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Feasibility of Nitrate Removal using Hydroxylamine Hydrochloride from Sundarijal River Water through a Laboratory Scale

Bhishma Karki, Jeevan Jyoti Nakarmi, Saddam Husain Dhobi

Abstract*: *Sundarijal River supply drinking water in Kathmandu city, Nepal and to study the nitrate concentration, 10 different sample from different locations of the Sundarijal River was taken. The method for the removal of presence nitrate in River was tested using hydroxylamine hydrochloride dose at 25±2^{0}C with 35 minutes contact time. Samples was tested for different dose of hydroxylamine hydrochloride and reduction of nitrate increase with increasing hydroxylamine hydrochloride dosages, up to certain limit. That mean with 0.5g, 0.6g and 0.8g dosages of hydroxylamine hydrochloride, reduction of nitrate was not observed when tested with 10mg/L, 50mg/L and 100mg/L river water, orderly. This tested samples shows the feasibility of nitrate removal from River water, Sundarijal.

Keywords*: *Kinetic study; Thermodynamic parameters; Intraparticle diffusion; Breakthrough analysis

I. INTRODUCTION

The Sundarijal River in Sundarijal is chosen for this research because this river supply water to different place of Kathmandu valley. Widespread of chemical fertilizers used and indecorous treatment of wastewater like industrial and urban spot led numbers of environmental difficulties. Among them nitrate-nitrogen concentration in ground and surface water are major issue developing counties (India, Nepal, Pakistan etc.). Large numbers of nitrogenous compounds like ammonia, nitrite and nitrate are frequently found in drinking and wastewater [27]. The water contaminated with nitrogenous compounds accompanying different infectious disease, example methemoglobinaemia found in newborn infants [1-3]. Studies also shows nitrate ion causes diabetes and carcinogen [4-5]. There are several ways to remove nitrate from water. Some of them are ion exchange, radsorption, reverse osmosis, catalytic hydrogenation electro dialysis, and biological denitrification and so on [6-9]. One of the best promising technique to remove high nitrate concentration is biological reactor although have different challenges and difficulties. Absorption is also one of the feasible process with lack of adsorbent for removal of nitrate. Instead of these difficulties, researcher are working on chemical reduction methods and other method to remove nitrate from water. Recently researcher used chemical methods for nitrate removal using zero-valent metals like iron, magnesium and aluminum reported in literature [10-17]. For the aqueous solution, iron reduce nitrate into nitrogen gas or ammonium ion and oxidizes itself into ferrous ion. At pH>10.5, aluminum reduce nitrate into nitrogen gas or ammonia and oxidize itself into aluminum ion. While in acid medium, Magnesium reduce nitrate into nitrogen gas or ammonium ion and oxidize itself into Magnesium ion [18, 10]. The stabilities and solubility of nitrate is low because nitrate has low tendency to go precipitation and adsorption phenomena, which drawback of conventional water treatment technologies. The major challenges to remove nitrate with aluminum powder from water is due to residual of aluminum ion (Al^{3+}) [19]. Therefore, cheap and easily readily available reducing agent to reduce nitrate effectively on drinking water and wastewater with moderate dose is one of challenges and solution. Using hydroxylamine hydrochloride is one of the novel method to remove nitrate from water are not been reported so far. Therefore, this method may be one of the solution to overcome the challenges of removal nitrate from water which is significant of this work. Advanced Oxidation Process is modern chemical method for the treatment of water containing nonbiodegradable /toxic substances and to get decontaminated drinking water [28]. Water treatment scheme is proposed where two variables are taken, authors also fabricated the device and tested for removal of organic contaminants from an aqueous solution using $BiVO_4$ photoanode [29].

II. EXPERIMENTAL SECTION

A. Reagents and chemicals

To test the removal of nitrate some chemicals and reagent are as Potassium nitrate, Hydroxylamine hydrochloride (Merck), KNO_3 solution (1.6305g in 1L distilled water), and other laboratory apparatus.

B. Batch experiments

To proceed the experiment all apparatus are washed with related laboratory regent and with necessity lab equipment experiments is carried out. The experiment is carried by using minimum (0.01g) to maximum (0.1g) amount of hydroxylamine hydrochloride and 0.01g of $FeCl_3$ (as catalyst) with nitrate solution (synthetic). This solution are continuous stirred at ambient temperature (25±2^{o}C) at 400rpm with magnetic stirrer.

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* Correspondence Author
Bhishma Karki*, Tri-Chandra Multiple Campus, Tribhuvan University, Ghanta Ghar, Kathmandu, Nepal. Email: magnum.photon@gmail.com
Jeevan Jyoti Nakarmi, Central Department of Physics, Tribhuvan University Kirtipur, Kathmandu , Nepal. Email: Nakarmijj@gmail.com
Saddam Husain Dhobi, Robotics Academy of Nepal, Lalitpur-44700, Nepal. Innovative Ghar Nepal, Lalitpur, Email: saddam@ran.edu.np / saddamdhobe@gmail.com

The test was done with the help of Nitrate Interference suppressor. Moreover all test was done at an ideal and same laboratory environment to avoid the error or disturbance in test. Large number of external factor effecting the removal rate and percentage. Some of factors are amount of hydroxylamine hydrochloride, nitrate concentration, pH value and so on.

C. Theory of nitrate reduction with hydroxylamine hydrochloride

Hydroxylamine hydrochloride is soluble in aqueous medium producing hydroxylammonium ion ($[NH_3OH]^+$) and chloride ion. Hydroxylammonium ion is responsible for the reduction of nitrate with Iron initiates and reduction take places from Fe (III) to Fe (II) as shown in (1a). After this, Nitrate is reduced to nitrite by Fe (II) ion as shown in (1b). The overall reaction is given by equation (1c).

$2NH_3OH^+ + 4Fe^{+3} \rightarrow 4Fe^{+2} + N_2O + H_2O + 6H^+$ (1a)

$2Fe^{+2} + NO_3^- + 2H^+ \rightarrow 2Fe^{+3} + NO_2^- + H_2O$ (1b)

$2NH_3OH^+ + 2NO_3^- \rightarrow N_2O + 3H_2O + 2HNO_2$ (1c)

The Nitrite produced in this reaction is reduced to nitrous oxide as per equation (1d)

$NH_3OH^+ + NO_2^- \rightarrow N_2O + 2H_2O$ (1d)

The overall nitrate reduction process is given by equation (1e)

$4NH_3OH^+ + 2NO_3^- \rightarrow 2N_2O + 5H_2O + 2H^+$ (1e)

Alternatively, Hydroxylammonium chloride react with nitrate ion to produce hydroxylammonium nitrate (HAN) and produce N_2O and N_2 with 2:1 to 4:1 in absence of iron catalyst. However in presence of iron, this ratio has been determined to be 36:1[20].

$[NH_3OH]Cl + NO_3^- \rightarrow [NH_3OH]NO_3 + Cl^-$ (2a)

$2[NH_3OH]NO_3 \rightarrow N_2O + 3H_2O + 2HNO_2$ (2b)

$[NH_3OH]NO_3 + HNO_2 \rightarrow N_2O + 2H_2O + HNO_3$ (2c)

$4[NH_3OH]^+ + 2NO_3^- \rightarrow 3N_2O + 7H_2O + 2H^+$ (2d)

$5[NH_3OH]^+ + NO_3^- \rightarrow 3N_2 + 8H_2O + 4H^+$ (2e)

This stoichiometric equations listed above show 2-5 moles hydroxylamine hydrochloride amount are necessary to remove nitrate from solution, but in practices amount of hydroxylamine hydrochloride is higher than theoretical.

III. RESULT AND DISCUSSION

A. Effect of hydroxylamine hydrochloride dose

Figure 1, below shows hydroxylamine hydrochloride dose with initial nitrate removal percentage at room temperature with small range (25±2^{o}C) for 35 minutes to each sample test (10mg/L, 50mg/L and 100mg/L). The reduction of nitrate increased from 51.7% to 87.7% for 0.01 to 0.1g of hydroxylamine hydrochloride with initial concentration of nitrate solution of 10 mg/L. 51.6% to 88.9 % for 0.01 to 0.1g of hydroxylamine hydrochloride with initial concentration of nitrate solution of 50 mg/L. 47.9% to 90.2 % for 0.01 to 1.0g of hydroxylamine hydrochloride with with initial concentration of nitrate solution of 100mg/L. But with different tests like for 0.5g, 0.6g and 0.8g not significant reduction percentage was observed at initial concentration of nitrate (10mg/L, 50mgL and 100mg/L), respectively.

On other hand, at lower dosage of hydroxylamine hydrochloride, the percentage removal of nitrate is high at 10mg/L and low at 100mg/L. This may be due to the fact that at lower dose, equal amount of hydroxylamine hydrochloride is added to all concentrations of nitrate and hence equivalent amount of nitrate is reduced. So, percentage reduction is least at higher nitrate concentration and maximum at lower nitrate concentration.

On increasing the dose of hydroxylamine hydrochloride the reduction of nitrate is also increase and finally an equilibrium state is obtain, this show the reduction of nitrate was depend on the initial concentration. Hence, nitrate reduction was found to be maximum at higher nitrate concentration and lowest at lower nitrate concentration.

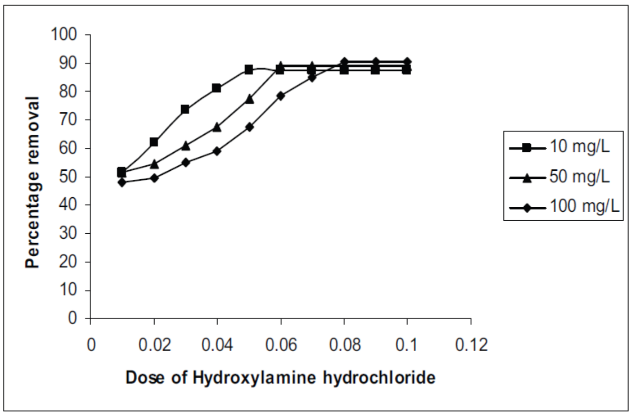

Figure 1. Removal Percentage of nitrate with Hydroxylamine hydrochloride

B. Impact of nitrate concentration on Nitrate removal Percentage

The study of nitrate concentration at initial phase studies with various dose of hydroxylamine hydrochloride at room temperature shown in figure 2. Figure 2, show with increasing concentration percentage removing nitrate is increase from 87.7% - 90.2%. Therefore, this process of nitrate reduction is suitable for water with high and low concentration of nitrate. It is also observed that reduction of nitrate by hydroxylamine hydrochloride brings nitrate concentration well below the permissible limit (45 mg/L) from water with wide range of initial nitrate concentration.

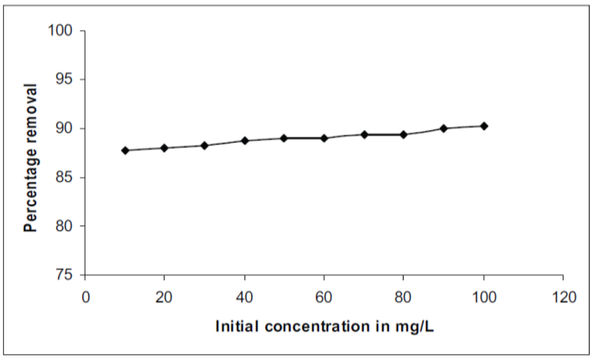

Figure 2. Initial nitrate concentration versus percentage removal of nitrate.

C. Impact of pH on Nitrate Removal percentage

Figure 3 show the impact of removing nitrate with pH and this shows that with increasing the pH of solution nitrate removal percentage decrease. The decrement is very slow for all consider initial concertation in this work.

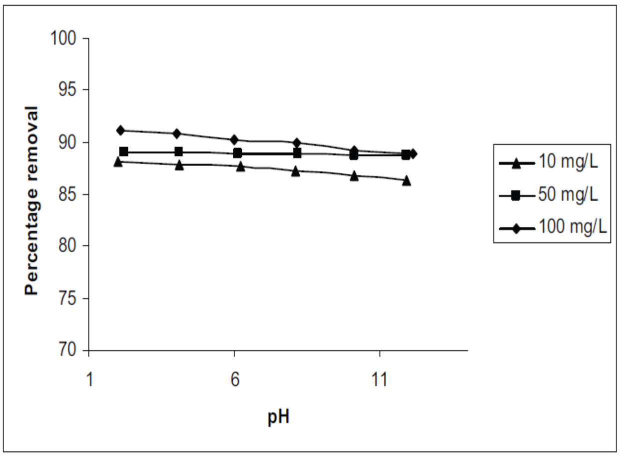

Figure 3: Impact of pH on nitrate removal Percentage.

The impact of pH on removal percentage of nitrate may be the existence of hydroxylamine (NH_2OH) at high pH and hydroxylammonium ion (NH_3OH^+) at low pH.

D. Impact of contact time on nitrate removal percentage

Figure 4, show the impact of contact time and removal percentage of nitrate. The impact of contact time and removal of nitrate percentage show that removal percentage of nitrate increase with increases in contact time. Initially, removal percentage of nitrate is fast and most of the nitrate ion was reduced to nitrogen gas or nitrous oxide within 5 minutes of initial contact, with increase times contact equilibrium is obtained after 35 minutes. Moreover, initially reaction is fast this is due to the concentration of nitrate as well as hydroxylamine hydrochloride was high initially and as time passes concentrations decreases and reaction rate slow.

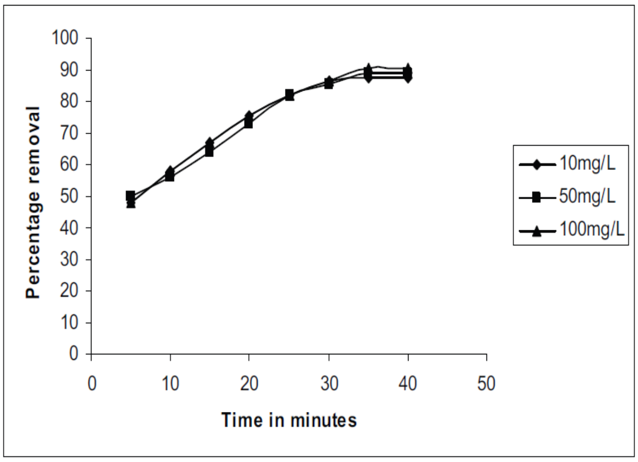

Figure 4: Removal percentage of nitrate with time contact.

E. *Kinetic study of reaction with contact time*

The kinetic studies of nitrate reduction by hydroxylamine hydrochloride was studies with rate constant equation and the first order rate expression [21] given by

$$\text{Log}\,(C_e) = \text{Log}(C_0) - K_1\left(\frac{t}{2.303}\right)$$

where C_e is equilibrium concentration and C_0 *is* initial nitrate concentration. The unit of centration is mg/L. K_l is first order rate constant and unit is min^{-1}. Plots of *Log*(C_e) versus t at different initial concentration is presented in Figure 6 below.

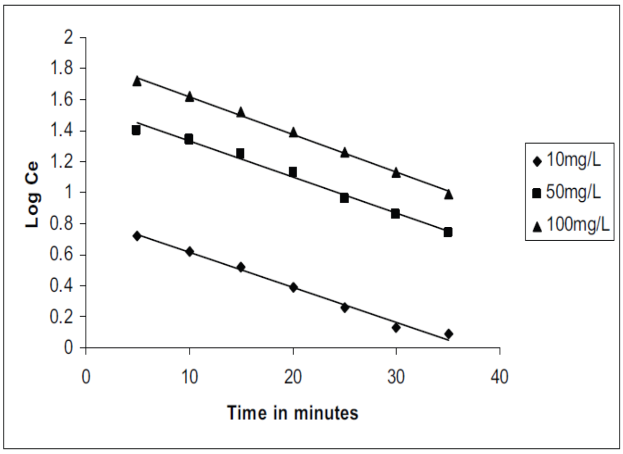

Figure 5. First order kinetics, time versus Log(C_e) with initial nitrate concentration.

The rate constant for first order (calculated from slope) and correlation coefficient for different initial concentration of nitrate is presented in Table 1. From graph, the equilibrium concentration goes decrease with time for this the rate constants was found around 0.05 min^{-1} and the correlation coefficients values indicated the validity of first order kinetics. For second order rate expression, [22] is given by,

$$\frac{1}{C_e} = \frac{1}{C_0} + K_2\, t$$

where K_2 is the rate constant and the plot of $1/C_e$ versus 't' is presented in Figure 7 below,

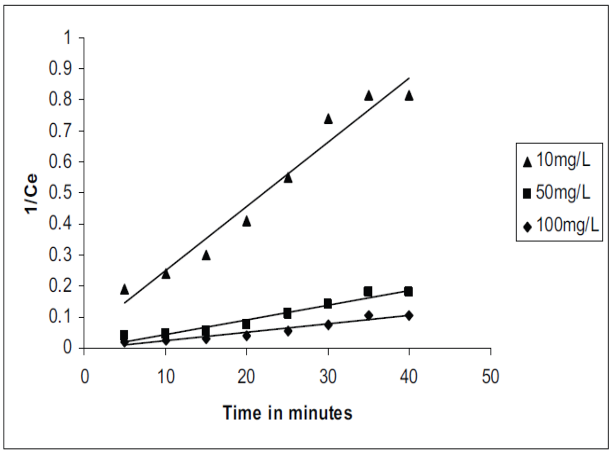

Figure 6: Second order kinetics, time versus 1/C_e with initial nitrate concentration.

The rate constant for second order (calculated from slope) and correlation coefficient for different initial concentrations are presented in Table 1. The value of R^2 for first order rate equation was found to be greater than 0.98 and that for second order rate equation was less than 0.96. Moreover the R^2 value of first order is greater than second order.

Table 1: First and second order rate constant with concentration.

Nitrate Concentration (mg/L)	First order kinetics		Second order kinetics	
	Rate Constant	R^2	Rate Constant	R^2
10	0.051524	0.990025	0.020685	0.960
50	0.053281	0.984926	0.004651	0.948
100	0.056591	0.995594	0.002688	0.943

F. Impact of Temperature on removal percentage of Nitrate

Figure 8 below show the impact of temperature on removal nitrate percentage from samples. To optimize the reaction different dose and concertation of hydroxylamine hydrochloride is taken. The study shows removal percentage decrease with increasing in temperature of concentration or sample which is taken in consideration

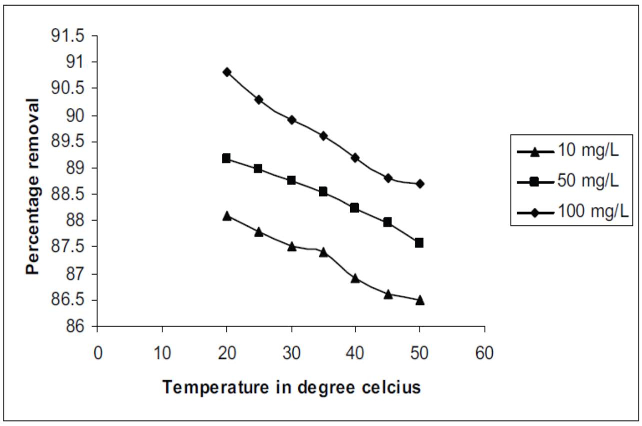

Figure 7: Removal percentage of nitrate with temperature

Observation result is shown in figure 8 shows nitrate removal percentage decreased in between 88.1 to 86.5, 89.16 to 87.56 and 90.8 to 88.7 for 10mg/L, 50mg/L and 100mg/L, respectively with incensement of temperature 20°C to 50°C. This continuous decrease of percentage removal with increasing in temperature show reaction is exothermic.

Gibbs free energy, enthalpy and entropy are some thermodynamic parameters used to study the nature of reaction and removal percentage [23-26].

$$log(K_c) = \frac{\Delta S}{2.303} - \frac{\Delta H}{2.303RT} \text{ and } \Delta G = \Delta H - T\Delta S$$

The visualization of rate constant and invers of time is for different nitrate concentration are shown in figure 9 and graph is linearly increase. The tabulated value in table 2 of ΔH and ΔS from graph shown below. The rate constant increase with inverse of temperature for different concentration of nitrate and hydroxylamine hydrochloride.

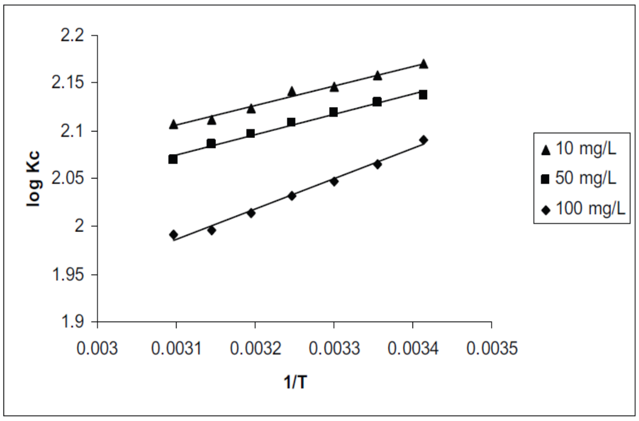

Figure 8: Rate constant vs 1/T at different concentration

Since the reaction is exothermic, therefore enthalpy is negative and entropy is positive. These both suggest Gibbs free energy is negative, therefore reaction is spontaneous.

Table 2: Enthalpy, Entropy and Gibbs free energy with different concentration.

Initial Nitrate Concentration (mg/L)	ΔH (kJ/mol)	ΔS (kJ/K /mol)	ΔG (kJ/mol)							R2
			20^oC	25^oC	30^oC	35^oC	40^oC	45^oC	50^oC	
10	-3.9502	0.02807	-12027.2	-12316	-12604.9	-12893.7	-13182.6	-13471.4	-13760.2	0.98
50	-4.02689	0.02724	-11795.6	-12096.1	-12396.6	-12697.1	-12997.6	-13298.2	-13598.7	0.983
100	-6.08212	0.01917	-11472.4	-11800.9	-12129.3	-12457.8	-12786.2	-13114.7	-13443.1	0.984

IV. CONCLUSIONS

From the above studies and experiment, it is found that reduction of nitrate from water is maximum at higher nitrate concentration and slowly decrease with a limit point. Also, reduction of nitrate is slowly increase with decrease in pH is also observed. In addition, with initial concentration the reduction of nitrate also increase. So, this removal method can be apply to treat water with wide range of nitrate concentration. This process can be apply to denitrify wastewater where the concentration is high as well as ground water. The reduction of nitrate was a rapid process and the optimum time for nitrate reduction was found to be 35 minutes. Kinetic studies show reduction process obeys first order kinetics. The temperature dependence reaction here show, the reduction of nitrate decrease as temperature increase which indicated reduction process is exothermic was confirmed by calculation thermodynamics parameters.

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AUTHORS PROFILE

Dr. Bhishma Karki is working as a Lecturer in Tri-Chandra multiple Campus. He has total of 11 years of experience at teaching and in Research. He has awarded Ph.D. in Physics from Tribhuvan University, Kirtipur, and Kathmandu, Nepal. He has published more than 10 research articles in national and International journals. He is recognized Researcher, Consultant and member of many renowned institutions in Nepal. His area of interest is Wastewater Treatment, Nanotechnology, Photocatalysis, Material Characterization, Photodegradation and Materials Chemistry.

Dr. Jeevan Jyoti Nakarmiis a professor of Physics at the Central Department, Tribhuvan University, Kirtipur. He is also a Head of Central Department of Computer Science and IT First Employment, 2009. His current research includes nan manufacturing, nanoscale magnetism, superconductivity, proton conductors, and electron transport in bacterial nanowires as well as magnetosphere, atmospheric physics, VLF data analysis, instrumentations, thin film deposition and their application. He has a bachelor's degree in Physics and a PhD in Plasma Physics from the Tribhuvan University. He was a President of Nepal Physical Society from 2013-2015.

Mr. Saddam Husain Dhobi pursed B. Sc., & M. Sc., in Physical Science from Tribhuvan University, Kathmandu-44600, Nepal 2016, & 2020. He is currently working as Sr. Researcher in Innovative Ghar Nepal Laboratory and Robotics Academy of Nepal, Lalitpur-44700, Nepal since 2013. He has published more than 37 research papers in reputed international journals including Thomson Reuters (SCI & Web of Science), it's also available online. His research work focuses on electron and photon properties beyond the general properties, Data Analytics, Virology, Nuclear Physics, and Computational Intelligence based education. He has 4 years of research experience.