer, an inlet for introducing formic acid (HCOOH)/nitrogen gas (N$_2$) mixture and arrangement for withdrawing samples. The known amount of catalyst was taken in the reactor containing 1000 mL de-ionized water. Nitrogen gas was used in batch process avoid interference of other gases. The contents of the reactor were flushed with nitrogen flow for 45 min to remove excess oxygen. Formic acid was used as a reducing agent. The flow rate of nitrogen was maintained at 50 mL min-1, by flow controller. Nitrite in the solution was determined byUV Spectrophotometer (HACH DR600 DOC 022.97.90368) using Cadmium reduction method (DOC316.53.01066, method 8039).
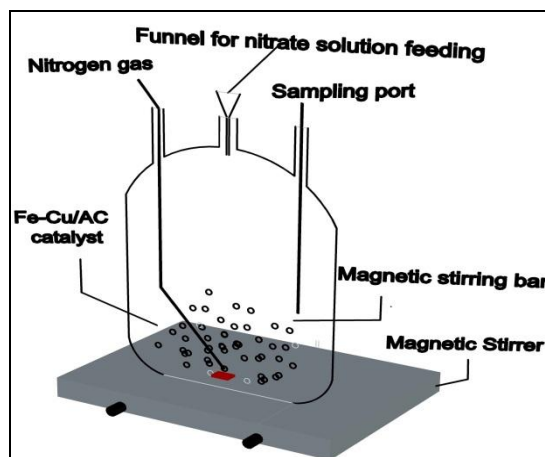
Fig. 2 Experimental setup for the batch reaction mode

III RESULT AND DISCUSSION

3.1 Effect of Metal Proportion

Effects of variation of metal proportion on granular activated carbon for catalytic activity towards catalytic reduction of nitrate were studied through batch experiments. The proportions of loading Fe-Cu metals were varied as (Fe: Cu) 4:1, 4:2, 5:1, 5:2, 6:1 and 6:2 by 5 weight % on activated carbon. The nitrate reduction batch reactions were conducted as aforesaid in order to determine the optimal proportion of Fe-Cu metals with the same dose of catalyst as 100 mg/L for each case. The variation in catalytic activity with respect to different metal proportions on nitrate reduction was observed. In case of the 4:1 Fe-Cu/C catalyst the nitrate concentration reduced from 100 to 70 ppm whereas at Fe : Cu proportions 4:2, 5:1, 5:2, 6:1, and 6:2 the final concentrations of nitrate in treated water, at 120 min from end of reaction, were observed to be 37, 68, 75, 90 and 81 ppm, respectively (Table 1). The catalytic activity has increased when Fe: Cuproportion increased from 4:1 to 6:1due to increase in number of active site.

Table 1 Catalytic activity of Catalyst proportion various Fe-Cu/C catalysts

Sr. No	Catalyst proportion (Fe:Cu)	Nitrate Reduction Percentage
1	4:1	30.42
2	4:2	36.64
3	5:1	67.89
4	5:2	74.62
5	**6:1**	**89.8**
6	6:2	79.26

3.2 Effect of Metal Loading

Effects of variation of metal loading on activated carbon for catalytic activity towards catalytic reduction of nitrate were studied through batch experiments. The percentage loading of Fe- Cu metals was varied as 2, 5, 7, and 10by weight % on activated carbon. The nitrogen gas flow was maintained at 50 mL/min.The Fig 3 shows nitrate removal % observed for different weight percentages of Fe-Cu on activated carbon, and reaction times. Blank experiment was carried out in similar conditions with bare activated carbon, indicated reduction in nitrate concentration from 100 to 88 mg/L. It could be attributed to adsorption on activated carbon. Blank experiment in the presence of only formic acid wasconducted wherein no nitrate reduction was observed.
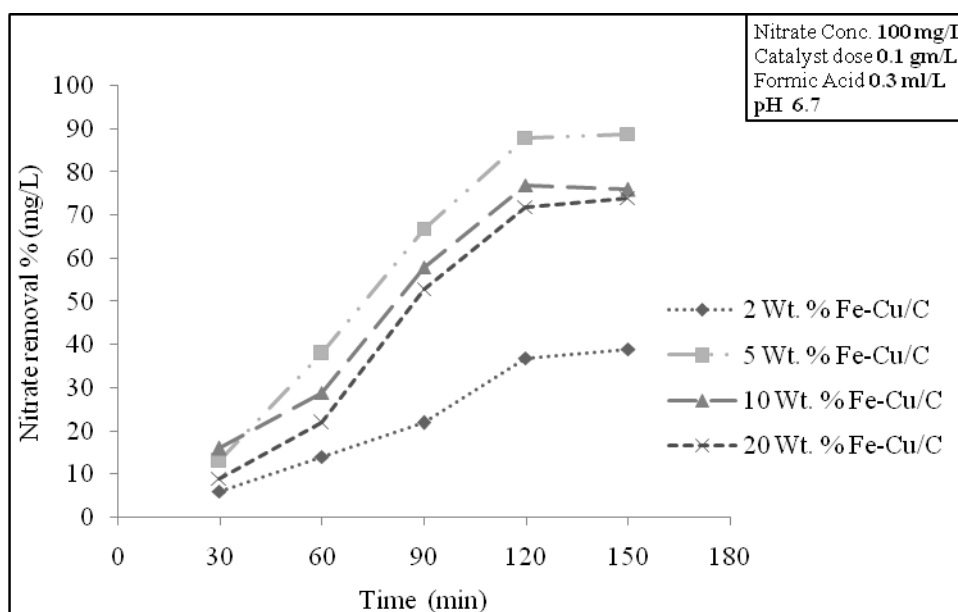

Fig. 3Nitrate removal for different wt. %ofbimetallic catalyst

As evident from Fig 3, the 5 weight % Fe-Cu bimetallic catalyst was more effective than the others. Further, the removal efficiencies improved with increase in reaction time. However, for the 5 weight % of Fe-Cu bimetallic catalyst there was no significant improvement in removal for reaction time larger than 120 min. So, the optimal weight % of Fe-Cu bimetallic catalyst and the reaction time was found respectively as 5 and 120 min.

3.3 Effect of Catalyst Dose

The dose of catalyst was varied as 0.05, 0.1, 0.5, 1 and 2 gm/L. The observed nitrate removal efficiencies are shown in Fig. 5. As seen from the Fig. 5, bimetallic catalyst dose – 0.1 gm/L was more effective than the others. For the catalyst doses 0.5, 1, and 2gm/L, the nitrate reduction efficiencies observed wereslightlylower. So, the optimal catalyst dose of Fe-Cu bimetallic catalyst was found as 0.1 gm/L.
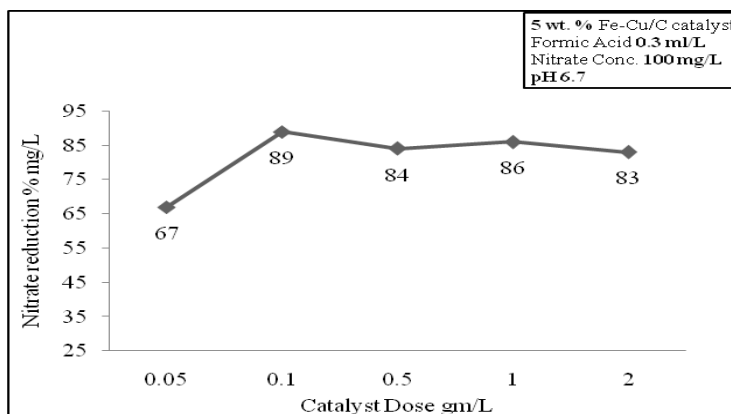
Fig. 5 Effect of dose variation of catalyst on catalytic activity

3.4 Effect of pH Variation

The catalytic reduction reaction was performed at near neutral pH (6.6 – 7.1) as well as acidic condition (2.6 – 3.0). The results show that the catalytic reduction for nitrate wasmore effective at near neutralpHin comparison with the acidic condition (Fig – 4). In order to avail near neutral condition for effective catalytic reduction reaction, initially pH of influent was raised to 11 by adding Sodium hydroxide flakes. Subsequently adding formic acid as a reducing agent resulted in decrease of the pH to near neutral condition. The faster nitrate reduction at lower pH was attributed to the greater production of H_2, which in turn refreshed the surface reactivity of the nanoparticles. Also the high pH value was a negative effect on the NO_3 conversion rate[14]. This was most likely due to H^+ consumption during the reactions. As evident from Fig. 4,in the near neutral pH conditionenhanced the nitrate removal rate as compare to acidic pH condition.As evident from Fig. 4,that the N_2 selectivity increased with an increase of pH value and the maximum N_2 selectivity (90%) was observed at pH value of 6.7.
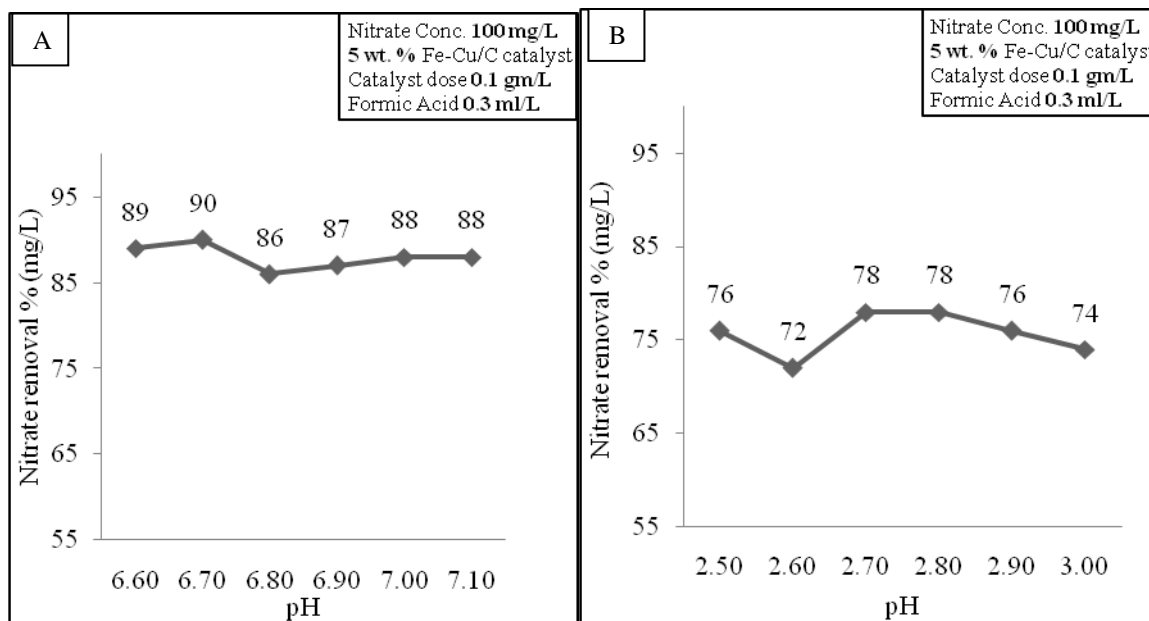

Fig. 4 Effect of pH on catalytic activity with A) near Neutral condition and B) Acidic condition

3.5 Effect of Formic Acid Dose

Retaining the optimal catalyst dose of Fe-Cu bimetallic catalyst as 0.1 gm/L, the dose of formic acid was varied as 0.1, 0.2, 0.3, 0.5 and 1ml/L to study its effect on nitrate reduction. The observed Nitrate removal efficiencies for the different doses of Formic acid are shown in Fig. 6.The results clearly show that the effect of introducing formic acid is significant in the nitrate reduction reaction.Fig. 6 shows that the formic acid dose – 0.3 ml/L, was more effective than the others. However, for the further increase the formic acid dose, there was no significant improvement in nitrate removal. So, the optimal formic acid dose was found as 0.3 ml/L for nitrate removal. The maximum nitrate removal efficiency obtained for the dose was 87 %.
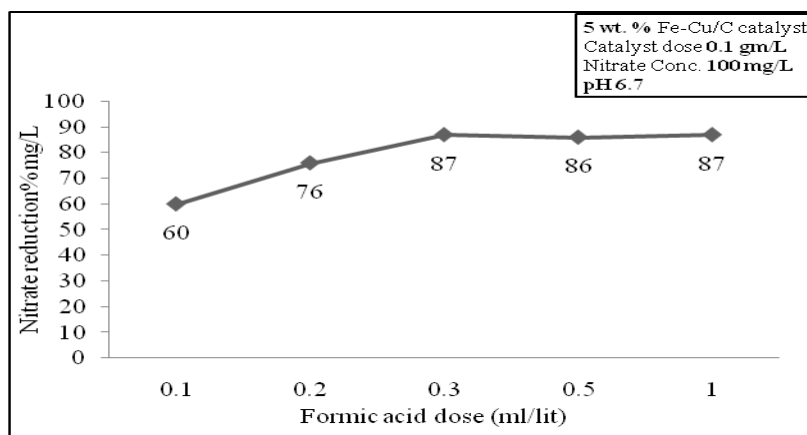

Fig. 6 Effect of dose variation of formic acid on catalytic activity

IV CONCLUSIONS

The process of developing the bimetallic Fe-Cu/C catalyst is successfully demonstrated through the present study.Based on the lab experiments, it can be concluded that bimetallic Fe-Cu/C catalyst along with formic acid as a reducing agent is effective for catalytic reduction of nitrates in water.The removal efficiency depends on pH of the water, dose of reducing agent as well as proportion of Fe and Cu. The removal efficiencies were more for near neutral pH. So, in order to achieve enhanced removal of nitrates it is essential to adjust initial pH of the water to be treated. In the present work the initial pH was raised nearly to 11, so as to attain near neutral pH subsequent to addition of formic acid as the reducing agent. Almost 90% removal of nitrates was achieved with 5 weight %Fe-Cu/C bimetallic catalyst (Fe: Cu ration (6:1), Dose – 100 mg /L), and 120 min as reaction time, in presence of Formic acid (85%, Dose – 0.3ml /L).

ACKNOWLEDGMENT

REFERENCES

[1]   Patil, S. R., Patil, D. B., Kulkarni, H. S., Bhamburdekar, S. B., (2014), "Assessment of physico-chemical properties of ground water from different villages of ShiralaTaluka, Sangli District (India)." International Journal of Advanced Research, 2 (3), 51-54

[2]   Archna, Sharma S. K., and Sobti R. C., (2012), "Nitrate Removal from Ground Water: A Review" E-Journal of Chemistry 9(4), 1667-1675

[3]   Khandare, H. W., (2013), "Scenario of Nitrate contamination in Groundwater: Its causes and Prevention" International Journal of ChemTech Research., 5 (4), 1921-1926.

[4]   U.S. EPA, Toxicity and Exposure Assessment for Children's Health, (2006), "Nitrates and Nitrites TEACH Chemical Summary"

[5]   Indian Standards IS: 10500 (2012), "Drinking water specification."

[6]   Ulf P., Marc H., Jörg D., Vorlop K.D.,(2000), "Improving the catalytic nitrate reduction", Catalysis Today 55, 79–90

[7]   Albin P.*, Jurka B., Janez L., Oshio T., Kajiuchi, (1996), "Kinetics of the catalytic liquid-phase hydrogenation of aqueous nitrate solutions", Applied Catalysis B: Environmental, 11 (81–98).

[8]   Hoorld S., Vorlop K.-D., Tacke T. and Sellb M., (1993), "Development of catalysts for a selective nitrate and nitrite removal fromdrinking water", Catalysis Today, 17 (21-30).

[9]   Salome, O., Soares, G.P., Jose, J.M., Orfao, Pereira, M. F. R., (2009), "Bimetallic catalysts supported on activated carbon for the nitrate reduction in water: Optimization of catalysts composition." Applied Catalysis B: Environmental, 91(1-7), 441–448.

[10]   Deganello, F., Liotta, L., (2000), "Catalytic reduction of nitrates and nitrites in water solution on pumice-supported Pd–Cu catalysts." Applied Catalysis B: Environmental, 24 (3–4), 265–273

[11]   Gauthard F., Epron F. and Barbier J., (2003), "Palladium and platinum-based catalysts in the catalytic reduction of nitrate in water: effect of copper, silver, or gold addition", Journal of catalysis 220 (182–191).

[12]   Ulf P., Marc H., Jörg D., Vorlop K.D.,(2000), "Supported bimetallic palladium catalysts for water-phase nitrate reduction", Journal of Molecular Catalysis A: Chemical 173 (2001) 313–328.

[13]   Wenliang G., Naijia G.∗, Jixin C., Xinxin G., Ruicai J., Haisheng Z., Zhiguang L., Fuxiang Z., (2003), "Titania supported Pd-Cu bimetallic catalyst for the reduction of nitrate in drinking water", Applied Catalysis B: Environmental, 46 (341–351).

[14]   Jialu S., Chao L., Aimin L., (2016), "Selective reduction of nitrate into nitrogen using Fe–Pdbimetallicnanoparticle supported on chelating resin at near-neutral pH" Chemical Engineering Journal, 286, 408–415.

[15]   Shukla, A., Pande, J. V., Bansiwal, A., Osiceanu, P., Biniwale, R. B., (2009), "Catalytic Hydrogenation of Aqueous Phase Nitrate Over Fe/C Catalysts." Catalysis Letters Journal, 131:451– 457.

[16]   Choi, E. K., Park, K. H., Lee, H. B. Cho, M., Ahn, S., (2013), "Formic acid as an alternative reducing agent for the catalytic nitrate reduction in aqueous media." Journal of Environmental Science, 25(8), 1696-1702.