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Modified Dalian Medical Stone for Removing Ammonium from Aquaculture Water

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To improve the ammonium exchange capacity of the medical stone, its modifications in different solutions have been tested, respectively. The ammonium-exchange isotherms of the modified medical stone have been determined and compared. The renewable ammonium exchange capacity of the medical stone has been further studied. The results indicated that the ammonium exchange of medical stone increased as the average pore diameter and the BET surface area increased, after the medical stone were soaked with HCl and H_2SO_4 solutions. The modified method soaking with NaCl solution was superior to them, because the sodium content of this modified medical stone increased, leading to a more improved ammonium exchange capacity. The ammonium exchange capacity decreased with modified ion in the order $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$. When the ammonium concentration was 150 mg/L, the ammonium exchange capacity of medical stone modified with 98 ºC NaCl solution increased 80.4 %. For the ammonium exchange isotherms of medical stones, the Freundlich isotherm model yielded a much better fit than that of Langmuir isotherm model. After three times regeneration, the ammonium uptake of medical stone was changed little. Its exchange capacity was stable.

Key Words: Ammonium, Medical stone, Ion exchange, Aquaculture water.

INTRODUCTION

Ammonium (NH_3-N) comes from the soil of the most fish species in aquaculture. Due to its high concentration, it is extremely toxic to most fish species and other water animals, leading to the eutrophication in aquaculture water. It has become a grave threat to environment and aquaculture now[1]. The ion-exchange method is widely regarded as the best choice of ammonium removal and researched by many scholars. The essence of an ion-exchange method is the ammonium exchange of the ion-exchanger[2,3].

Medical stone is a kind of compound or medicinal mineral rocks with exchange ability[4,5], which has been widely used for the removalof metal ions[6], but few for removal of ammonium from aquaculture water. This paper tried to modify the medical stone with different ways for the improvement of its ammonium exchange capacity. Its modifications in HCl, H_2SO_4, NaCl, KCl, $CaCl_2$, $MgCl_2$ solutions has been tested, respectively. The ammonium-exchange isotherms of the modified medical stone have been determined and compared. The renewable ammonium exchange capacity of the medical stone has been further studied.

EXPERIMENTAL

Samples of the natural medical stone (denoted herein as natural) originated from Dalian city (China). The medical stone was crushed and classified to a size range of 0.45-0.9 mm. The fragments were washed with deionized water to remove water-soluble residues and dried in an oven at 100 ºC for 1 h.

Modification of medical stone: The 10 g natural medical stone was soaked in 50 mL of 1 M solutions of HCl, H_2SO_4, KCl, NaCl, $CaCl_2$ or $MgCl_2$ for 2 h, respectively. These medical stone samples were then washed four times with deionized water and dried in an oven at 100 ºC for 1 h.

The 10 g natural medical stone was soaked in 50 mL of 1 M NaCl solution, then incubated at 50, 80, or 98 ºC for 2 h, respectively. These medical stone samples were then washed four times with deionized water and dried in an oven at 100 ºC for 1 h.

Measuring experiment for the ammonium exchange of medical stone: 0.5 g Samples of medical stone were added to 50 mL aliquots of NH_4Cl solutions with different concentrations (0-240 mg/L) and the respective mixtures were shaken at a rate of 100 r/s at 25 ºC. After 24 h, the two phases were separated by filtration through a 0.2 μm microporous membrane filter after different time intervals (0.5-6 h). The ammonium concentration in the aqueous phase was analyzed by a colourimetric method using Nessler's solution[7]. This approach was adopted to test the different medical stones.

Measuring experiment for the ammonium exchange of regenerative medical stone: 0.5 g Samples of NaCl modified medical stone were added to 50 mL aliquots of 200 mg/L NH_4Cl solution. The respective mixtures were shaken at a rate of 100 r/s at 25 ºC. After 24 h, the ammonium concentration in the liquid phase was analyzed. Then the medical stone was soaked in 1 M regeneration of NaCl, NaOH, HCl, respectively. The ammonium exchange and exchanger regeneration experiments were repeated three times.

Calculation of the uptake of ammonium: Ammonium uptake (q_t) was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (1)$$

where, q_t is the total amount of exchanged ammonium (mg/g), C_0 and C_t are the initial and equilibrium concentrations of ammonium solution (mg/L), respectively, V is the solution volume (L) and M is the weight of adsorbent (g).

RESULTS AND DISCUSSION

Ammonium exchange of the different treatment medical stones: From Table-1 and Fig. 1, the ammonium exchange of medical stone increased as the increasing of the average pore diameter and the BET surface area, after medical stone soaking with HCl and H_2SO_4 solutions. The modified method soaking with NaCl solution was superior to them, because the sodium content of this modified medical stone increased, leading to a more improved ammonium exchange capacity. Ion exchange played with the most profound effect on the ammonium exchange.

TABLE-1
POROUS STRUCTURE PARAMETERS (at $P/P_0 = 0.98$)

Modification methods of medical stone	BET surface area (m^2/g)	Total porous volume (cm^3/g)	Average pore diameter (Å)
Natural	1.0203	0.000348	13.6615
H_2SO_4	1.7116	0.000846	20.0530
HCl	1.9803	0.001148	25.4563
NaCl	1.3203	0.000489	15.6615

Ammonium exchange of the metal ion treatment medical stones: From Fig. 2, the ammonium exchange capacity decreased with the modified ion in the order $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$, because of the smallest radius of Na^+ ion and its binding force to medical stone. Thus, it was easier to exchange with ammonium than other ions. It was similar to most other minerals.

Ammonium exchange of the heat treatment medical stones: As is shown in Fig. 3, the ammonium-exchange capacity of the medical stone increased on increasing the temperature at which it was soaked in NaCl solution. As the temperature was raised, the porous structure of medical stone changed little, but the rate of movement of Na^+ ions in the solution was accelerated and so more Na^+ ions in the free solution replaced metal ions in the medical stone owing to the enhanced force of the collisions. When the temperature of the NaCl solution reached 98 ºC, the modified medical stone obtained had the highest Na content and thus attained the best exchange capacity. When the ammonium concentration was 150 mg/L, the ammonium exchange capacity of medical stone modified with 98 ºC NaCl solution increased 80.4 %.

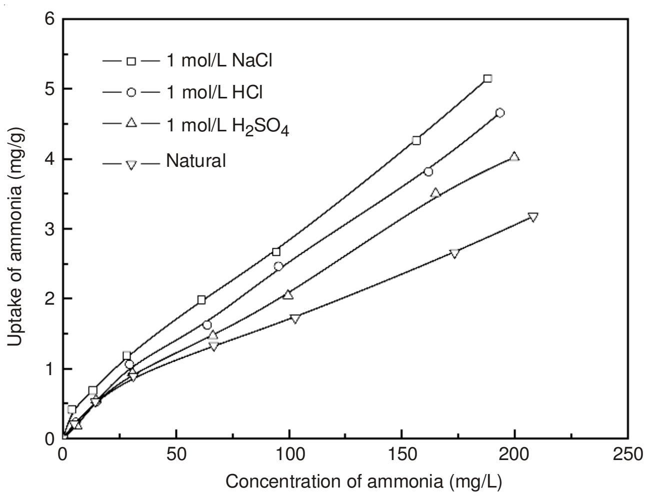

Fig. 1. Ammonium-exchange isotherms of medical stone modified with different solutions (T, 25 ºC; initial ammonium concentration, 0-240 mg/L; contact time, 24 h)

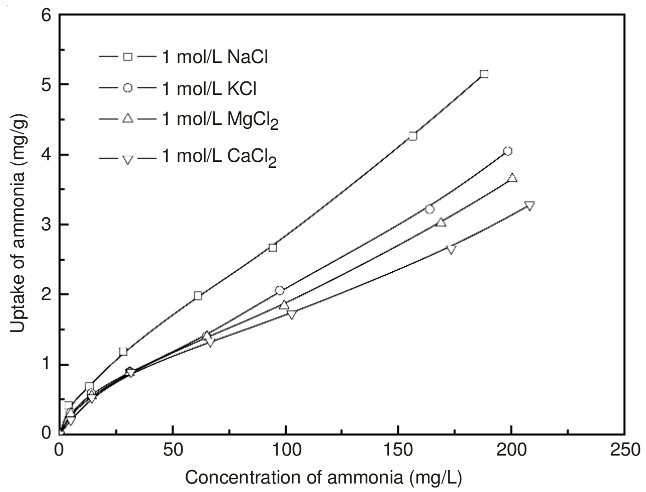

Fig. 2. Ammonium-exchange isotherms of medical stone modified with different metal ions (T, 25 ºC; initial ammonium concentration, 0-240 mg/L; contact time, 24 h)

Ammonium exchange of the regenerative medical stone: From Table-2, through the NaCl modified medical stone were regenerated with HCl, NaOH and NaCl solution three times, respectively, the ammonium uptake of medical stone was changed little. Its exchange capacity was stable, which is favour for the application of ammonium removal.

Exchange equilibrium isotherms: According to the experimental data in Figs. 1 to 3, the equilibrium relationships between the ammonium uptake of medical stone and its equilibrium concentration in the solution are characterized by the exchange isotherms. To characterize the exchange equilibrium of ammonium for the natural and modified medical stones, the Langmuir and Freundlich models were used. After fitting the experimental data, it was found that the Freundlich model yielded a much better fitting (R^2 = 0.999-0.982) of the data compared with the Langmuir model (R^2 = 0.989-0.743).

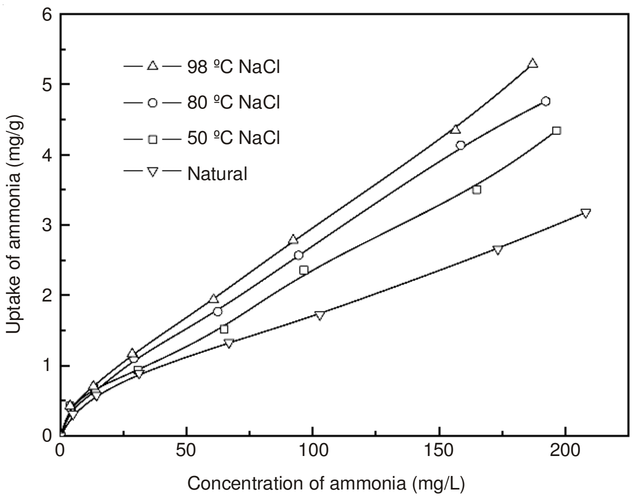

Fig. 3. Ammonium-exchange isotherms of medical stone samples modified with NaCl solutions at different temperatures (T, 25 ºC; initial ammonium concentration, 0-240 mg/L; contact time, 24 h)

TABLE-2
AMMONIUM UPTAKE OF THE REGENERATION MEDICAL STONES

Regene -ration	Ammonium uptake before regenerating (mg/g)	Ammonium uptake after the first regenerating (mg/g)	Ammonium uptake after the third regenerating (mg/g)
HCl	4.1338	4.1601	4.1665
NaOH	4.1556	4.1338	4. 1900
NaCl	4.1348	4.1873	4.2137

Conclusion

The results have shown that the ammonium exchange of medical stone increased as the increasing of the average pore diameter and the BET surface area, after the medical stone were soaked with HCl and H_2SO_4 solutions. The modified method soaking with NaCl solution was superior to them because of the increasing of the Na content of this modified medical stone, leading to a more improved ammonium exchange capacity. Ion exchange played with the most profound effect on the ammonium exchange. The ammonium exchange capacity decreased with the modified ion in the order $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$. This was similar to most of other minerals. When the ammonium concentration reached 150 mg/L, the ammonium exchange capacity of medical stone modified with 98 ºC NaCl solution increased 80.4 %. For the ammonium exchange isotherms of medical stones, the Freundlich isotherm model yielded a much better fit than that of Langmuir isotherm model. Further, through the medical stone were regenerated with HCl, NaOH and NaCl solution three times, respectively, the ammonium uptake of medical stone was changed little, showing a stable exchange capacity.

In addition, medical stone, with adsorption, solubility, pH adjustment, biological activity and mineralization, is good to aquatic organism. This modified medical stone would apply in the ammonium removal from aquaculture water.

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