Revista de Ciências Agroveterinárias
Universidade do Estado de Santa Catarina (UDESC)

Research Note

Vermiculite as a sustainable alternative for ammonia removal in aquaculture: Comparison with zeolite and activated carbon

Vermiculita como alternativa sustentável para a remoção de amônia em aquicultura: Comparação com zeólita e carvão ativado

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Submission: January 04th, 2025 | Acceptance: September 15th, 2025

ABSTRACT

Vermiculite was assessed for efficacy in removing ammonium compounds in an aquaculture context. Vermiculite performance was then compared with that of zeolite and activated carbon, which are commonly used as adsorbents in this process. Adsorption tests were carried out with adsorbent dosages of 22, 34, 46 g.L-1 at total ammonium nitrogen (TAN) concentration of 3 mg.L-1 for 5, 15, 25 and 35 minutes. All adsorbents removed ammonium ions from the water rapidly, with adsorption equilibrium being reached in less than 5 minutes in all tests. Zeolite and vermiculite showed higher removal efficiency and adsorption capacity than activated carbon, and both zeolite and vermiculite reduced the TAN concentration to less than 1 mg.L-1. It is estimated that 400 grams of zeolite and vermiculite will be required for efficient removal of ammonium in aquariums up to 20-40 L. In addition, vermiculite and zeolite are more economical, costing less to remove ammonium than activated carbon. Combined with the reactivation capacity of the adsorbents, zeolite and vermiculite are viable alternatives from an economic and environmental standpoint.

KEYWORDS: Adsorbents. Aquaculture. Ammonium removal. Sustainability.

RESUMO

Testes com vermiculita foram realizados para avaliar sua eficiência na remoção de compostos de amônio no contexto da aquicultura. O desempenho da vermiculita foi comparado com o da zeólita e do carvão ativado, que são adsorventes comumente utilizados nesses processos. Os testes de adsorção foram realizados com dosagem de adsorvente de 22, 34, 46 $g.L^{-1}$ a uma concentração de nitrogênio amoniacal total (TAN) de 3 mg L^{-1} durante 5, 15, 25 e 35 minutos. Todos os adsorventes removeram rapidamente os íons de amônio da água, na qual o equilíbrio de adsorção foi atingido em menos de 5 minutos em todos os ensaios. A zeólita e a vermiculita apresentaram eficiência de remoção e capacidade de adsorção maiores do que o carvão ativado, e ambos reduziram a concentração de TAN para menos de 1 $mg.L^{-1}$. Estima-se que serão necessários 400 gramas de zeólita e vermiculita para uma remoção eficiente de amônio em aquários de até 20-40 L. Além disso, a vermiculita e a zeólita são mais econômicas e com menor custo para remover amônio do que o carvão ativado. Aliado à capacidade de reativação dos adsorventes, a zeólita e a vermiculita são alternativas mais viáveis do ponto de vista econômico e ambiental.

PALAVRAS-CHAVE: Adsorventes. Aquacultura. Remoção de amoníaco. Sustentabilidade.

The global trade of ornamental fish transports approximately 1.5 billion live fish annually, generating revenues of around 30 billion US dollars (STEVENS et al. 2017). However, ensuring the health of the specimens during breeding, handling and transport remains a challenge for the success of the activity. It is estimated that 73%

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of individuals exported die due to poor water quality and excessive stress (STEVENS et al. 2017). With the intensification of aquaculture in the past decades, the removal of ammonium compounds is becoming a key concern (GHASEMI et al. 2018, FAO 2022). Exposure to these toxic compounds can lead to tissue damage, haematological alterations, and death in extreme situations (BARBIERI & BONDIOLI 2015). Several fast and effective methods have become standard practice to keep these pollutants at safe levels. One such method involves the use of adsorbents (FARHAD & MOHSEN 2016).

Removal of pollutants with adsorbents is an efficient process, offering a rapid response with minimal additional expense. This efficiency is further enhanced by the potential to regenerate adsorbents after use, thereby reducing overall operational costs. Research shows that adsorbents, such as vermiculite, can be reused up to five cycles in high concentrations of ammonia (>100 $mg.L^{-1}$) and still maintain an adsorption capacity above 75% (REN et al. 2022). Many of these adsorbents are non-toxic and considered environmentally friendly (GHASEMI et al. 2018). Certain classes of adsorbents are also used in the treatment of effluents in sewage systems, reducing the concentration of ammonium and various other pollutants to levels considered environmentally safe (HALIM et al. 2010, WANG et al. 2011). However, there is limited reporting on the applicability of these removers in culture systems, where low ammonium concentrations can cause alterations in organisms (ZHOU & BOYD 2014), and there is particularly a lack of information on the ideal amount and cost-effectiveness of using each type of adsorbent.

Vermiculite is a highly charged hydrated phyllosilicate mineral that exhibits high performance as a natural adsorbent for ammonium removal (SOLISMAA et al. 2019). Its ecological profile and environmental benefits make it a preferred option for many water treatment applications and researchers are currently exploring the potential reuse of vermiculite (MORAES et al. 2019). As vermiculite is typically discarded after being used to protect chemical products during transportation (MORAES et al. 2019) and is less costly than zeolite and activated carbon (the two most used adsorbents in the aquarium sector), the present study aimed to assess the adsorption capacities and removal costs of all three adsorbents.

The vermiculite employed for ammonium adsorption in this work was the same material tested by MORAES et al. (2019). This material was reused following its initial application as a thermal insulator and adsorbent in Sigma-Aldrich chemical product packaging. MORAES et al. (2019) characterized the sample by XRD (Panalytical X'PERT PRO MPD - PW3040/60) at CuKα (λ=1.540598 Å), 40 Kv, 30 mA; range 5 to 65°, rate 0.016° and 99.7 s count. This method is used to identify different phases of crystalline materials. The performance of vermiculite as adsorbent was compared with two other products commonly used in aquaculture: zeolite (Ocean Tech, Clinoptilolite) and activated carbon (Boyu). These are both aquarium products used to remove ammonium from water, and were purchased from an aquarium store. All adsorbents were standardized to grain size of less than 1mm.

Adsorption experiments were conducted utilising a solution of 3 $mg.L^{-1}$ of total ammonium nitrogen (TAN). This solution concentration was selected because it was very close to the median lethal concentration (CL_{50}) of *Piaractus mesopotamicus*, an

Amazonian fish species widely used in Brazilian aquaculture (BARBIERI & BONDIOLI 2015). All solutions were obtained by mixing ammonium chloride (Synth, P.A) in deionized water.

The experimental design comprised three factors: adsorbent (3 types), dosage of adsorbent (3 levels) and time (4 levels), resulting in a total of 36 treatments in triplicates. A control was conducted in triplicate to confirm that only the adsorbents were responsible for ammonium removal. A quantity of 0.32, 0.48 and 0.65g of each adsorbent was added to 14 mL of ammonium solution in conical tubes (15 mL), resulting in adsorbent dosages of 22, 34, and 46 $g.L^{-1}$, respectively. The suspension was stirred (75 rpm) during 5, 15, 25 and 35 min (experimental time). After these experimental times, the solutions were centrifuged (300 rpm) and the supernatant was separated. The TAN concentration was then measured using a spectrophotometer (Hanna, mod. HI33099). The pH and temperature parameters were monitored using a pH-indicator (Merck®) and glass thermometer.

Ammonium removal (AR) was determined using Eq. (1): %AR = (Ci – Cf / Ci) x 100, where: Ci and Cf are initial and final ammonium concentrations (mg L^{-1}), respectively. Adsorption capacity of the material "Q" ($mg.g^{-1}$) was determined using Eq. (2): Q = (Ci – Cf)V/m, where: Ci and Cf are initial and final concentrations ($mg.L^{-1}$), V is the volume (L) and m is the mass of adsorbent (g).

To study the market price dynamics of each adsorbent and to analyse the possibility of using vermiculite to replace the adsorbents currently used in aquaculture, a price ($) survey was carried out on the Amazon International website between 2 and 5 May 2023. The relationship between the price per 1 kg of adsorbent and the cost of removal (CR) was obtained using Eq. (3): CR ($US\$.mg^{-1}$) = PA/q, where: PA is the average price of the adsorbent ($US\$.kg^{-1}$) and q is adsorption capacity of material ($mg.kg^{-1}$). The adsorption capacity of the adsorbents was expressed in kilograms, as this is the most suitable unit for aquarists and fish farmers in a removal cost analysis.

The differences in TAN due to: (i) adsorbent type, (ii) adsorbent dosage and (iii) time were assessed using a three-way ANOVA, followed by Tukey's *post-hoc* test. The same approach was applied to adsorption capacity values. The removal cost analysis was performed using a Kruskall-Wallis test, followed by a Ranks test, which evaluated the cost of each adsorbent in removing ammonium (OSTERTAGOVÁ et al. 2014). Data analyses were performed using Past software (HAMMER et al. 2001).

The X-ray diffraction (XRD) patterns of vermiculite showed relative intensities of six basal reflections (002-6.13 º, 004-12.28 º, 006-18.46 º, 008-24.69 º, 0010-31 º, and 0012 - 377. 46 º) very similar to the standard sample (ICSD 01-074-1732) characteristic of this clay mineral (Figure 1).

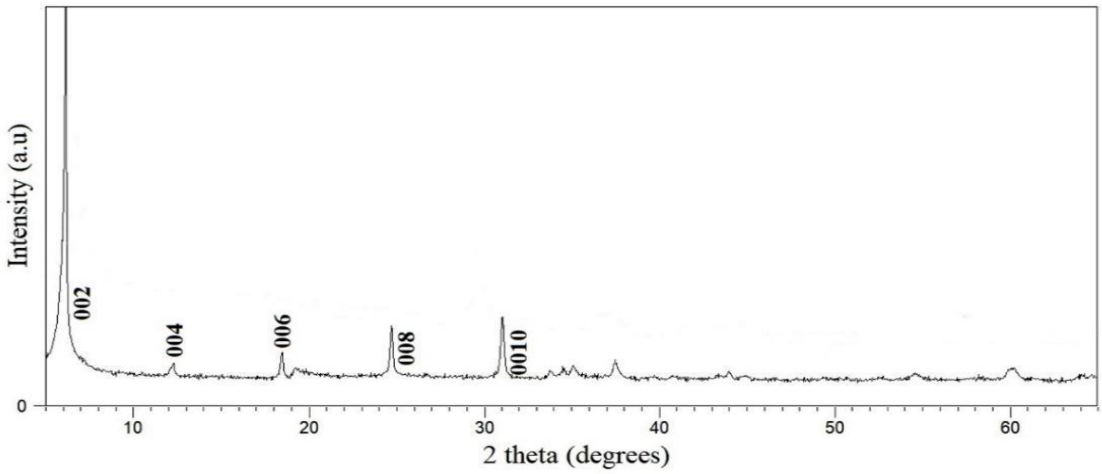


Figure 1. XRD patterns of vermiculite sample, source: (MORAES et al. 2019).

The adsorption tests were carried out at a temperature and pH range of 26° C (± 0.7° C) and 6.8 (± 0.6), respectively. Adsorption equilibrium was reached for all adsorbents after 5 minutes of testing. The results showed significant difference in ammonium removal capacity among the adsorbent examined ($F_{(8, 90)}$ = 23.79, p = 0.001). Zeolite showed the highest removal capacity of the three materials evaluated, with almost 100% more removal than activated carbon (Tukey; p = 0.001), and approximately 33% higher than vermiculite (Tukey; p = 0.001) (Figure 2).

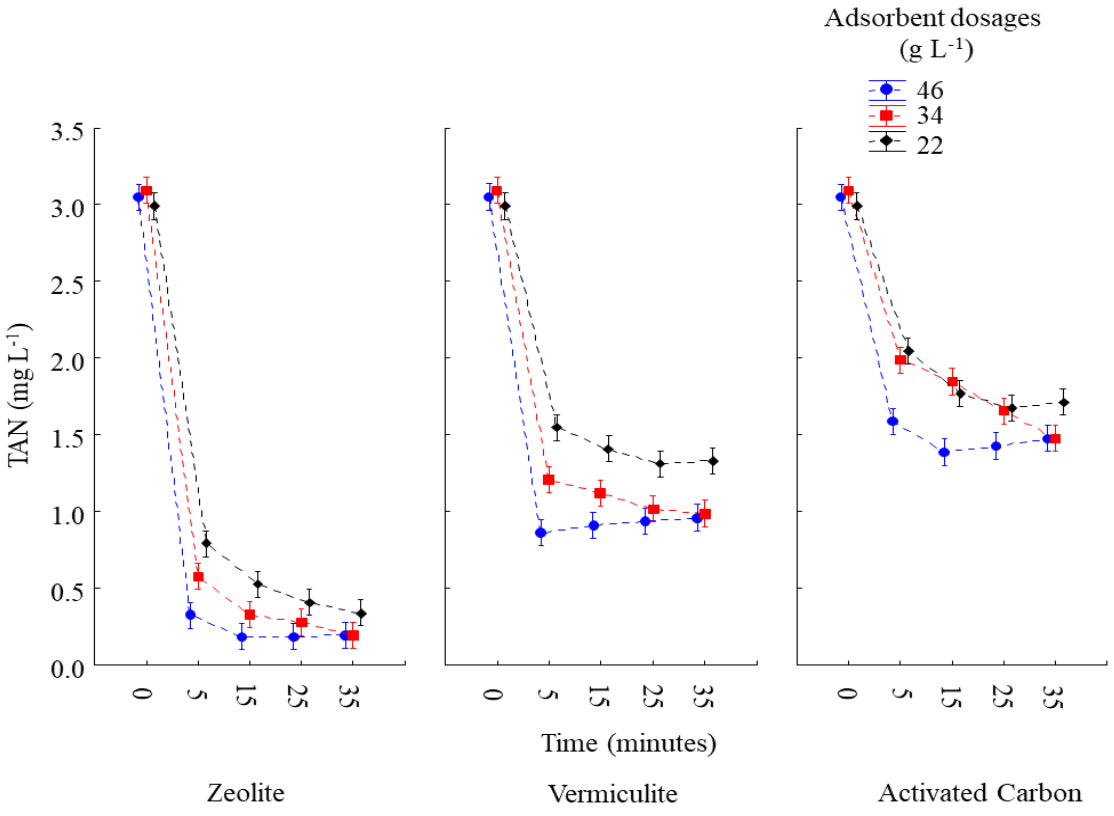


Figure 2. Concentration of total ammonia nitrogen, TAN (mg L^{-1}) (mean ± Standard Error of the Mean) at dosages of 22, 34, 46 (g L^{-1}) for each adsorbent tested (zeolite, vermiculite and activated carbon) in relation to the respective time levels (0, 5, 15, 25, 35 minutes).

In this study, significant differences in adsorption capacity (Q) were found only between 22 and 46 (g L^{-1}) for both zeolite and vermiculite ($F_{(4, 72)}$=111.96, p = 0.001). At 34 g.L^{-1}, the mean adsorption capacity of zeolite was 0.08 mg.g^{-1}, while vermiculite was 0.06 mg.g^{-1} and activated carbon was 0.04 mg.g^{-1} (Figure 3). However, no difference was observed in adsorption capacity of the zeolite, vermiculite and activated carbon treatments at dosages of 34 and 46 g.L^{-1}, respectively (Tukey; p = 0.1294).

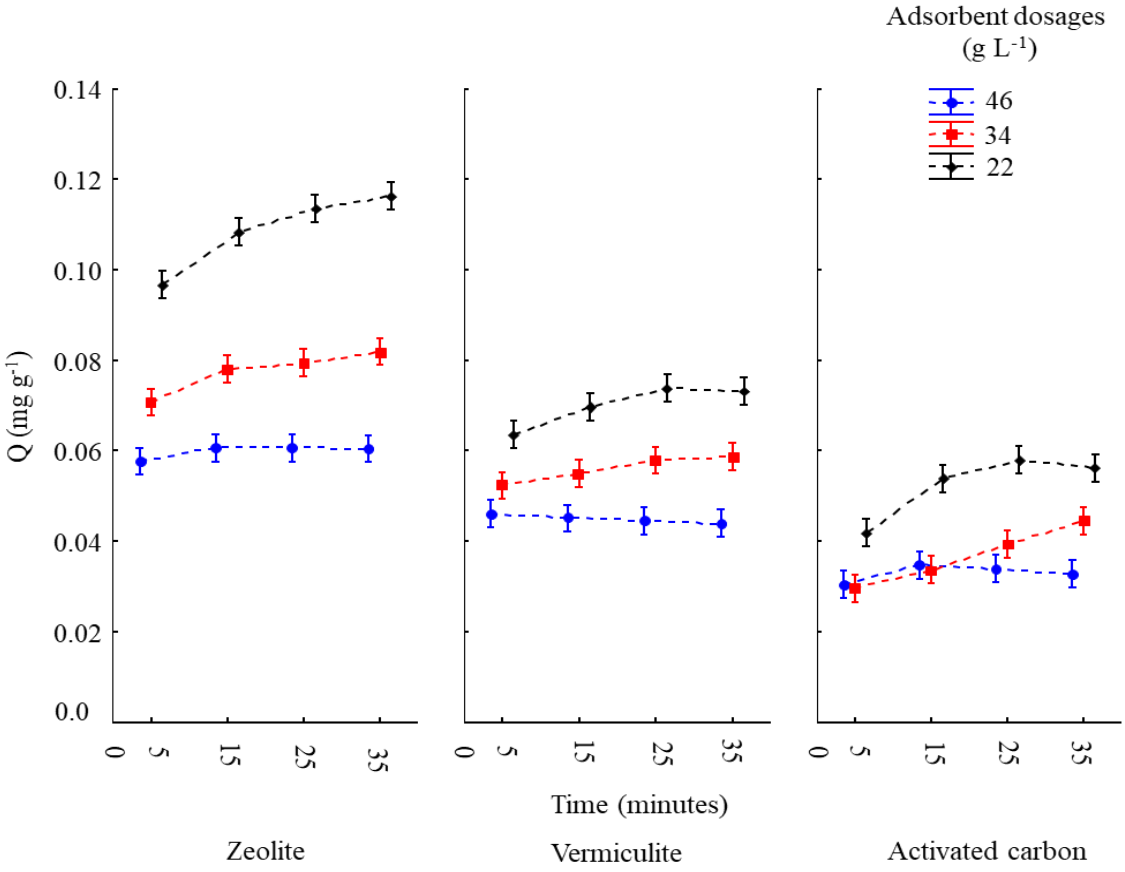


Figure 3. The adsorption capacity "Q" (mg.g^{-1}) (mean ± Standard Error of the Mean) at dosages of 22, 34, 46 (g.L^{-1}) for each adsorbent (zeolite, vermiculite and activated carbon), in relation to the respective time levels (5, 15, 25, 35 minutes).

Cost comparisons among adsorbents for ammonium removal revealed that zeolite and vermiculite did not differ significantly in cost-benefit (Ranking Test, p = 0.120). Both materials were found to be approximately half as expensive as activated carbon ($H_{(2, 21)}$ = 7.67, p = 0.021). A further evaluation of material costs indicated that activated carbon was consistently more costly than the other adsorbents included in this analysis (see Table 1 for detailed cost-benefit data).

All materials removed ammonium rapidly within 5 minutes of initiating the experiment. Vermiculite and zeolite were particularly efficient, reducing ammonium concentration to less than 1 mg.L^{-1}. The adsorption capacity was observed to vary depending on both the type and quantity of adsorbent, with zeolite exhibiting the highest capacity and activated carbon the lowest. In addition, the removal cost (RC) analysis indicated that activated carbon is not the most suitable adsorbent for removing ammonium from water.

Table 1. Final concentration (FC), percentage ammonia removal (R), adsorptive capacity (Q), price per kg, and removal cost (RC) of the experimental treatments using 46 g L^{-1} adsorbent (mean ± standard deviation) in 96 hours, except for the control group. The symbol "*" between treatments indicates p<0.05 between the treatments within the same columns. The presence of "a" indicates p > 0.05 in the same columns. The symbol "x" = no data.

Adsorbent	FC ($m.L^{-1}$)	R (%)	Q ($mg.kg^{-1}$)	Price per kg (US$)	RC (US$/ mg)
Zeolite	0.22 ± 0.06*	90	81*	24.13 ± 10.69	0.40 ± 0.17a*
Vermiculite	0.91 ± 0.13*	75	69*	19.22 ± 3.78	0.43 ± 0.08a*
Activated Carbon	1.46 ± 0.13*	54	44*	27.12 ± 11.48	0.82 ± 0.34**
Control	3.05 ± 0.07	x	x	x	x

The rapid removal of ammonium from water is attributed to the small particle size of the adsorbent materials (< 1mm). Smaller particles have a higher surface-to-volume ratio, and research has indicated that particles of 1 to 2 mm can reach adsorption equilibrium within a very short time (TAYLOR & MASOUDI SOLTANI 2023). In addition to the rapid removal of ammonium, the stability of pH observed throughout our study emerges as another positive feature.

While maintaining pH levels between 6.2 and 7.4, the adsorbents showed no significant influence on this parameter and underscores its suitability for aquaculture applications. This stability is especially noteworthy because even minor pH fluctuations can adversely impact aquatic organisms and compromise water quality. In contrast, SALLAM et al. (2024) reported a slight increase in pH, attributing this to the exchange of sodium for hydrogen ions by certain acidic adsorbents such as zeolite. Nevertheless, the adsorbents maintained pH levels within ranges considered safe for fish farming, demonstrating the safety of using adsorbents in terms of this physical-chemical parameter (BALDISSEROTTO 2011, YU et al. 2019, SALLAM et al. 2024). Ultimately, the capacity of these adsorbents to maintain pH within a narrow, safe range is as vital to their effectiveness as their ability to remove ammonium efficiently.

Vermiculite and zeolite have a high capacity to remove ammonium pollutants due to their affinity for attracting these ions (FARHAD & MOHSEN 2016, FERREIRA et al. 2023). The adsorption mechanism by zeolite and vermiculite is probably caused by the greater selectivity of both adsorbents for cationic substances, due to the negative charges dispersed by the surface and pores of both materials (MORAES et al. 2019). Although other ions in the solution may compete with the ammonium ion (NH_4^+) for binding sites in vermiculite, the ammonium ion generally forms stronger bonds with these sites than magnesium (Mg^{2+}), calcium (Ca^{2+}), sodium (Na^+), and potassium (K^+) (FERREIRA et al. 2023). In activated carbon, the lower adsorption shown must depend on its porous structure and the functional group on the surface. In addition, the zeolite and vermiculite surfaces are hydrophilic and have a greater affinity for ammonium ions than the hydrophobic surface of activated carbon. (HALIM et al. 2010, HUANG et al. 2020).

The required dosage of adsorbent for effective ammonium ion removal is influenced by multiple factors, including pollutant concentration, water volume, and the

presence of competing ions (FARHAD & MOHSEN 2016). ZHOU & BOYD (2014) tested the efficiency of zeolite application in a pond with a large volume of water. They used a 20 L aquarium with a TAN concentration of 3 $mg.L^{-1}$, the adsorbents were applied at 50 $mg.L^{-1}$, equivalent to 500 kg per hectare in a fish pond. Their results indicated limited efficacy at this dosage, with only 8% of the initial ammonium concentration being removed. It should be emphasized that the adsorbent dosage employed by ZHOU & BOYD (2014) was approximately 1000 times lower than the dosage applied in the present study. This substantial difference in dosage likely contributed to the observed discrepancy in removal efficiency between the two studies.

However, the use of adsorbents for ammonium removal in small volumes of water, such as in transport systems, biofilters and intensive fish farming, is considered a cost-effective alternative (ZHOU & BOYD 2014, SHAH & MRAZ 2020). The use of zeolite to transport the armoured catfish *Ancistrus triradiatus* has been shown to reduce the ammonium concentration from 51 to 15 $mg.L^{-1}$ (70% removal) and to lower the number of deaths after transportation by 30% (RAMÍREZ-DUARTE et al. 2011). Furthermore, the combined use of zeolite and activated carbon during fish transportation showed better ammonium removal efficiency and survival rates compared to the use of either adsorbent alone (MUSTAHAL et al. 2021).

Adsorbents can be used in conjunction with biofilters because they promote the conversion of ammonium to nitrate due to the action of nitrifying bacteria on these materials and are 30% more efficient at removing ammonium and nitrate than when used separately (MOTESHAREZADEH et al. 2015, YU et al. 2019). When zeolite was applied to intensive sea bass farming, the adsorbent was able to reduce the amount of ammonia present in the water, improve the animals' performance parameters, and lower the amount of heavy metals present in the fish tissues, thus highlighting a number of benefits of using this material in aquaculture systems (SALLAM et al. 2024).

Additionally, adsorbents can be combined to enhance the efficiency of the adsorption and nitrification processes. YU et al. (2019) observed that the use of $15g.L^{-1}$ zeolite and activated carbon were able to maintain the recommended levels of ammonium ($<1mg.L^{-1}$) and nitrate ($< 40mg.L^{-1}$) for freshwater fish (BARBIERI & BONDIOLI 2015, KOCOUR KROUPOVÁ et al. 2018). Although there is still a lack of studies demonstrating the use of vermiculite in aquaculture, there is great potential for the use of this adsorbent in these systems. Thus, based on our results, we estimated that aquariums with a volume of less than 20-40 L should be supplied with either 400 g of zeolite, 400 g of vermiculite, or 800 g of activated carbon.

The use of zeolite and vermiculite can help maintain water quality, reduce chronic stress and mortality and improve animal welfare during farming, handling and transport (RAMÍREZ-DUARTE et al. 2011, STEVENS et al. 2017). The efficiency of zeolite and the low price of vermiculite make them more viable alternatives than activated carbon, which is more expensive, and the price is not proportional to the lower efficiency of this compound. Combined with the reactivation capacity of the adsorbents, the discovery of efficient and low-cost alternatives to remove ammonium from the water, such as vermiculite, contributes to the development of increasingly sustainable aquaculture (GHASEMI et al. 2018, EL MESSAOUDI et al. 2022).

NOTES

AUTHOR CONTRIBUTIONS

Conceptualization, methodology, formal analysis, R.R.F, D.S.M and J.T.L; investigation, R.R.F and L.F.S; resources and data curation, R.R.F, L.F.S, D.S.M and J.T.L; writing-original draft preparation, R.R.F, D.S.M and J.T.L; writing-review and editing, R.R.F, L.F.S, D.S.M and J.T.L; supervision, validation and visualization, D.S.M and J.T.L; project administration and funding acquisition, R.R.F, D.SM, J.T.L. All authors have read and agreed to the published version of the manuscript.

FUNDING

This work was supported by the National Council for Scientific and Technological Development (CNPQ) under grant number 300927/2022-3 for R.R.F.

INSTITUTIONAL REVIEW BOARD STATEMENT

Not applicable for studies not involving humans or animals.

INFORMED CONSENT STATEMENT

Not applicable because this study did not involve humans.

DATA AVAILABILITY STATEMENT

The data can be made available under reasonable request.

ACKNOWLEDGEMENTS

We would like to thank the Paraense Museum Emílio Goeldi for providing R.R.F. with an institutional training grant (PCI-DC/CNPq).

CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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