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Removal of Ammonia and Nitrite from Coastal Water Using Low-Cost Agricultural Waste

V. Parimala · K. K. Krishnani · B. P. Gupta · R. Ragunathan · S. M. Pillai · P. Ravichandran

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Nitrogenous contaminants such as ammonia and nitrite have been found to appear frequently in the source water used for coastal aquaculture (Krishnani et al., 2002; Krishnani et al., 2003). Presence of excessive nitrogenous compounds in source water may cause eutrophication in the receiving water aquaculture ponds. Ammonia is the major end product of protein catabolism, which remains in the form of unionized ammonia (NH_3) and ionized ammonia (NH_4^+). The proportion of unionized and ionized ammonia varies with pH and temperature. Unionized ammonia is a critical water quality parameter and toxic to aquatic life, but the ammonium ion is harmless except in extremely high concentrations. The problem of keeping the undissociated ammonia concentration within non-harmful limits is reduced, in practice, to control over the total ammonia concentration. Nitrite is an intermediate product in bacterial nitrification and denitrification processes. Therefore, the reduction of the impact of total ammonia and nitrite on the receiving environment may be essentially obtained upstream by optimizing shrimp/fish farming management practices regarding feeding and water quality (Porrello et al., 2003).

V. Parimala · K. K. Krishnani · B. P. Gupta · R. Ragunathan · S. M. Pillai · P. Ravichandran
Central Institute of Brackishwater Aquaculture, 75, Santhome High Road, Chennai, India

R. Ragunathan
Department of Organic Chemistry, University of Madras, Chennai, India

V. Parimala (✉)
Patent Office, Guindy, Chennai, India
e-mail: parimalavarsini@yahoo.com

Most of the previous works highlight the use of commercially activated carbons and ion exchange resins in fresh water aquaculture (Chiayvareesajja and Boyd, 1993). The high capital investment and regeneration costs of activated carbon and ion exchange resins resulted in the idea of using agricultural wastes (Krishnani et al., 2006a; Krishnani et al., 2006b). Many of the fibrous materials from agricultural wastes are generally used as fertilizers (Hepher and Pruginin, 1981), as ingredient of formulated feed (Bombeo-Tuburan et al., 1993) for enhancement of natural productivity of ponds, especially in freshwater culture systems, and also as biosorbents for the removal of heavy metals (Krishnani et al., 2004; Krishnani and Ayyappan, 2006). India is an agricultural country and produces a considerable amount of agricultural waste such as coconut husk. This is a highly lignocellulosic material. Previously, we have reported the removal of chromium from coastal water using five different products prepared from coconut husk (Parimala et al., 2004). In the present paper, a study has been carried out to investigate the use of these products in the remediation of ammonia and nitrite from coastal water, and to examine their effect on other water quality parameters.

Materials and Methods

Five different kinds of materials were prepared from coconut husk

i. Raw coconut husk fibre (CRF): This was dried in oven at 50°C in order to get constant moisture content.
ii. Dried coconut husk fibre (CDF): Raw coconut husk was thoroughly washed with deionized water and then dried.

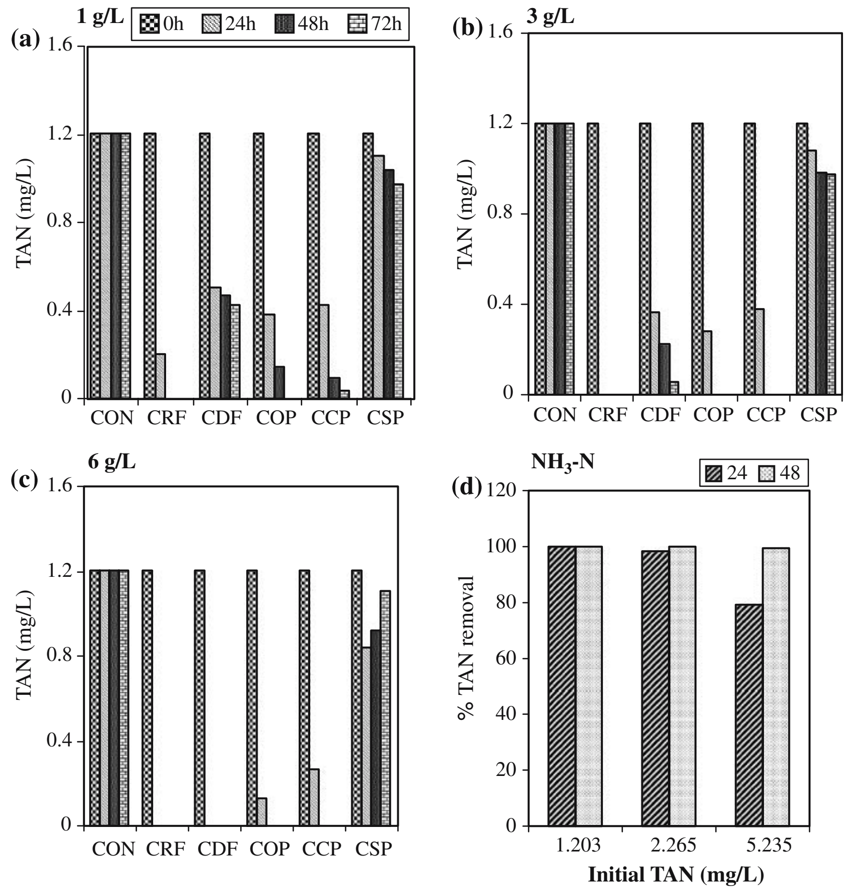

Fig. 1 Effect of coconut husk materials at (a) 1 g/L, (b) 3 g/L and (c) 6 g/L and (d) initial ammonia concentration using CRF at 3 g/L, in the removal of TAN from coastal water

iii. Oven-dried coconut husk powder (COP): Dried material (CDF) was further dried at 100°C and then powdered.
iv. Charred material powder (CCP): Dried material (CDF) was charred at 250 °C in the muffle furnace and then powdered.
v. Charred with acid (CSP): Dried material (CDF) was charred with concentrated sulphuric acid for 24 h. After complete charring, charred material was thoroughly washed with water to remove sulphuric acid, dried at 100°C, and then powdered.

Coastal water (25–26 g/L) for the experiment was collected from the coastal lagoon, Muttukadu, near Chennai. The appropriate amounts of ammonium sulphate and potassium nitrite (E. Merck) were added into the water to attain various ammonia and nitrite concentrations. For each experimental run, 1 L water was taken in 2 L capacity beakers and treated with five different materials prepared from coconut husk at 1, 3 and 6 g/L, with a separate set of controls. Further, water samples were analyzed for measurement of total ammonia nitrogen (TAN) and NO_2-N concentrations at daily intervals for the period of 4 days. At the end of the experiment, water samples were collected from all the treatments and analyzed for measurement of other water quality parameters: Ammonia, nitrite and phosphates in coastal water were analyzed by standard method (Strickland and Parsons, 1972; APHA, 1989) using UV-visible spectrophotometer (Hitachi- U–2000); other parameters such as pH and salinity were measured using pH meter and salinometer, respectively. The data was statistically analyzed using 4 (duration) × 5 (materials) factorial completely randomized design with two replications for each dose. Duncan's multiple range test was applied to identify significant differences between main effects and interaction effects. M-STATC statistical software was employed to perform statistical analysis.

Results and Discussion

The effect of five different types of materials from coconut husk at 1, 3 and 6 g/L on the removal of 1.203 mg/L ammonia is presented in Fig. 1. This shows that ammonia removal was most effective with raw coconut husk fiber (CRF) followed by oven dried coconut husk powder (COP) and charred coconut husk powder. These materials at 1 g/L decreased ammonia from 1.203 mg/L to 0.201 (83.29%), 0.379 (68.49%) and 0.423 (64.83%), respectively, in 24 h and 97–100% removal was achieved in 72 h; whereas these materials at 3 g/L decreased ammonia from 1.203 mg/L to nil (100%), 0.279 (76.81%) and 0.377 (68.67%), respectively, in 24 h and 100% removal was achieved in 48 h. In the case of 6 g/L, 100% removal was achieved within 24 h. Coconut husk fibers dried in oven (CDF) at 1, 3 and 6 g/L were effective in removing ammonia from 1.203 mg/L to 0.504 (58.10%), 0.363 (69.83%) and nil (100%), respectively, in 24h and 0.472 (60.76%), 0.226 (81.21%) and nil (100%), respectively, in 48 h. Coconut husk charred with acid (CSP) at all three doses was not effective to remove ammonia efficiently.

The effect of initial ammonia concentrations at 1.203, 2.265 and 5.235 mg/L on the ammonia removal with CRF at 3 g/L is shown in Fig. 1d. The ammonia values decreased from 1.203, 2.265 and 5.235 mg/L to nil (100%), 0.038 (98.3%), 1.09 (79.2%) in 24 h and, after 48 h, the ammonia concentrations were nil (100%), nil (100%) and 0.026 (99.5%) mg/L respectively.

The effect of five different types materials prepared from coconut husk at 1, 3 and 6 g/L on the removal of 1.024 mg/L nitrite is presented in Fig. 2. This shows that ammonia removal was effective with raw coconut husk fiber (CRF) followed by powder charred with acid (CSP). Oven-dried coconut husk powder (COP) and charred coconut husk powder (CCP) were also found to be effective. These preparations at 1 g/L decreased nitrite from 1.024 mg/L to 0.97 (5%), 0.863 (16%), 0.873 (15%) and 0.848 (17%) in 48 h. Further, there was a slight decline in nitrite concentration and, after 96 h, they decreased nitrite levels to the extent of 21%, 19%, 20% and 22% respectively. These materials at 3 g/L decreased nitrite from 1.024 mg/L to 0.338 (67%), 0.615 (40%), 0.993 (3%) and 0.91 (11%) in 24 h; 0.12 (88%), 0.403 (61%), 0.365 (64%) and 0.46 (55%) in 48 h; and nil (100%), 0.225 (78%), 0.126 (88%) and 0.124 (88%) in 96 h respectively. In the case of 6 g/L, these materials have reduced nitrite concentration from 1.024 mg/L to 0.054 (95%), nil (100%), 1.005 (1.86%) and 0.745 (27.25%) in 24 h, and 100% nitrite removal was achieved in 48 h. CDF was found to be least effective and this material at 3 and 6 g/L decreased nitrite concentration from 1.024 mg/L to 0.834 (19%) and 0.54 (47%), respectively, in 96 h.

The effect of initial nitrite concentrations at 1.024, 2.35 and 5.04 mg/L on the nitrite removal with CRF at 3 g/L is shown in Fig. 2(d). The nitrite values decreased from 1.024, 2.35 and 5.04 mg/L to 0.338 (67%) 0.856 (63.57%) and 2.44 (51.6%) in 24 h and after 48 h, values were 0.12 (88.28%), 0.34 (85.53%) and 0.812 (83.89%) mg/L, respectively. The results show that percent removal was found to decrease with increasing initial toxicant concentration.

Statistical analysis for the comparison of efficacies of five different types of materials from coconut husk with respect to 1.203 mg/L initial ammonia concentration is given in Table –1. This shows that efficacy of CRF with the doses of 1 and 3 g/L for the removal of ammonia is significantly different from all other materials. However, at the higher dose (6 g/L), all other materials, except CSP, were equally effective. Similarly, COP and CCP at 1 and 3 g/L were equally effective as there was no significant difference in their values. Ammonia removal was highest for CRF at 1 g/L throughout the experiment. Analysis of the interaction effect between experiment duration and materials for ammonia removal relvealed that, in the case of CRF at 3 and 6 g/L, there was no significant effect of duration on ammonia removal and maximum ammonia removal was achieved within 24 h (Table 1). However, in the case of CRF at 1 g/L, maximum ammonia removal was achieved after 48 h. It is also observed that there is a significant difference in ammonia removal between 24 h and 48–72 h. In the case of COP and CCP at 1, 3 and 6 g/L, ammonia removal within 24 h was significantly different from 48 h, and thereafter there was no significant difference as maximum ammonia removal was achieved within 48 h. In the case of CDF at 1 g/L, ammonia removal was not effective and there was no significant effect of duration on the removal. However, in the treatment with 6 g/L, maximum removal was achieved within 24 h. The same levelof ammonia removal by COP and CCP at 6 g/L within 48 h can be achieved by using CRF at 3 g/L within 24 h.

Result of statistical analysis of data for the removal of nitrite is given in Table –1. This shows a significant difference among efficacies of all the five materials at 6 g/L for nitrite removal. However, there was no significant difference between COP, CCP and CSP at 1 g/L and 3 g/L. In the case of CRF, COP, CCP and CSP at 6 g/L, there was no significant effect of duration (from 48–96 h) on nitrite removal and maximum nitrite removal was achieved in 48 h. However, efficacies of these materials at 1 and 3 g/L were significantly different at all the durations. This also has been substantiated by statistical analysis.

Other water quality parameters, such as salinity, did not show much change in the presence of CRF, CDF, COP, CCP and CSP throughout the course of the experiment. These materials at 1 g/L decreased pH from 8.33 to 8.09, 8.12, 7.88, 7.68 and 7.46, respectively; at 3 g/L, decreased pH from 8.33 to 7.76, 8.18, 8.03, 7.98 and 5.7, respectively; and at 6 g/L, decreased pH from 8.33 to 7.7, 8.25, 8.25, 8.15 and 4.08, respectively. We also observed little change in phosphate values with CDF, COP and CSP at 1, 3 and 6 g/L. Raw coconut husk fiber at 1, 3 and 6 g/L increased phosphates from 0.044 mg/L to 0.202, 0.236 and 0.314 mg/L, respectively. Whereas, in the case of charred coconut husk powder (CCP) at 6 g/L, phosphate concentration increased from 0.044 mg/L to 0.271 mg/L.

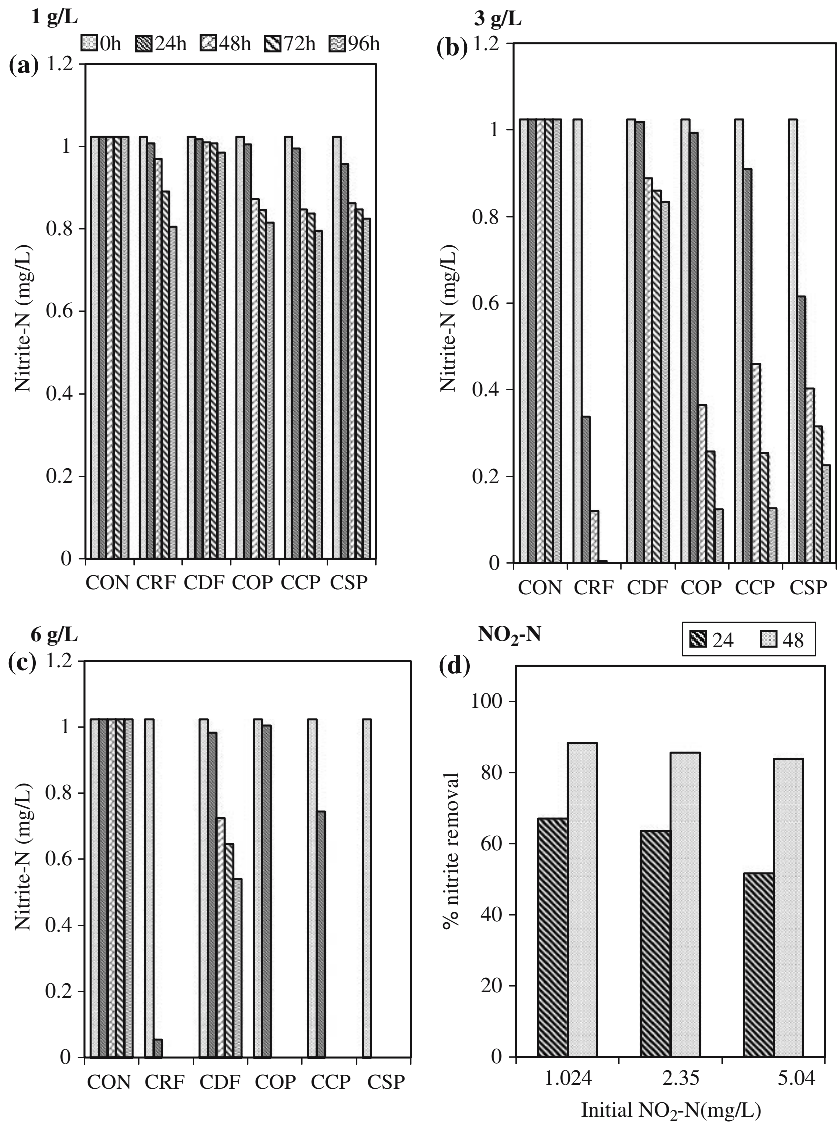

Fig. 2 Effect of coconut husk materials at (a) 1 g/L, (b) 3 g/L and (c) 6 g/L and (d) initial nitrite concentration using CRF at 3 g/L on the removal of nitrite from coastal water

There are many other reports (Pandey et al., 2000 and Chavez-Gomez et al., 2003) on the use of lignocellulosic materials for enhancing the growth of microorganisms. Azim et al. (2002) reported lower ammonia concentration in a pond treated with bamboo, and observed that periphyton improved water quality in aquaculture system by increasing nitrification. The reduction in total ammonia content in bagasse-based treatment has also been observed by Mridula et al. (2003), and it was estimated that autotrophic productivity could be doubled by providing a substrate area similar to the pond water surface area. They also reported that ponds with substrates had lower total ammonia levels than control ponds, and concluded that enhanced bacterial biofilms on the substrates might reduce ammonia levels through promotion of nitrification. The effective removal of nitrite with raw coconut husk fiber might be due to an increase in autotrophic bacterial growth combined with PO_4^{2-} ion exchange mechanism.

The present study shows that coconut husk can be used for the effective removal of ammonia and nitrite from coastal water. The removal of ammonia was found to depend on materials, dose and time. Raw coconut husk fiber (CRF) and oven dried coconut husk powder (COP) at 1–3 g/L are effective in decreasing ammonia and nitrite levels from coastal water in 24–48 h; whereas, CDF was least effective in 24 h and this was found to be effective at 3–6 g/L in 48–72 h. Statistical data shows that ammonia and nitrite removal by CDF at 6 g/L in 24 h can be achieved by using CRF at 1 g/L in 48 h and at 3 g/L in 24 h. Hence, from this study, it may be concluded that raw coconut husk fiber (CRF) at 1–3 g/L is the most effective material followed by oven-dried powder for detoxification of ammonia

Table 1 Comparison of coconut husk material efficacy for the removal of ammonia and nitrite from coastal water

Effect of materials

Coconut husk	Mean					
	Initial TAN (1.2030 mg/L)			Initial nitrite (1.0240 mg/L)^{A}		
	1 g/L	3 g/L	6 g/L	1 g/L	3 g/L	6 g/L
CRF	0.3639^{D}	0.3008^{D}	0.3008^{C}	0.9396^{B}	0.2974^{D}	0.2156^{C}
CDF	0.6513^{B}	0.4615^{B}	0.3008^{C}	1.0090^{A}	0.9248^{A}	0.7836^{A}
COP	0.4322^{C}	0.4403^{C}	0.3643^{C}	0.91260^{C}	0.5528^{BC}	0.4058^{B}
CCP	0.4375^{C}	0.3950^{C}	0.3680^{B}	0.9000^{C}	0.5548^{B}	0.3538^{D}
CSP	1.0798^{A}	1.0598^{A}	1.017^{A}	0.9036^{C}	0.5164^{C}	0.2048^{E}

Interaction effect of materials and duration

Coconut husk	Mean				Mean			
	Hr	(Initial TAN 1.203 mg/L)			Hr	Initial nitrite (1.0240 mg/L)^{A}		
		1 g/L	3 g/L	6 g/L		1 g/L	3 g/L	6 g/L
CRF	0	1.203^{A}	1.203^{A}	1.203^{A}	24	1.008^{B}	0.338^{L}	0.054^{H}
	24	0.201^{H}	0.000^{I}	0.000^{G}	48	0.970^{EF}	0.012^{Q}	0.000^{I}
	48	0.000	0.000^{I}	0.000^{G}	72	0.891^{G}	0.005^{R}	0.000^{I}
	72	0.000^{L}	0.000^{I}	0.000^{G}	96	0.805^{KL}	0.000^{S}	0.000^{I}
CDF	0	1.203^{A}	1.203^{A}	1.203^{A}	24	1.018^{BC}	1.080^{B}	0.983^{C}
	24	0.504^{E}	0.363^{E}	0.000^{G}	48	1.010^{CD}	0.888^{E}	0.725^{E}
	48	0.472^{EF}	0.226^{G}	0.000^{G}	72	1.008^{DE}	0.860^{F}	0.646^{F}
	72	0.426^{F}	0.054^{H}	0.000^{G}	96	0.985^{EF}	0.834^{G}	0.540^{G}
COP	0	1.203^{A}	1.203^{A}	1.203^{A}	24	1.005^{CD}	0.993^{C}	1.005^{B}
	24	0.379^{G}	0.279^{F}	0.127^{F}	48	0.873^{GH}	0.365^{K}	0.000^{I}
	48	0.144^{I}	0.000^{I}	0.000^{G}	72	0.846^{GHIJ}	0.258^{N}	0.000^{I}
	72	0.003^{KL}	0.000^{I}	0.000^{G}	96	0.815^{IJK}	0.124^{P}	0.000^{I}
CCP	0	1.203^{A}	1.203^{A}	1.203^{A}	24	0.995^{DEF}	0.910^{D}	0.745^{D}
	24	0.423^{F}	0.377^{D}	0.269^{E}	48	0.848^{GHIJ}	0.460^{I}	0.000^{I}
	48	0.091^{J}	0.000^{I}	0.000^{G}	72	0.838^{HIJ}	0.254^{N}	0.000^{I}
	72	0.033^{K}	0.000^{I}	0.000^{G}	96	0.795^{JKL}	0.126^{P}	0.000^{I}
CSP	0	1.203^{A}	1.203^{A}	1.203^{A}	24	0.958^{F}	0.615^{H}	0.000^{I}
	24	1.100^{D}	1.080^{B}	0.838^{D}	48	0.863^{GHI}	0.403^{J}	0.000^{I}
	48	1.040^{C}	0.984^{C}	0.918^{C}	72	0.848^{GHIJ}	0.315^{M}	0.000^{I}
	72	0.976^{B}	0.972^{C}	1.109^{B}	96	0.825^{HIJK}	0.225^{O}	0.000^{I}

Means in the vertical row with different superscripts are significantly different ($p \leq 0.05$)

and nitrite in 24–48 h. Proportion of ammonia and nitrite removal was found to increase with an increased concentration, while the time taken for ammonia removal decreased with an increased concentration. Successful studies on the use of these materials for the remediation of coastal source water for aquaculture could be useful for the agricultural countries like India, which generates considerable amount of coconut husk.

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