Application of Modified Bentonites (SMB and ATB) for Decreasing the Environmental Effects of Phosphate and Sulphate Anions Existing in RAS

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Introduction

Aquaculture wastewaters when discharged to the environment or another receiving body of water can create serious problems. These effluents contain large amounts of harmful material such as organic compounds, anionic and cationic species, uneaten food and etc., which have undesirable effects on the health of aquatic ecosystems and aquaculture facilities. Aquaculture systems produce large quantities of nutrients (phosphorus and sulphate) that require treatment and/or disposal. Principal sources of aquaculture wastes are uneaten foods. The presence of trace amounts of phosphate (even less than 1 ppm) in treated wastewater is often responsible for eutrophication; particularly in lakes and slow moving rivers. Sulphate and phosphorus, discharged with these effluents, result in enhanced growth of organisms associated with eutrophication. However, regulatory agencies are becoming increasingly concerned over elevated sulfate concentrations in effluents, owing largely to its impact on the salinity of receiving waters. There are several methods to treat wastewater containing sulfate anions. The removal of the anion by means of adsorption on the activated carbon, neutralization with $CaCO_3$, biological treatment, reverse osmosis and dialysis and ion exchange were studied. Aiming for the high quality of receiving waters in aquaculture systems, various techniques such as settling systems, centrifugal systems, mechanical filters (media filter and screen filter) and biological processes have been introduced and were applied. Inorganic ion exchanger materials such as zeolites are utilized to remove ammonia from fish raring facilities. Clay is another material that can be used as an ion exchange adsorbent. However, it is utilized very poorly in the existing aquaculture wastewater treatment facilities. The use of clay as anion exchanger in aquaculture has not been considered yet. After modification, clay is also capable of removing anions and other compounds with negative charges. In this study, by using a cationic surfactant TDTMA, and acid thermo activation methods, the surface of bentonite was changed and the capability of the exchanged clay for the adsorption of anionic compounds such as sulfate and phosphate from aquaculture effluent was analyzed.

Materials and Methods

Bentonite, natural clay, was acquired from Tabas Iran Co. in Tehran and was used without any further purification. All chemicals were of analytical reagent type and were used as received. The standard solutions were prepared using $NaNO_3$, $NaNO_2$, Na_3PO_4 and Na_2SO_4 salts in Milli-Q water.

Fish culture system containing two 200-L fish tanks and a sump tank was designed and constructed. Each tank was stocked with 30 trout of 120g mean weight (9.37 Kg/m^3). It also included a combined unit of sand and biological filter to remove faces and other suspended particles and biological inter-conversion of nitrogenous wastes, respectively .The X-Ray diffraction pattern of the mineral sample showed that the major clay material present in the sample is bentonite.

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The main mineralogical impurities are Quartz, hydrated silicates of sodium, calcium, magnesium and aluminum, Stellerite-(Na), Illite, Muscovite and Gypsum. The composition of bentonite in terms of its oxide forms provided by the manufacturer is listed in Table 1. Elemental analysis of the sample using XRF showed that the raw material had Si/Al ratio of 3.46.

The Na-exchanged form of bentonite was prepared by stirring samples for 6h with a 1M aqueous solution of NaCl. Excess NaCl and other exchangeable cations were removed from the exchanged bentonite via filtering. Then, it was washed several times with deionized water until a negative chloride test was obtained with 0.1M $AgNO_3$. The Na-saturated bentonite (50g) was dispersed in 1L of distilled water. TDTMA–bentonite was prepared by adding quantities of the respective surfactant equal to twice the cation exchange capacity of the bentonite and was stirred for 6h. After treatment, bentonite was washed with deionized water to obtain salt-free minerals and a negative chloride test was carried out with 0.1M $AgNO_3$. Finally, it was dried, grounded and sieved to a size range of 0.8-1.2mm.

The acid thermo activated clay was obtained from a natural sodium bentonite. The raw material was first decarbonated and homoionized. Acid thermo activation is a process that allows controlled extraction of aluminum ions from crystalline structure of clay, also introducing an acceptable acidity level. This process modifies the textural properties of clays, favoring a greater porosity and surface area. To carry out acid thermo activation, the purified clay was put in a flask with an acid solution (10 mL acid/1 g clay), stirred and refluxed and heated to 105°C for 3h. The utilized acid solution was: HNO_3 (2N). Thereafter, the clay was washed with de-ionized water and dried at 70°C. The powders were ground to a particle size of 0.8-1.2mm and then heated for 4h at 300°C.

The solution pH was carefully adjusted by adding small amounts of HCl or NaOH solutions and measured using a pH-meter (corning 120). The samples were filtered and the equilibrium concentrations ascertained by photometer (palintest® 8000). The amount of anions adsorbed onto TDTMA–Bentonite (SMB) was determined by the difference between the initial and remaining concentrations of anionic solutions. The distribution coefficient (K_d) was determined by using the following equation:

$$K_d = \frac{(C_i - C_e)}{C_i} \cdot \frac{V}{m}$$

Where C_i and C_e are the initial and the equilibrium anions concentrations (mg/L), V is the volume of solution (mL) and m is the amount of the used adsorbent (g).

Results and Discussion

Structural comparisons between modified and natural bentonite imply that modification procedures have changed crystal lattice and layered structure of the mineral smoothly (Figs. 3 and 4). Heating resulted in increased distance between layers and consequently yielded higher anion uptake compared with natural bentonite. Surfactant layer grafted on surface and within the layers of mineral resulted in anions removal by the modified bentonite.

The present study was set out in a laboratory condition to evaluate the anion absorption capacity of surfactant acid thermo modified bentonites so as to reveal the potential of the compound as an alternative water remediation method for aquaculture recirculation system. The research clearly suggests that modified bentonite acts as a proper adsorbent for the removal of harmful anions from aquaculture and aqueous solutions. Because of the importance of generating a viable ion uptake tool for toxic species, different studies have been carried out regarding the use of a low-cost adsorbent for the selective removal of anions from aqueous solutions.

Conclusion

It has been shown that bentonite modified by TDTMA and acid thermo activation method provides a considerable ion uptake capacity. The main advantages of this procedure are as follows:

1- Natural bentonite is very cheap and abundant.

2- Results showed that bentonite modified by TDTMA was efficient for removing harmful ions from aquaculture wastewater and decreasing anions under the critical levels.

3- Since the bentonite clays even in modified forms can remove cationic species, so this adsorbent is very effective for the simultaneous removal of cationic and anionic species from aquaculture recirculation effluents.
4- This new adsorbent can be utilized as a supportive filter in RAS to remove toxic compounds such as NO_3^-, NO_2^-, $PO4_3^-$ and SO_4 from aquaculture systems.

Key words
Recirculation system, Anionic compounds, Bentonite, surfactant, anion adsorption, BMPs