

# Recovery of Nitrate from Water Using Chitosan/Bentonite Biocomposite in a Continuous Stirred Tank Reactor

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## Abstract

In this study, Chitosan/Bentonite (ChBT) biocomposite was prepared and utilized for the recovery of nitrate from water in continuous stirred tank reactor under various operational conditions. The results revealed that nitrate recovery efficiency of ChBT was significantly affected by the variation of flow rate, initial concentration and ChBT loading. The nitrate recovery efficiency increased with increase in ChBT load and decreased with increase in influent nitrate concentration and flow rate. In addition, the service time increased with increase in ChBT load. The result show that ChBT biocomposite could be used in continuous flow reactors for the recovery of nitrate from water.

**Keywords:** Biosorption; Chitosan/Bentonite biocomposite; CSTR; Recovery of nitrate;

## Introduction

Anthropologic activities including industrialization and agricultural practices contribute immeasurably to the pollution of the environment and pose a threat to the global water supply [1-5]. Among various inorganic pollutants, nitrate is possibly one of the most prevalent chemical pollutants in water resources and has become a worldwide crucial apprehension [6]. Agriculture is a major contributor of nitrate to surface waters and groundwater pollution due to excessive and long-term use of chemical fertilizers and animal manures on cropland [7-9]. The epidemiological studies show that drinking water is the main source of nitrate and intake of water with high nitrate concentrations has considerable health effects [6]. The toxicity of nitrate to humans is mainly attributable to its *in vivo* reduction to nitrites. Ingested nitrate is reduced to nitrite, which binds with hemoglobin to form methemoglobin by oxidation of ferrous iron (Fe<sup>2+</sup>) in hemoglobin to ferric form (Fe<sup>3+</sup>). This prevents or reduces the ability of blood to transport oxygen and leads methaemoglobinaemia, the so-called "blue-baby syndrome" which is dangerous especially in infants causes cyanosis, asphyxia and consequently to death, at higher concentrations [6, 7, 10-13]. This is the primary adverse health effect associated with human exposure to high level of nitrate in water.

Moreover, the reduction of nitrate to nitrite in the alimentary canal and nitrite readily reacts with amide and amino compounds to generate N-nitroso compounds (NOC), most of which are potentially carcinogenic for humans [7, 12, 14-16]. Other diseases associated with intake of high concentration of nitrate in water are hypertension, increased infant mortality, central nervous system birth defects, diabetes, weakness, mental depression, headache, diarrhea, spontaneous abortions, and

changes to the immune system [7, 6]. High nitrate concentrations in water bodies contributes to eutrophication and this can lead to development of anoxic conditions by depleting dissolved oxygen, increase in plant and animal biomass, and affects the biodiversity [6, 7, 17]. The World Health Organization (WHO) and US Environmental Protection Agency (USEPA) set the Maximum Contaminant Level (MCL) of nitrate ions in drinking water to be 50 mg/L and 45mg/L as NO<sub>3</sub><sup>-</sup>, respectively [7, 15, 18] and many countries have formulated their own MCLs according to their domestic conditions.

The removal of nitrate from water has been a subject of extensive academic and industrial research to limit the risks associated with high nitrate concentration and to meet the regulatory limit. Various technologies are currently available to remove nitrate from water [2, 19]. Among the unit operations in water treatment, adsorption is an economical and environmentally friendly treatment technique with ease of operation, simplicity of design, allows nitrate recovery, and feasibility to implement in field conditions and in point of use treatment systems. Furthermore, this process can remove multiple pollutants from water and wastewater [19-22].

Several types of materials such as activated carbon, such as activated carbon, activated waste sepiolite, layered double hydroxides (LDHs) and agricultural wastes [19] have been explored for removal of nitrate from water. However, modification and production process of such materials consumes great quantity of energy and chemicals which intern involving environmental costs. Therefore, there is a need of alternative low-cost, eco-friendly, locally available in nature, biodegradable, and sustainable adsorbent materials for the removal of nitrate from water and wastewater that have pollutant binding capacities has increased to replace the conventional and expensive adsorbent materials based on economic and environmental point of views [19-22]. This need has promoted the increased scientific study of adsorbent materials from biological origin during the last decades. Recently, great attention has been driven towards the natural materials and their derivative products, such as cellulose, lignin, starch, alginate, gelatin, chitin, and chitosan for the removal of aquatic pollutants [24-28]. These biomaterials obtained from biomass by relatively simple process that uses considerably lower quantities of chemical substances and energy, compared to the production of conventional adsorbents. Besides, most adsorbents materials are obtained from byproducts of waste during industrial or agricultural processes [24-28]. Among these biomaterials, chitosan has received wide attention in the

**Received date:** May 23, 2018; **Accepted date:** June 20, 2018; **Published date:** June 25, 2018

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**Citation:** Golie WM, Ambethkar Y, Sreedevi U (2018) Recovery of Nitrate from Water Using Chitosan/Bentonite Biocomposite in a Continuous Stirred Tank Reactor. *J Environ Bio Res.* 2(1)

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environmental engineering field as effective adsorbents for the removal of various aquatic pollutants [29-32]. The presence of functional group like amino and hydroxyl in its molecules contributes many possible adsorption interactions between chitosan and pollutants [32]. However, chitosan in its original form is not suitable for practical use due to its poor chemical and low mechanical stability and finally, these properties restrict its field applications. Therefore, chitosan needs certain modifications to overcome the abovementioned limitations. Bentonite is an attractive immobilization inorganic material for chitosan due to its environmental benignity, low cost as well as chemical and mechanical stability. The previous report [33] demonstrated that chitosan based organic-inorganic hybrid biocomposites are efficient, cost effective, and eco-friendly materials for the removal of nitrate from water.

Numerous studies on the removal of nitrate from water and wastewater using a various of adsorbents which has been reported in the literature and most of the studies on nitrate adsorption were focused on batch equilibrium studies [19, 20, 34]. However; batch studies are only limited to investigate the characteristics of the adsorbent and the results obtained cannot easily applied directly to continuous process [35]. Continuous process is simple to operate and can be controlled easily, can be easily scaled up from a laboratory-scale procedure, and it is economical process [36, 37]. In a continuous adsorption, adsorbent is continuously in contact with fresh nitrate solution and therefore efficient utilization of adsorbent can be achieved. Moreover; continuous adsorption study can be used to identify the feasibility of the adsorbent under continuous loading with nitrate ion [34, 38]. Therefore, it is important to study the dynamic behavior in a continuous operation. Once the biosorbent is saturated, it can be regenerated for cyclic use or can apply on the cropland as an alternative fertilizer. These uses ensure both economic and environment benefits by avoiding contamination of the ground water [39-41].

The present work demonstrates the use of chitosan/bentonite biocomposite for the removal of nitrate from water in continuous stirred tank reactor with the aim of minimizing the negative impact of nitrate pollution and recovery of nitrate. The objectives of this study were to investigate the effect of operational conditions, such as influent nitrate concentration, flow rate, and biosorbent dose on the performance of continuous flow system for continuous removal and recovery of nitrate from water.

## Materials and Methods

### Materials

Chitosan pure (85% deacetylated and M.W 193400 g/mol) and

potassium nitrate were purchased from Sisco Research Laboratory (SRL), New Delhi (India). Glutaraldehyde solution (25%) was purchased from Central Drug House (CDH), New Delhi (India). Glacial acetic acid, bentonite, and potassium hydroxide were purchased from Fisher Scientific, New Delhi (India). Hydrochloric acid (GR, 35%) was purchased from Merck, New Delhi (India).

### Preparation of chitosan/bentonite biocomposite

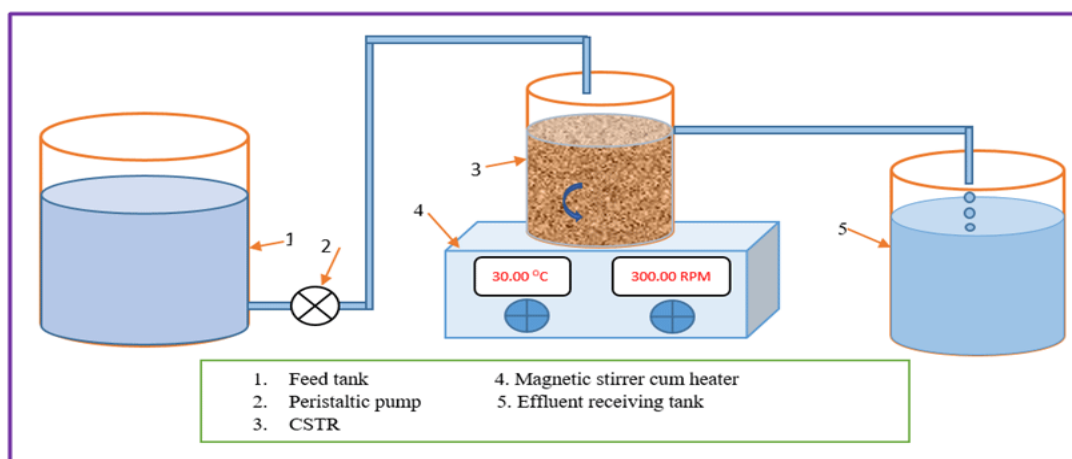
The chitosan/bentonite biosorbents was prepared with modifications of the procedure of previous reports [33, 34]. Chitosan solution was prepared by dissolving 5.0 g of chitosan powder in 200 ml of 5% (v/v) acetic acid solution and kept stirred at room temperature for 24 h to ensure that the chitosan was completely dissolved. Chitosan/bentonite mixture was prepared by dispersing 5g of bentonite powder into chitosan solution. The mixture was stirred at 50°C for 1h and ultrasonicated for another 1h. Subsequently, glutaraldehyde solution (25% v/v) was added drop wise to chitosan/bentonite mixture a cross linker to chitosan solution ratio of 1:40 and stirred vigorously for 15 min. The mixture was kept in refrigerator at 4°C for 24h to undergo cross linking reactions. The cross linked chitosan/bentonite biocomposite was washed several times with deionized water to remove any unreacted glutaraldehyde. Cross linked chitosan/bentonite biocomposite was modified by acid treatment in order to activate bentonite as well as to protonate the amine groups of chitosan. In this case the crosslinked biocomposite was treated with 1 M HCl solution at 50°C for 1h. The resulting biocomposite was separated from acidic solution by filtration and rinsed with deionized water several times to neutral pH, dried in an oven at 60°C for 24h, and then pulverized to a uniform size and stored in a sealed container for further use. The prepared biosorbent is denoted as "ChBT".

### Characterization

Surface morphology study and elemental analyses of samples were conducted using SEM and EDX, respectively on ZEISS EVO 18 model. Fourier transform infrared spectroscopy (FT-IR) spectra were collected with NICOLET iS50FT-IR model using KBr pellets. Point Zero Charges (PZC) of the biosorbents were determined through solid addition method as reported by Sharma et al [42]. Characterization results are presented in the previous report [33].

### Experimental set-up

Continuous biosorption studies were conducted in a continuous stirred tank reactor to evaluate the performance and biosorption profile of chitosan/bentonite biocomposite on the recovery of nitrate from



**Figure 01:** Schematic diagram of semi-continuous stirred tank reactor

water. Continuous stirred tank biosorption experiments were carried out in a magnetically stirred glass reactor of effective volume 300 ml. The experiments started by loading a known quantity of biosorbent into the reactor and which was then completely filled with nitrate solution. Afterwards, nitrate solution was continuously fed into the reactor tank at a particular flow rate and influent nitrate concentration and the magnetic stirrer continuously stirred at 300 rpm. The flow rates were adjusted by operating a peristaltic pump. Microfilter was fixed at the outlet of the reactor tank to avoid loss of biosorbent material during out flow of solution from the reactor. A schematic diagram of the experimental set-up used is shown in figure 1.

### Continuous flow biosorption experiments

Continuous stirred tank biosorption experiments were carried out at temperature of  $25 \pm 2$  OC and at the solution pH value of  $6.8 \pm 0.2$ . The effects of significant parameters such as influent nitrate concentration, flow rate, and mass of biosorbent on the amount of nitrate removed were investigated. Effect of influent nitrate concentration on nitrate removal was investigated with initial nitrate concentrations of 100, 150, and 200 mg/L, at a flow rate of 0.36 L/h, and biosorbent load of 10 g. Effects of contact flow rate (0.12, 0.24, and 0.36L/h) on the removal of nitrate from water was investigated at the influent nitrate concentration of 200 mg/L and biosorbent load of 10 g. The effects of varying the biosorbent load (5, 10, and 15 g) were studied, while flow rate of 0.36 L/h and initial influent concentration of 200 mg/L were kept constant. Sampling of reactor and column effluents were done at certain time intervals and analyzed for the remaining nitrate concentration using methods reported in the previous study [34].Regeneration experiment was conducted by passing 0.1 KOH solution through the reactor at flow rate of 0.36 L/h for 1 h followed by rinsing with deionized water for another 1 h with the same flow rate after each cycle of regeneration. figure 2.

## Results and Discussion

### Biosorption Studies

Studies conducted on the recovery of nitrate from water in continuous stirred tank reactor biosorption system indicated that the biosorption process is influenced by various operational parameters. These included the influent nitrate concentration, the flow rate of the feed solution, and the mass of biosorbent at an optimum temperature of  $25 \pm 2$  OC and at the solution pH value of  $6.8 \pm 0.2$ . For the evaluation of the experimental data, the total amount of nitrate removed by the biosorbent for a given feed nitrate concentration and flow rate were calculated from the difference between the total amount of nitrate fed to the reactors and the amount present in the bulk of the effluent immediately after column saturation. The maximum adsorption capacity for each experimental set up was determined as the total amount of nitrate ions adsorbed per gram of biosorbent to the total amount of nitrate ions fed to the column. Breakthrough curves for different flow rates, influent nitrate concentration and biosorbent dose

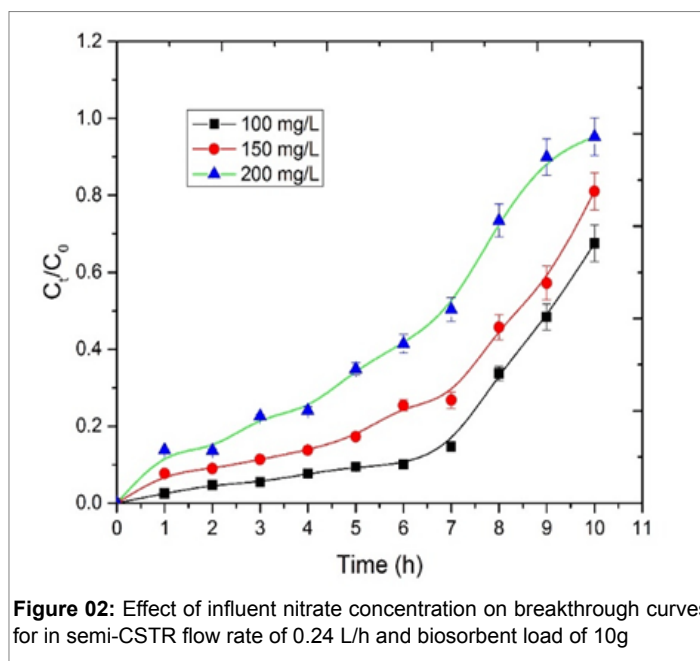


Figure 02: Effect of influent nitrate concentration on breakthrough curves for in semi-CSTR flow rate of 0.24 L/h and biosorbent load of 10g

were plotted as the ratio of influent nitrate concentrations to effluent nitrate concentration ( $C/C_0$ ) versus time.

### Effect of influent nitrate concentration

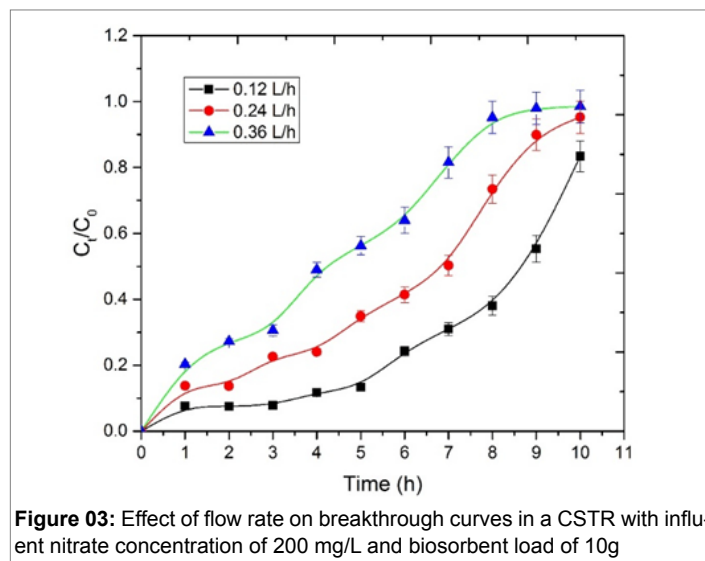
Effect of influent nitrate concentration on nitrate removal was investigated with initial nitrate concentrations of 100, 150, and 200 mg/L, at constant flow rate of 2.5 ml/min and biosorbent load of 11.76 g. The changes of effluent nitrate concentration vs. time experiment are illustrated in Fig 2 and continuous flow biosorption parameters at different influent nitrate concentration are presented in Table 1. In the initial hours, the biosorbent effectively removed nitrate at all the influent nitrate concentrations studied in both reactors. As the experiments continued, the concentration of nitrate in the effluent increased slowly indicating that the biosorbent became saturated. On the other hand, the percentage removal and time required for attaining breakthrough decreased with increase in influent nitrate concentration. Increasing the influent concentration from 100 mg/L to 200 mg/L resulted a steeper breakthrough curve, while the broader curves were obtained at lower concentration values. At higher influent nitrate concentrations available biosorbent sites are quickly filled and resulting in reduced breakthrough time and nitrate removal efficiency [34]. However, it was observed that the total amount of nitrate removed by the biosorbent increased with the increase in initial nitrate concentration. This may be due to concentration gradient of the adsorbate which is the driving force for higher mass transfer rate and this is directly related to the initial concentrations [45].

Table 1: Parameters in continuous flow biosorption of nitrate by ChBT biocomposite at different influent nitrate concentrations, flow rate, and biosorbent load

$C_0$ (mg/L)	Q(L/h)	Biosorbent load (g)	$t_b$ (h)	$t_e$ (h)	$V_b$ (L)	$V_e$ (L)	$q_{tot}$ (g)	%R
100	0.24	10	7	10	1.68	2.4	430.06	89.6
150	0.24	10	6	9	1.44	2.16	579.5	80.49
200	0.24	10	4	8	0.96	1.92	615.08	71.19
200	0.12	10	6	10	0.72	1.2	393.57	81.99
200	0.36	10	2	9	0.72	3.24	678.41	67.30
200	0.24	5	2.75	8	0.66	1.92	454.23	65.79
200	0.24	15	10	1.68	2.4	776.07	90.84	90.84

### Effect of flow rate

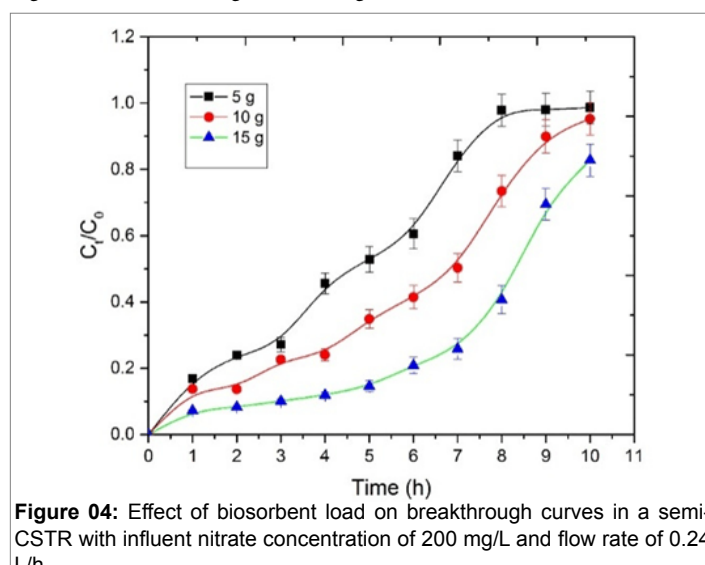
Contact time is an important parameter to determine the minimum time required for substantial biosorption to take place [46]. Effect of flow rate on the removal of nitrate from water was investigated at the influent nitrate concentration of 200 mg/L and biosorbent load of 11.76 g. The changes of nitrate removal vs. time profile are shown in Figure 3 and continuous flow biosorption parameters at different flow rate are presented in Table 1. The results revealed that there was a negative relationship between flow rate and nitrate removal efficiency. Higher nitrate removal efficiencies were obtained at lower flow rate. A lower flow rate resulted in a longer residence time in the reactor which resulted sufficient contact time between biosorbent and nitrate [34]. figure 3.



**Figure 03:** Effect of flow rate on breakthrough curves in a CSTR with influent nitrate concentration of 200 mg/L and biosorbent load of 10g

### Effect of biosorbent dose

Biosorbent dosage was an important parameter influencing adsorption capacity and effluent concentration. The effect of biosorbent dose was investigated with influent nitrate concentration of 200 mg/L and flow rate of 2.5 ml/min. The effect of biosorbent dosage on nitrate removal was depicted in Fig. 4 and Table 1. It was evident that the nitrate removal efficiency increased with the increase in biosorbent dosage. The increment can be elucidated by the fact that for a fixed initial nitrate concentration, the number of active site will be higher and surface area will be larger at higher biosorbent dosage [47, 48]. figure 4.



**Figure 04:** Effect of biosorbent load on breakthrough curves in a semi-CSTR with influent nitrate concentration of 200 mg/L and flow rate of 0.24 L/h

### Conclusions

The recovery of nitrate from aqueous solutions was conducted in a CSTR and fixed-bed column system using ChBT biocomposite. The effects of process parameters such as flow rate, initial nitrate concentration and biosorbent load on the performance of the continuous flow system were investigated. The change in biosorbent dose significantly affected the column performance by increasing the breakthrough and exhaustion time and total removal percentage of nitrate was greatly increased. Conversely, the increase in flow rate and initial concentration tended to decrease in the breakthrough and exhaustion time and hence lower percentage of nitrate removal. Hence, appropriate parameters are important for the operation of the continuous system in order to achieve optimum performance. The result show that ChBT biocomposite is effective biosorbent and could be applied in large scale continuous flow system for the recovery of nitrate from water. Moreover, ChBT biocomposite is low-cost and saturated biosorbent could be applied in a cropland as an alternative fertilizer. These uses ensure both economic and environment benefits by avoiding contamination of the ground water.

### Acknowledgements

The authors are thankful to College of Engineering, Deffence University for funding the research.

### Nomenclatures

C <sub>b</sub>	Breakthrough concentration (mg/L)
C <sub>o</sub>	Initial adsorbate concentration (mg/L)
C <sub>t</sub>	Effluent adsorbate concentration (mg/L)
M	Biosorbent load (g)
q <sub>total</sub>	Total amount of nitrate adsorbed (mg)
R	Total percentage removal of nitrate (%)
t <sub>b</sub>	Breakthrough time (h)
t <sub>e</sub>	Exhaustion time (h)
V <sub>b</sub>	Breakthrough volume (L)
V <sub>e</sub>	Total effluent volume (L)

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