

Removal of Nitrate from Water by Chitosan, Clay and Activated Carbon as Adsorbents: A Mini Review

Rakshitha R*, Yashas S R**

**(Department of Environmental Engineering, JSS Science and Technology University, Mysuru, India,*

***(Department of Environmental Engineering, JSS Science and Technology University, Mysuru, India,*

Corresponding Author: Ms. Rakshitha R

ABSTRACT

Nitrate contamination in the drinking water has posed threat to human health from decades, which has attracted many novel techniques for its removal over the years. Nitrate transforms into nitrite, increasing toxicity of the water to cause health impact. Adsorption of nitrate onto Activated Carbon, Chitosan and Organoclays has been studied in this study. The surface modification and chemical activation of these selected adsorbents have proved to be reliable in efficient nitrate removal. Effects of variables such as pH, contact time, initial concentration, adsorbent concentration, selectivity of ion exchange, adsorption kinetics and thermodynamics on nitrate adsorption have been reviewed. The Pillared Bentonite clay composed primarily of Na⁺ montmorillonite, with cation exchange capacity of 115 c mole / kg was used with modification by zero valent iron and cationic surfactant which showed high pore volume, large specific surface area and simultaneous reduction of nitrate. The activated carbon prepared by sugar beet bagasse and the commercially available one, have been tested with modifying it by alkaline and cationic surfactant for nitrate removal. Increment of the functional groups on the surface of adsorbent has been observed to be the key for efficient nitrate removal. Chitosan has been regarded as effective biosorbent. Particle diffusion in the adsorption process is the controlling step for nitrate uptake by the hydro-beads prepared by chitosan. The chitosan showed high reusability traits and was cost effective over activated carbon and organoclays.

Keywords- Activated Carbon, Pillared Bentonite, Chitosan Hydrobeads, Cationic Surfactant, Adsorption Isotherms, Adsorption Kinetics

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I. INTRODUCTION

Water resources are highly polluted by several nitrogen containing compounds, such as nitrate, nitrite, and ammonium, which may cause severe environmental problems including eutrophication. Nitrate and nitrite are naturally occurring ions that are part of the nitrogen cycle. Nitrogen compounds are essential nutrients for plants, which take them from the soil. Nitrate can reach both surface water and groundwater as a consequence of agricultural activity (including excess application of inorganic nitrogenous fertilizers and manures), from wastewater treatment and from oxidation of nitrogenous waste products in human and animal excreta, including septic tanks. Nitrogen, apart from carbon, Hydrogen and oxygen, is one of the basic elements present in organic compounds which form living matter. In nature, nitrogen and its compounds are subject to changes; mainly synthesis process which results in creation of organic nitrogen compounds from nitrates and gaseous nitrogen, and decomposition of organic dead matter in which initially released ammonia changes subsequently into nitrates and free nitrogen.

Nitrates are an inorganic compound composed of one atom of Nitrogen (N) and three atoms of Oxygen (O). Nitrate is the primary form of oxidized nitrogen in groundwater. It is soluble in groundwater and may be found in high concentration, if there is a nearby source of nitrate and oxygen is present. If there is no oxygen, bacteria in the soil use the nitrate as a food source, releasing nitrogen gas.

Nitrate can occur naturally in surface and groundwater at a level that does not generally cause health problems. High levels of nitrate in groundwater often result from improper well construction, well location, overuse of chemical fertilizers, or improper disposal of human and animal waste. Sources of nitrate that can enter into the well include fertilizers, septic systems, animal feedlots, industrial waste, and food processing waste. Nitrate concentrations are monitored in municipal water supplies and foods to prevent exposing people to the potential harmful effects of high levels of nitrates. Nitrates are highly soluble, meaning that they easily dissolve in water. For many people in rural areas, the primary source of drinking water is well water, which may be contaminated with nitrates. Nitrates can interfere with the ability of our

red blood cells to carry oxygen. Infants are more at risk of nitrate poisoning than older children or adults. Babies can turn “blue” when there is not enough oxygen being transported by their blood. This “blue baby syndrome” (technically known as methemoglobinemia) is a serious condition that can cause brain damage or death. Water with nitrite levels exceeding 1.0 mg/l should not be used for feeding babies.

Nitrogen is abundant on earth, making up about 80 % of our air as N_2 gas and most plants cannot use nitrogen in gaseous form. However, blue-green algae and legumes have the ability to convert N_2 gas into nitrate (NO_3^-), which can be used by plants. Plants use nitrate to build protein, and animals that eat plants also use organic nitrogen to build protein. When plants and animals die or excrete waste, this nitrogen is released into the environment as NH_4^+ (ammonium). Ammonium is eventually oxidized by bacteria into nitrite (NO_2^-) and then into nitrate, which is abundantly found in fresh water aquatic ecosystem. US EPA gives 10 mg/L as the maximum concentration allowed in human drinking water by the. As per BIS IS 10500: 2012, of India, the acceptable limit of nitrate in drinking water is 45 mg/L and no relaxation for nitrate in the absence of alternate sources. The World Health organization and the European Standards have prescribed 50 mg/L of acceptable nitrate levels in drinking water.

The most commonly used treatment methods to remove/reduce NO_3^- include chemical denitrification using zero-valent iron (Fe0), zero-valent magnesium (MgO), ion exchange (IX), reverse osmosis (RO), electrodialysis (ED), catalytic denitrification and biological denitrification. World Health Organization (WHO) has suggested biological denitrification and IX as nitrate removal methods, while IX, RO, and ED are approved by US EPA are the Best Available Technologies (BAT) to treat NO_3^- contaminated water. However, current available technologies for NO_3^- removal have their own strength and limitations and are found to be expensive, less effective and generate additional by-products. Nevertheless, these traditional technologies do not solve the problem related to the excess of NO_3^- in the environment; in turn, they generate NO_3^- concentrated waste streams that pose a disposal problem due to the high saline content. BATs are relatively expensive and moreover, cause process complexity to be used in in situ application for direct decontamination of groundwater. Zero-valent iron (ZVI) has been extensively studied for its ability to reduce different contaminants including NO_3^- in groundwater. However, it has few limitations which were discussed by various researchers, these include; NO_3^- reduction using ZVI are ammonium production and the pH control

requirement (by initial pH reduction or use of buffer). Furthermore, biological denitrification processes are difficult to apply to inorganic wastewater treatment because additional organic substrates are required to serve as electron donors.

The main objective of this article is to review the mechanism of removal of Nitrate from water by adsorption process, using Chitosan, Clay and Activated Carbon as adsorbents.

II. REMOVAL OF NITRATE FROM WATER USING CHITOSAN AS ADSORBENT

Masheane et al. (2016) developed novel CTs beads embedded with Al and functionalized-multiwall carbon nanotubes (f-MWCNTs) for the denitrification of water and to investigate the interaction between the composite beads and nitrates during the adsorption process. The adsorption of nitrates from water by the CTs-Al/f-MWCNT beads was carried out in a batch adsorption process. Exactly 50 mL nitrate solution of desired concentration (50 mg/L optimal concentration) was placed in a flask and a known amount (1 g) of CTs-Al/f-MWCNT beads was agitated at room temperature for a certain time after which the concentration of nitrates in the solutions were analysed using Dionex ion chromatography spectroscopy 2000 (ICS). The adsorption of nitrates was higher at low pH values. CTs had poor adsorption capacity since the highest adsorption of 23 % was observed at pH 4. Below pH 4 CTs dissolved since its solubility was very high at that pH. CTsAl/f-MWCNTs gave high adsorption capacity and had percentage removal up to 96.8% over a pH range of 2-6. It is observed that there was a rapid uptake within the first 30 min and the adsorption equilibrium was achieved within 60 min for all the adsorbents. Therefore 60 minutes was chosen as the optimal contact time for adsorption. The rate of nitrates adsorption on the surface of CTs and CTs nanocomposite beads was studied using adsorption kinetics models. These models examined the rate of the adsorption. The pseudo first order and pseudo second order kinetics were obtained and plotted. Langmuir and Freundlich models were used to quantify the adsorption capacity of nitrates on CTs and CTsAl/f-MWCNTs. CTsAl/f-MWCNT nanocomposite beads have been found to be effective adsorbents for the removal of nitrate. Compared to CTs which only showed 23% removal at pH 4, Al and f-MWCNTs improved the removal efficiency of CTs and decreased the solubility and swelling capacity of CTs.

Patil et al. (2013) have conducted studies on groundwater nitrate removal by using ‘Chitosan’ as an adsorbent. Powdered chitosan and chitosan solution was used as adsorbent for nitrate removal

from water. 130 samples were collected from agricultural belt. Spectrophotometer method was used for determination of nitrate concentration in groundwater samples collected. Steep decrease in pH with increase in chitosan solution dosage was noted. Chitosan in solution form was found to remove hardness and chlorides and there were significant reductions in nitrate and fluoride concentrations and exhibited disinfection efficiency up to 99.5%.

Sudipta Chatterjee and Seung Han Woo (2009) have worked to determine the efficiency of chitosan in the form of hydrobeads to remove nitrate from its aqueous solution and to investigate the interaction between nitrate and chitosan during adsorption. The effect of pH on nitrate adsorption process was studied over the pH range 3.0–8.0 and the initial nitrate concentration was fixed at 50, 100, 250, 500, and 1000 mg/l. The kinetic behavior of this process was studied at pH 5 and 30 °C using four different initial nitrate concentrations. Langmuir isotherm was acceptable and the adsorption process was homogeneous. The paper concluded that Chitosan hydrobeads were found to be an effective biosorbent for the removal of nitrate from an aqueous solution. Maximum adsorption capacity of nitrate was 92.1 mg/g at 30 °C. Desorption of nitrate from the loaded beads was accomplished by increasing the pH of the solution to the alkaline range.

III. REMOVAL OF NITRATE FROM WATER USING CLAY AS ADSORBENT

Yun Zhang et al. (2011) investigated on the Enhanced removal of nitrate by a novel composite: Nano scale zero valent iron supported on pillared clay. They conducted studies on the PILC, which was prepared from bentonite by intercalation with poly hydroxyl Al (III) cations, and used as the carrier of NZVI. The performance on removing nitrate of this novel composite NZVI/PILC was tested by batch experiments, and compared with that of the bare NZVI. Effect of dissolved oxygen on the removal efficiency was investigated, and the kinetics of reactions and end products of reduction were also analyzed. The results indicated that the PILC is an excellent matrix to carry NZVI. Effectively, it prevented the NZVI particles from aggregating together. The PILC also promoted the mass transfer of nitrate from solution onto iron surface, leading to the enhanced removal efficiency. The kinetics of nitrate removal by NZVI or NZVI/PILC fitted well with the Langmuir–Hinshelwood model. The reaction constant and adsorption constant of NZVI/PILC treatment were both much higher than those of NZVI alone, indicating the reaction rate is positively related to the adsorption.

Mahmoud El Ouardi et al. (2015) has conducted studies to determine the adsorption capacity of locally available natural clay materials originated from a dam situated in Morocco (Agadir city) and to remove nitrate from its aqueous solution. Hence, the effect of various parameters on the adsorption process has been investigated. It is notable that the kinetic of nitrate adsorption consists of two phases, an initial rapid phase when the process is very fast and a second slower phase when it reaches equilibrium. The initial high rate of nitrate uptake is probably due to the greater availability of binding sites near the surface of the clay. The adsorption equilibrium state was reached after a contact time of 180 min with $Q_e = 215.69$ mg/g. Adsorption kinetic study revealed that the adsorption process followed first order Kinetics. Theoretical correlation of the experimental equilibrium and adsorption data for the Nitrate-New Clay system was properly explained by the Langmuir isotherm mode with $R^2 = 0.9$. The maximum adsorption capacity was $Q_m = 244.06$ mg/g at 20 °C and at natural pH. An increase in adsorbent dosage increased the percentage removal of nitrate. 1 g/l was considered as optimum dose and was used for further study. The pH heavily affected the adsorption capacity, and the percentage removal was found to decrease with increase in pH. The obtained results indicated that this New Clay (NC) was very good adsorbent for NO_3^- , and interesting alternative material with respect to more costly adsorbent used.

Jianfa Li et al. (2010) aimed to enhance the efficiency of Fe (0) on removing nitrate by using the pillared bentonite as adsorbent. For this purpose, the pillared bentonite was prepared by intercalation of poly hydroxo Al (III) cations. The continuous column experiments were performed to examine the efficiency on nitrate removal by Fe (0) mixed with the pillared bentonite. For the comparison study, the nitrate reduction by Fe (0) alone and the nitrate adsorption on the pillared bentonite were also investigated. The nitrate removal efficiency was at 100% for 10–40 h depending on the initial pH of influent nitrate solution and the amount of OH-Al-bent used. The pillared bentonite played multiple roles in the mixture including, adsorption to nitrate ions, which facilitated the mass transfer of nitrate from solution onto solid surface, acid catalyst for the nitrate reduction due to its surface acidity, the sustained release of hydrogen protons through cation exchange with iron cations which could explain the high efficiency on nitrate removal even when the solution was fed at nearly neutral pH.

Saeed Bagherifam et al. (2014) selectively removed the nitrate and perchlorate from aqueous solution by organoclays which was prepared using montmorillonite and hexadecylpyridiniumchloride (HDPyCl). The cationic surfactant modified

organoclay was prepared at room temperature using HDPyCl corresponding to 4 times the cation exchange capacity (CEC) of Na-montmorillonite. Powder X-ray diffraction (XRD) analysis of the above organoclays showed a large basal spacing of 40.27 Å with the intercalation of HDPy cations in the interlayers probably as a result of a paraffin-type bilayer arrangement. The nitrate and perchlorate uptakes by this organoclay could be described well using the Langmuir isotherm while their uptake kinetics fitted well to the pseudo-second order model. The maximum adsorption capacities of nitrate and perchlorate by the organoclay, HDPy-montmorillonite were calculated at 0.67 and 1.11 mol g⁻¹. Nitrate and perchlorate uptake kinetics were found to be fast as equilibrium was reached within 4 hours. Furthermore, the uptakes of nitrate and perchlorate by HDPy-montmorillonite were found to be highly selective in the presence of Cl⁻, SO₄²⁻ and CO₃²⁻, the most abundant naturally occurring anions. Therefore, the HDPy-montmorillonite could be used as a highly efficient adsorbent for the separation of nitrate and perchlorate from drinking water.

IV. REMOVAL OF NITRATE FROM WATER USING ACTIVATED CARBON AS ADSORBENT

Kashefi Asl et al. (2016) have studied on activated carbon and Clinoptilolite sorbents for the removal of nitrates from water. Effects of contact time, temperature, pH, adsorbent dosage, initial nitrate concentration, adsorption isotherms and adsorption kinetics in the nitrate removal process was determined. The results showed that activated carbon sorbent is much better than Clinoptilolite and has more ability to remove the activated carbon. The best efficiency for nitrate removal from 60ml water for activated carbon in a 4 g dose sorbent, contact time of 60 min, temperature of 20° c, pH=6.5 and the initial concentration of 100 mg/lit is 62.61 % and from Clinoptilolite, in terms of 4 g adsorbent dosage, contact time of 60min, temperature of 20° c, pH=5.5 and the initial concentration of 100 mg/lit was 8.7 %. Nitrate adsorption by activated carbon had a correlation coefficient of 0.968 which followed Freundlich isotherm. Clinoptilolite with a correlation coefficient of 0.976 followed the Langmuir isotherm. Pseudo-second order kinetics for activated carbon and pseudo-first order kinetics for clinoptilolite was observed.

Mazarji et al. (2017) investigated on a commercial granular activated carbon which (AC) was treated with sodium hydroxide followed by a cationic surfactant (acetyl trimethyl ammonium bromide) to increase its efficiency for nitrate removal. They intended to study the effect of the alkaline treatment on the texture properties of the commercially activated carbon and to evaluate the

combination of two treatments on adsorption of nitrate in batch and small continuous column experiments. The results of SEM analysis were consistent with the results obtained from analyzing the activated carbons using N₂ adsorption isotherm. The micro pore volume increased to 0.400 cm³g⁻¹ (in AC-2). These results are consistent with BET surface area where lower surface area was observed for AC compared to AC-1. However, the cationic surfactant modification leads the surface area to become smooth. As a result, the surface area and pore volume of the activated carbon decrease. AC and AC-1 exhibited a poor performance for nitrate adsorption. In case of the quaternary ammonium functional groups, left after cationic surfactant modification on the surface of AC-2, led to increase the affinity towards the nitrate. These results indicated that higher specific surface area is not necessarily guaranteed a higher adsorption capacity towards nitrate anion. In this study, AC-2 exhibited the lowest value of specific surface area among other adsorbents, in spite of its highest amount of nitrate uptake. Due to the better removal efficiency evidenced for AC-2, the subsequent batch experiments were carried out by using AC-2. When the pH changes, the amount of nitrate adsorbed on AC-2 does not significantly change. The highest nitrate adsorption occurred at pH 5 (almost the same value compared to pH 7). However, the lower pH value did not favor the higher adsorption of nitrate. Besides, the sharp decrease of nitrate adsorption below pH 5 may be related to the competition of Cl⁻ ions with nitrate anions. The results showed that as the adsorbent dosage increases from 0.05 to 0.5 gL⁻¹, the nitrate percentage removal increases from 25 to 83%. Whereas the adsorption capacity decreases from 11 to 3.3 mg/g. This was because of the fact that the increased percentage removal of nitrate with increasing AC-2 dose provided the availability of more active surfaces sites of the adsorbent form adsorption. The effect of contact time on nitrate adsorption with two different initial nitrate concentrations of 40 and 80 mgL⁻¹ at an optimum adsorbent dosage and optimum pH. The availability of plenty active sites on the AC-2's surface led to a rapid uptake of nitrate in the beginning. The time required for equilibrium adsorption is 120 min. Equilibrium time does not change with increasing initial nitrate concentration from 40 to 80 mg/L, while the amount of nitrate adsorbed is increased with increase in initial nitrate concentration. The obtained values of the used kinetic models best fitted to the pseudo-second-order kinetics. The feasibility of each adsorbent to treat synthetic nitrate solution was investigated in small column experiments. Modifications lead to increase in the lifetime of adsorbents. For AC-2, the breakthrough was 54 bed volume (BV), while BV was 6.8. This improvement

in the lifetime indicates the feasibility of using AC-2 in continuous condition to remove nitrate from aqueous solution compared to the other adsorbents. Gunduzoglu et al. (2010) have conducted studies on removal of nitrate from aqueous solutions by activated carbon prepared from sugar beet bagasse and chemically activating with $ZnCl_2$. Activated carbon was prepared by 10-30g of $ZnCl_2$ in 300ml distilled water and 10g dried bagasse is stirred for 6hrs at 80° c. Use of $ZnCl_2$ as activator increased pore volume and size of adsorbent. The effects of pH, temperature and contact time were investigated. Isotherm studies were carried out and the data were analyzed by Langmuir, Freundlich and Temkin equations. Three simplified kinetic models were tested to investigate the adsorption mechanism. Maximum removal of nitrate 41.2% was obtained at pH 3. The kinetics studies indicated that the pseudo-second-order equation provided the better correlation of the adsorption data. The Langmuir model was found to provide the best fit of the experimental data.

V. CONCLUSIONS

The presence of elevated concentrations of nitrate in potable water has become a serious concern worldwide. Adsorption is promising process due to being economical and less production of sludge and fewer disposal problems in removal of nitrate from water. This seminar report discusses three different adsorbents for its use in nitrate removal in its original as well as modified forms. Effects of pH, contact time, surface modifications, initial nitrate dosages and check for the kinetic studies have been observed. The Chitosan was used as powder, hydro-beads as well as in solution form because it exhibits properties of biodegradability and non-toxicity. The solution showed greater nitrate removal without imparting turbidity and showed up to 99.5% disinfection capacity. It is also absorbed that surface modification of chitosan with acid treatment increased surface area by putting carboxyl function group on surface this improved removal of impurities. Chitosan also has high reusability property when treated with alkaline solution. Also, chitosan could be a suitable matrix for immobilizing microalgae with *Scenedesmus* sp. which was more efficient in removing phosphate and nitrate from water than the conventional free cell system. The pillared bentonite, i.e. Organoclays with montmorillonite prepared by intercalating poly cations in to interlayers which made the particles hydrophobic to improve its cation exchange showed higher removal of nitrate from aqueous solution. Nitrates were selectively removed over chlorides and sulphates in the water. The pillared bentonite played multiple roles in adsorption to nitrate ions, which facilitated the mass transfer of nitrate from solution

onto solid surface, acid catalyst for the nitrate reduction due to its surface acidity, the sustained release of hydrogen protons through cation exchange with iron cations which could explain the high efficiency on nitrate removal even when the solution was fed at nearly neutral pH. The activated carbons used in the selected studies are obtained from sugar beet bagasse, commercially available one and modified activated carbons. The adsorption study was influenced by impregnation ratio of activators and activated carbon. The batch experiments conducted with the activated carbons showed high efficiency in removal of nitrate because of high pore volume and specific surface area. The activated carbons also showed its regenerative capacity and have let researchers think of developing the synthetic activated carbons in near future.

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