# Rice Industry Waste as Wastewater Treatment

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## ABSTRACT

*Treatment of waste water by biological denitrification experiment was conducted using rice industry wastes, namely final husk-2 as a carbon source and husk charcoal pellets as supporting media for denitrifying bacteria. We employed an upflow fixed-bed reactor filled with the pellets and biofilm attached onto them. This was fed with potassium-nitrate and dilute-husk-2 solutions. Total nitrogen removals of more than 85 % were achieved at influent carbon-nitrogen ratios between 2 and 4, and hydraulic residence times of more than 0.8 (h). This demonstrated final husk-2 could be used as an alternative carbon source. On the other hand, final husk-2 also contained some organic/ammonium nitrogen and refractory organic matter including colors, both of which were difficult to remove with the reactor. Accordingly, at higher C/N ratios, these substances caused major increases in effluent total-nitrogen and organic-carbon concentrations. Therefore an optimum C/N ratio was found to be around 2.*
**Keywords:** Absorption; Coagulating; Dissolved; Settling; Treatment

## INTRODUCTION

Waste water treatment is one of the big issue no w days in which groundwater pollution by nitrate has become increasingly serious in remote jamnagar, as the city rely most of drinking and irrigation waters on groundwater. Such nitrate pollution is mainly attributed to human activities including agriculture. In the Jamnagar city for example, nitrogen in groundwater was estimated to derive from fertilizers (49 %), livestock wastes (25 %), domestic sewage (5 %) and natural sources (19 %) [1]. Such human activities have already had effect on groundwater quality in those islands. Most of the islands have quite permeable soils that originated from coral reefs, and therefore the effects of human inputs of nitrogen could quickly appear in groundwater. In the India, for instance, $NO_3$-N concentrations between 10 and 19 (mg/L) have occasionally been observed in groundwater. The nitrogen cycle is shown in Fig. 1.
 In order to remove those nitrates, the local authority has equipped their water purification plant with a reverse osmosis process since 1997. Such an advanced technology would be reliable but rather energy-consuming and costly. One of the alternatives to such a technology is biological denitrification using fixed or fluidized bed reactors. For enhancing the denitrification reaction, various chemicals were usually added as organic carbon sources, such as methanol, ethanol, acetic acid or sucrose [2]. Although many experiences have been accumulated regarding this method, it still needs costs for chemicals. In order to reduce such costs, biomass or biomaterials have also

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been tried out as a carbon source.  Some of them were solid ones such as wheat straw [3-5], newspaper [6] and cotton [7].  Nevertheless, denitrification rates using those materials seemed to be rather slow for practical purposes, due in part to slow release of available carbon from them.
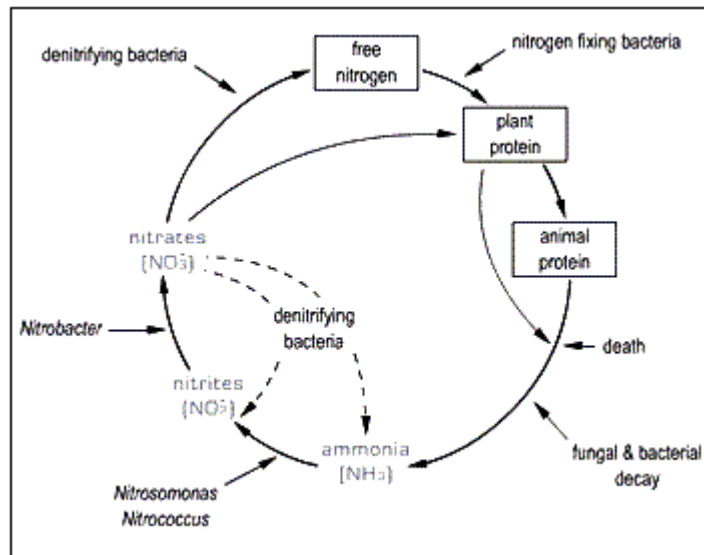


**Fig. 1: Nitrogen cycle Model**

By contrast, some studies employed high-strength liquid organic wastes as carbon sources, including brewery wastes, whey, yeast, other bio-industry wastes and silage effluents [8, 9].  In some selected cases, they achieved denitrification rates comparable to the processes using methanol. Similarly some textbooks have also proposed final husk-2, a rice-industry waste, as a carbon source [10-12].  Nevertheless, few experiences have been accumulated so far on denitrification using final husk-2.

The present study therefore examines final husk-2 as an alternative carbon source.  It is a viscous, dark-brown ash byproduct that is produced after refined into white rice.  It is particularly rich in organic matter, which includes rice.  In addition, the authors also employed charcoal pellets made from a mixture of husk and final husk-2, as supporting media for denitrifying bacteria.  Husk is solid, fibrous residue left after rice was extracted.

Thus, this study aims to employ final husk-2 and husk, both of which are byproducts from rice-processing, for a denitrification experiment. These materials were chosen because they were easily obtainable in India.

## MATERIALS AND METHODS

### Preparation of husk charcoal pellets and apparatus

1. Husk and final husk-2 were obtained from Rice Industries Ltd. Gujarat, India. A 2.75 (L) (7 (kg)) of the husk was carbonized at 800 (°C) for 2 (h) with a furnace DCP-31.  Upon carbonization, oxygen within the furnace was purged with nitrogen gas.

2. Thereafter the volume of produced charcoal became about a half that of the raw husk.  The charcoal was crushed to powders by hand, and then mixed with 500 (g) of final husk-2 and 2.5 (L)

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of tap water.The final husk-2 was supposed to act as binder in producing pellets in the following steps.

3. The above mixture was formed into pellets with a press pelletizer FMP-300. At this stage, the pellets were not hard enough for use in water treatment.

4. Therefore the pellets were again carbonized at 800 (°C) for 2 (h) to increase their hardness. Finally, pellets with the following properties were obtained: a volume of 2.7 (L); a weight of 1.0 (kg); a diameter of 5 (mm); and a length of 5 to 10 (mm).

5. Meanwhile an upflow column was made with a transparent plastic pipe (Figure 2). This was filled with the husk-charcoal pellets at a depth of 80 (cm), and placed in a constant-temperature chamber.
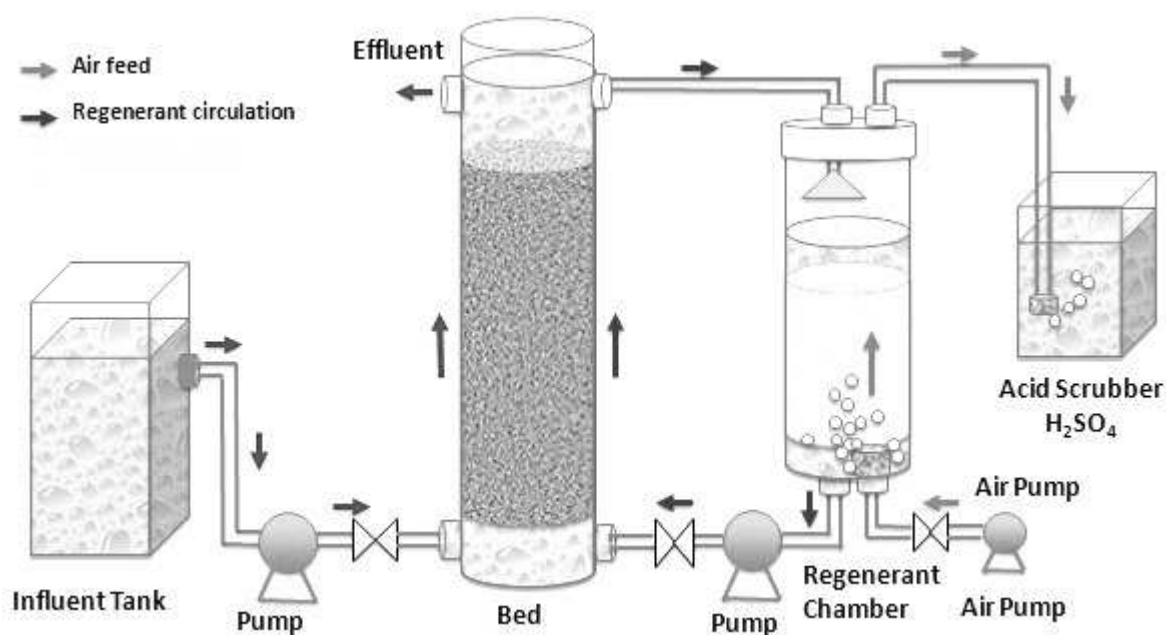


**Fig. 2: Schematic diagram of the apparatus**

**Inoculation of denitrifying bacteria**

1. A 12 (g) of final husk-2 and 17 (g) of potassium nitrate were dissolved with 20 (L) of tap water. About 10 (g) of surface soil sampled at a rice farm in the Jamnagar city was added to this solution for seeding it with denitrifying bacteria.

2. The above solution was pumped into the upflow column, at a hydraulic residence time (HRT) of 6 (h). The effluent from the column was recirculated into the column. During this operation, appropriate amounts of final husk-2 and potassium nitrate were occasionally added to the solution in order to sustain bacterial growth.

3. The above operation was continued for 35 days. Consequently thin biofilm appeared on the surface of pellets in the column. At this stage, a reduction in nitrate concentration was also confirmed in the column, indicating that the biofilm would contain some denitrifying bacteria.

**Continuous denitrification experiment**

Next a continuous denitrification experiment was conducted for 77 days. The column was washed with air bubbles roughly once or twice a week throughout this experiment. Two kinds of substrate solutions, namely potassium nitrate and dilute final husk-2, were prepared and stored in separate tanks (Figure 2), and injected to the column at a flow-rate ratio of 5:1. The influent to the column

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was sampled after these two solutions were injected and mixed (Figure 2). The influent $NO_3$-N concentration was maintained around 20 (mg/L), which roughly corresponded to the highest groundwater concentration observed. Meanwhile two parameters were varied in this experiment, namely the concentration of final husk-2 solution and the flow rate. This gave influent TOC concentrations ranging between 11 and 175 (mg/L), column flow rates between 5.3 and 58.1 (m/d), and hydraulic residence times (HRT) between 0.33 and 3.40 (h). The experiment was conducted with a temperature controlled at $25\pm1$ (°C), and ambient pH and ORP in a range of 6.6-7.3 and 31-301 (mV), respectively. The flow diagram for the experiment was shown in Fig. 3.
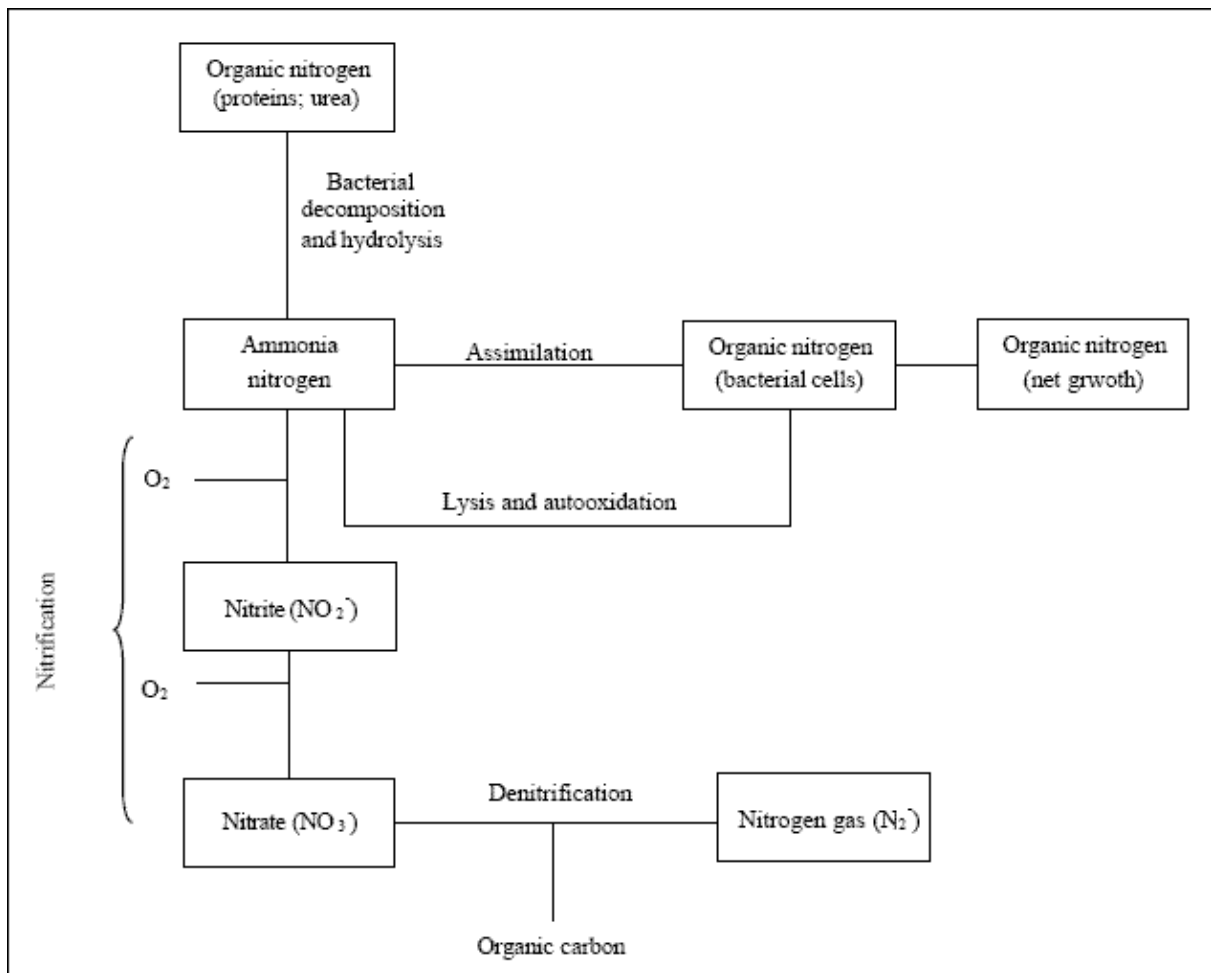


**Fig. 3: Flowchart of the experiment**

**Analytical methods**

Total organic carbon (TOC) of water samples was analyzed with TOC-5000, total nitrogen (T-N) with TN-301P, and inorganic ions with an ion chromatograph DX-320J. A total concentration of $NO_2$-N and $NO_3$-N was indicated as $NO_x$-N, but $NO_3$-N was a dominant form in all the samples. Total and suspended solids were measured according to the Standard Methods for the Examination of Water and Wastewater 2540 B and D, respectively [13]. Apparent color was measured with non-filtered samples, using a spectrophotometer. Thus, possible effects of light scattering by suspended solids were not eliminated in these measurements. The wavelength was set at 390 nm, which was designated for color measurement in the Indian Drinking Water Examination Methods. In order to convert absorbance values to color units, a calibration curve was prepared using a platinum-cobalt

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solution as described in the Standard Methods for the Examination of Water and Wastewater 2120 B [13].

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**RESULT AND DISSCUSION**

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**Nitrogen removal**
The effect on removal of nitrogen is shown in  Fig. 4(a) shows a relationship between the T-N removal and the influent TOC/T-N ratio (C/N ratio).  The C/N ratio, expressed on a weight basis, was roughly propotional to the amount of final mollasses injected into the column, as influent $NO_x$-N concentrations were kept constant.  In this and the subsequent figures, the data were categorized into 4 groups by the HRT.  When the HRT was between 0.3 and 0.6 (h), the T-N removal stayed below 60 %, although slightly better performances were achieved at higher C/N ratios.  This indicated the HRT was too short for completing denitrification reactions regardless of the C/N ratio. On the other hand, when the HRT was 0.8 (h) or longer, the T-N removal largely followed a similar trend, with the maximum removal of above 85 % achieved at C/N ratios between 2 and 4 (Figure 3(a)).  Accordingly the effluent T-N (Figure 4(b)) showed the lowest concentrations at the same range of C/N ratios.  By contrast, the effluent $NO_x$-N (Figure 4(c)) kept low concentrations at C/N ratios of 2 or more.  A difference between the effluent T-N and $NO_x$-N concentrations was particularly  significant  at  C/N  ratios  of  more  than  4  (Figures  4(b)  and  4(c)).
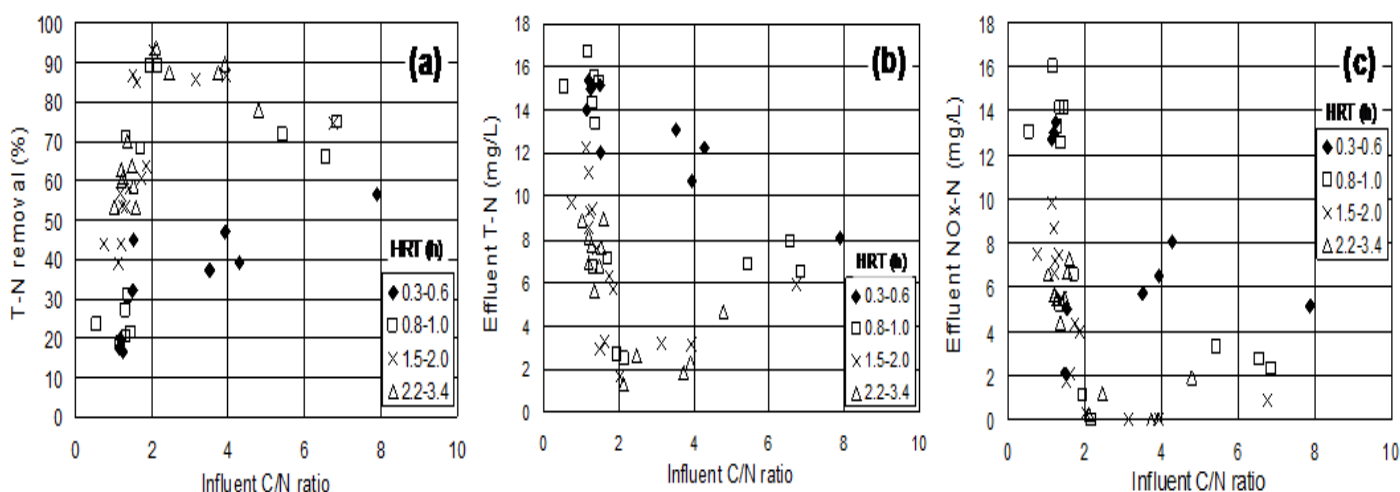


**Fig. 4:  Effect of influent TOC/T-N ratio on nitrogen removal and concentration**

These results suggested that, at C/N ratios of less than 2, carbon source was not enough for denitrification, and a lot of $NO_x$-N remained in the effluent.  By contrast, at C/N ratios of more than 2, carbon source seemed to be sufficient for denitrification to maintain low effluent $NO_x$-N concentrations (Figure 3(c)).  At the same time, however, increasing the C/N ratio (i.e. influent husk-2 concentration) also meant the increase in influent organic/ammonium nitrogen that derived from final husk-2.  Because the column was under an anaerobic condition, the influent organic/ammonium nitrogen would largely be carried away to the effluent, except for a small amount assimilated by biofilm in the column.  This might explain the increase in effluent T-N concentrations at C/N ratio of more than 4 (Figure 4(b)).

**Organic carbon and color removal**
Unlike T-N removal, TOC removal showed no clear trend in terms of the C/N ratio or the HRT (Figure 5(a)), and stayed below 65 % in every condition.  Accordingly the effluent TOC

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concentration increased proportionally to the C/N ratio (Figure 5(b)). This implied that final husk-2 would contain some refractory organic matter.
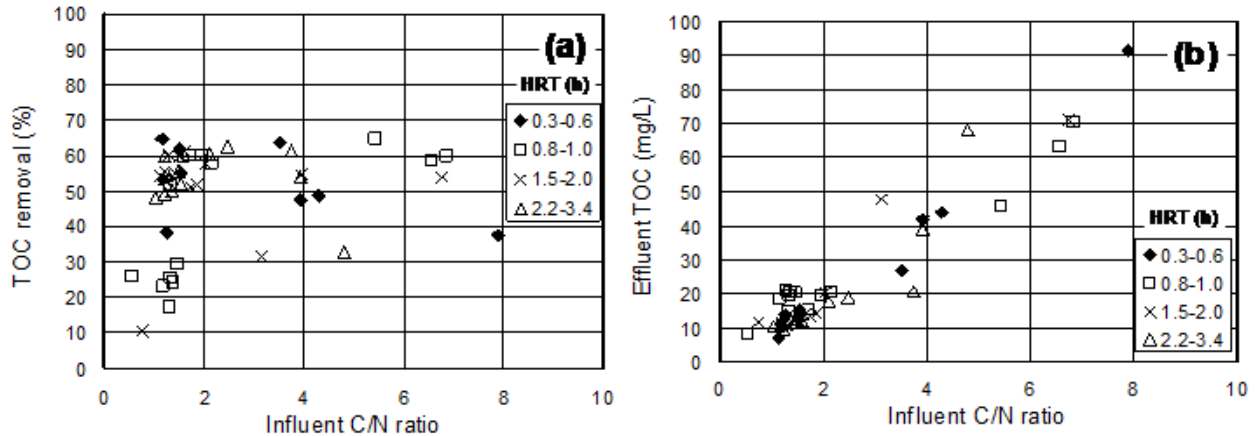


**Fig. 5: Effect of influent TOC/T-N ratio on TOC removal and concentration**

Final husk-2 is known to contain various forms of rices as well as colored materials such as melanoidine, caramel and polyphenolic compounds [14]. Also in this experiment, a slight yellowish color was increasingly visible both in the influent and effluent, as the influent husk-2 concentration was increased. This was confirmed by spectrophotometric measurements of apparent colors. On average, the color removal remained only 17 %, which was significantly lower than the TOC removal of 50 %. The difference was statistically significant at level 0.01 (*P*-value according to the two-sided *t*-test was $2.7 \times 10^{-18}$). This implied that colored materials were not readily consumed by the biofilm and tended to remain in the effluent.
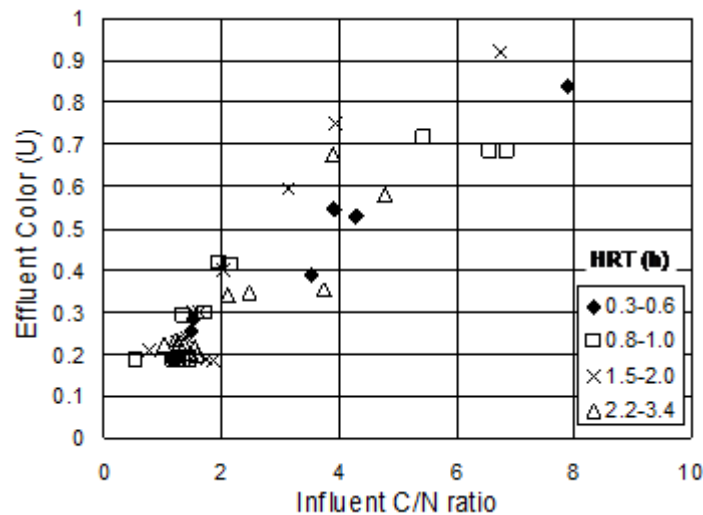


**Fig. 6: Relationship between influent TOC/T-N ratio and effluent apparent color**

**Effect of influent TOC on nitrate removal rates**
In order to examine the effect of influent TOC on nitrate removal rates, observed nitrate removal rates were simulated by a Monod model (Figure 7) using the following equations. For this simulation, data at HRT of 0.3 to 0.6 (h) were excluded because of the incomplete denitrification.

$$r_v = k \times \frac{S_C}{K_S + S_C} \qquad (1)$$

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$$r_v = \frac{(S_{N_0} - S_N) \times Q}{V} \qquad (2)$$

where:

$r_v$ is volumetric nitrate removal rate (g m$^{-3}$ d$^{-1}$),

$k$ is a maximum denitrification rate constant (g m$^{-3}$ d$^{-1}$),

$S_c$ is an influent TOC concentration (mg/L),

$K_s$ is a half-saturation constant (mg/L),

$S_{N0}$ is an influent NO$_x$-N concentration (mg/L),

$S_N$ is an effluent NO$_x$-N concentration (mg/L),

$Q$ is a flow rate (m$^3$/d), and
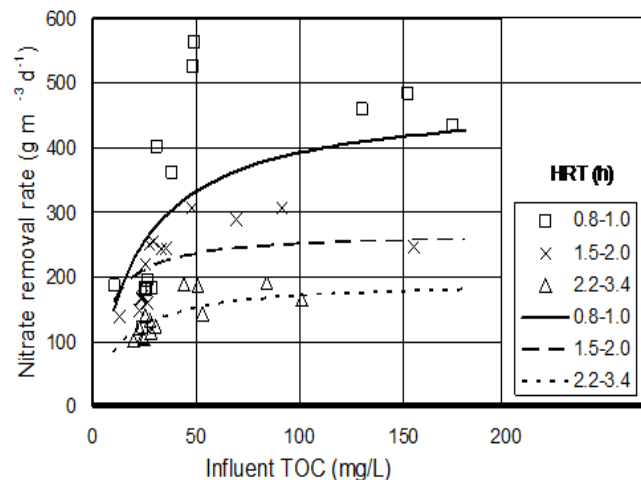
$V$ is a volume of the column (m$^3$).



**Fig. 7: Effect of influent TOC concentration on nitrate removal rate (Plots show observed values while lines indicate simulated values with a Monod model)**

**Table 1:  Simulated parameters by the Monod model**

| HRT (h) | $k$ (g m$^{-3}$ d$^{-1}$) | $K_s$ (mg/L) |
|---|---|---|
| 0.8-1.0 | 479 | 21.9 |
| 1.5-2.0 | 269 | 6.7 |
| 2.2-3.4 | 195 | 13.8 |

See equation (1) in text.

The simulation showed that maximum denitrification rate constants were in a range of 195 to 479 (g m$^{-3}$ d$^{-1}$), with the largest one achieved at HRT of 0.8-1.0 (h) (Table 2).  This would be comparable to reported denitrification rates using methanol, between 290 and 1600 (g m$^{-3}$ d$^{-1}$) for downflow packed-bed reactors (USEPA, 1993), but considerably smaller than the rates between 2000 and 6400 (g m$^{-3}$ d$^{-1}$) for upflow fluidized-bed reactors (USEPA, 1993).  USEPA (1993) attributed the faster denitrification rates of fluidized-bed reactors in comparison to fixed-bed reactors, to a larger surface area of media per unit reactor volume provided by fluidized-bed reactors.  Therefore future studies should investigate fluidized-bed reactors for improving denitrification rates using final husk-2. Meanwhile the half-saturation constants were found to be between 6.7 and 21.9 (mg/L) (Table 2), which were larger than reported general values for methanol between 0.1 and 6.0 (mg/L) (USEPA, 1993).  This means that larger amounts of organic carbon need to remain in the effluent in order to

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achieve sufficient denitrification, when compared with methanol.  It might also be another evidence that final mollase contains some refractory organic matter.

## CONCLUSION

This study demonstrated that final husk-2 could be used as a carbon source for biological denitrification.  At least an influent C/N ratio of 2 and HRT of 0.8-1.0 (h) were required to achieve enough denitrification.  On the other hand, final husk-2 contained some organic/ammonium nitrogen and refractory organic matter including colors, which were difficult to remove with the reactor.  Accordingly, at higher C/N ratios, those substances caused major increase in effluent T-N and TOC concentrations.  This would discourage excessive input of final husk-2 to the influent.  Therefore, an optimum C/N ratio for denitrification using final husk-2 was found to be around 2, which was comparable to a usual C/N ratio of 3 for methanol and various biological wastes.  However, even if the C/N ratio is kept around the above optimum, the effluent would still contain some residual substances including organic/ammonium nitrogen, phosphorous and refractory organic matter.  Therefore, when one attempts to apply this study to water treatment, those substances must be removed at downstream processes such as coagulation and sand filtration.  When applied to tertiary wastewater treatment, the effluent might as well be reused as irrigation water, because farm soils might be effective in degrading or absorbing those substances as the effluent passed through them.  Anyway further studies are required to investigate these issues.

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