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Research paper



Phosphorus and Nitrogen Treatment of Reservoir Water using Zeolite

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Abstract

Eutrophication in reservoir and tributaries causes obstruction of water flow and increased concentration of organic matter and plant production. The purpose of this project is to research about development of a cost-effective, affordable, efficient and portable Total Phosphorus (TP) and Total Nitrogen (TN) removal agent, transferrable across the target market to facility owners and individuals in the world. Two types of pellet composition were chosen for this project which is zeolite plus clay and the other one is clay only. Implementing a chemical adsorption technique of a clay-zeolite media is unique to the industry. The project outcome was intended to create and test a bench scale apparatus with engineered adsorption clay-zeolite media, and prepared for further field analysis, such as pH stabilization and many more. From the result analysis, we have found that as the contact time increases, the removal efficiency of the pellets also increases. It is clear that pellet with clay and zeolite composition has a better adsorption rate on removal efficiency about 53% for TP and 82% for TN rather than clay only pellet about 48% TP and 67% TN. Since the synthetic solution has a concentration of 5mg/L for both phosphorus and nitrogen, the only variables are pellet composition, pH, temperature and contact time. Both pellets have their pH increasing as the contact time increases.

Keywords: *Eutrophication; Clay-zeolite; Nitrogen; Phosphorus; Zeolite*

1. Introduction

In recent decades water quality deprivation has been a fundamental worry for social orders, since this impacts affects biodiversity, biological communities, human well-being, and drinking water utilization and food creation. A great part of water quality deprivation is identified with exorbitant loadings of nutrients. Nitrogen and Phosphorus compounds are basic nutrients to all forms of life, however in the event that it displays in significant amounts in getting waters, for example, lakes and waterways can cause their eutrophication [1]. N and P more often than not enters the surface water bodies through diffuse (e. g. horticulture keep running off) and point (e. g. release of mechanical wastewater from various industries, landfill leachates) sources, bringing about over the top development of green growth and different microorganisms, and additionally in expanded broke up oxygen consumption and fish lethality [2]. Thusly, these nutrients must be eliminated from wastewaters to control eutrophication in lakes and others water bodies. This is a critical factor in ecological sustainability.

Eutrophication results from the improvement of a waterway with preparing components which, within the sight of daylight, stimulate development of green growth and other sea-going plants [3]. Broad development of these plants can have numerous unfortunate impacts [3]. They tend to stop up streams and to frame drifting mats which diminish water clarity [3]. They frame rearing justification for flies and bugs and the disintegration of green growth can prompt offensive scents [3]. In addition, they can have different unfriendly consequences for seized water utilized for water supplies [3]. Numerous components are basics for the development of green growth; be that as it may, in characteristic water mixes of nitrogen and phosphorus are every now and again in restricted supply, which tends to control the degree of development that happens [3].

These aquatic biological communities are immaculate when the supplements' concentrations are low. Nitrogen and phosphorus are exhibited to the biological community as microbial and creature digestion, where a generally consistent state is accomplished with essential generation of new plant biomass. Once the water bodies are misleadingly improved with abundance phosphorus and nitrogen, rate of plant generation will increment and natural issue will begin to aggregate [4]. Different treatment strategies have been utilized utilizing substance, physical and natural frameworks to point of confinement or control the sum and type of supplements released by the treatment frameworks. At first the genius ceases most ordinarily utilized were organic nitrification for nitro-gen expulsion, and substance precipitation for phosphorus evacuation. Lately, various natural treatment forms have been created for the expulsion of nitrogen and phosphorus alone or in blend [5, 6]. Treatment technologies presently available include:

Physical: application of membrane innovations, filtration for particulate substance bearing phosphorus and nitrogen. There are a few downsides of utilization of membranes innovations: high starting investments, costly membrane substitution, and higher energy utilization in contrast with different techniques, and generally enormous measure of sludge produced by the concentrate treatment [2].

Biological: Biological Nitrogen Removal (BNR) is a combination of nitrification and denitrification, taking place as consecutive procedures. BNR is process; where conditions are are made that empower certain kinds of microbes to take-up over the top measures of phosphorus. The microscopic organisms are then

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expelled from the treatment procedure before they have sufficient energy to discharge back this phosphorus [2].
A mix of small scale green growth (Chlorella Vulgaris or C. sorokin-iana) and a miniaturized scale green growth development advancing bacterium (Azospirillum brasi-lense starin Cd), co-immobilized in little alginate dabs, was produced to expel phosphorus and nitrogen from metropolitan wastewater[7].
Chemical and physical-chemical: adsorption, precipitation, ion exchange (utilizing a mix of a cation and an anion exchanger) [2].
An audit of the distributed writing uncovered significant earlier innovative work of nutrients (P and N) adsorption forms utilizing zeolites, particularly clinoptilolite, in view of zeolites' appealing particle trade, adsorption, and hydration properties, various examinations have been completed [2, 3].
Given the ion specifically attributes of clinoptilolite, it ought to be appropriate for use in ammonia removal from aqueous solutions or effluents. A survey of the distributed writing revealed considerable prior research and development of ammonia ion-exchange process utilizing zeolite. Abroad studies, which utilized zeolites from a wide range of stores, have built up that zeolite, particularly clinoptilolite, has the potential to eradicate ammonia from municipal, industrial, and aquaculture wastewaters.
Recently, the research has been pointed at consuming bottomless naturally happening ease materials in the wastewater treatment, for example, characteristic and adjusted zeolites and bentonites, as well as zeolites synthesized from waste materials [2].
The practicality of using natural and Fe modified bentonites as adsorbents for phosphate removal from natural waters was contemplated [8]. he outcomes demonstrated that the adsorption limits of Fe-changed bentonites were near the limit of the Phoslock (a business bentonite item covered with lanthanum) and substantially higher contrasted with unmodified bentonite. Over 75% were evacuated (at introductory PO43-convergence of 50 mg/L) inside 60 minutes.
The removal of ammonium by natural and modified zeolitic materials has been broadly researched recently since utilization of zeolites would contribute to creating an environmentally friendly and sustainable technology for contaminants evacuation.
Clinoptilolite and mordenite were found as the best common zeolites for NH4+, because of their high selectivity for ammunition nium particle within the sight of contending cations, (for example, K+, Ca2+ and Mg2+), over an extensive variety of NH4+ concentrations [9]. It was discovered that Australian regular zeolite-clinoptilolite, might be effectively utilized in a settled bed particle trade procedure to accomplish high smelling salts expulsion efficiencies from fluid arrangements at rates commensurable with sand filtration [10]. A consolidated framework with zeolite and lime was proposed for removal of nutrients from wastewater. Removals of 98 % NH4+ and 100% aggregate phosphorus were accomplished [11]. Zeolite integrated from fly cinder and adjusted by corrosive treatment (with 0.01 mol/L H2SO4) indicated promising evacuation productivity for both NH4+ and PO43-at low focuses [12].
The utilization of Natural Bulgarian zeolite (clinoptilolite) indicates relatively great removal efficiency as for NH4+ from wastewater [2]. It shows low ability to remove PO43-from wastewater. Zeolite change with Na+ fundamentally enhances its take up ability as for NH4+. Just in one hour and in one stage, by utilizing Na-adjusted zeolite, the ammonium concentration was diminished from 5 times MAC to the level required by the standard. The take-up of NH4+ takes after the pseudosecond-order active model. Zeolite change with Mg2+ and particularly with Fe2+ enhances its capacity to take up PO43-from wastewater, at essentially keeping the capacity displayed by regular zeolite as for NH4+ immobilization [2]. Use of naturally taking place, low-cost materials, such as zeolites for handling waste discharges will contribute to the sustainable development of our society.

2. Materials and Methods

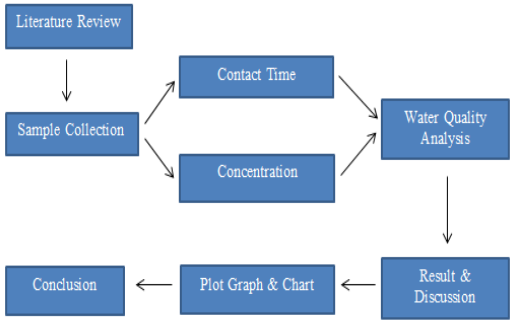


Fig 2.1: Methodology flowchart for Total Phosphorus and Nitrogen treatment

Figure 2.1 explained the process of this project to accomplish the water treatment for total phosphorus and nitrogen by using clay based pellet of zeolite mix with clay (kaolin+bentonite).
Total Phosphorus (TP) is a mix of all filterable and particulate structures. TP is the most broke down and inspected phosphorus division [13]. TP is portrayed in light of how much phosphorus is available to be oxidized into orthophosphate. Scientific tests for assimilation and analysis varies, which present error and information impediments; which must all be seen and connected in like manner [14]. The real results caused by eutrophication can be recorded as takes after: Diversity of plant and creature species declines, plant and creature biomass increment, turbidity builds, rate of sedimentation aggregation expands, shortening the life expectancy of the lake and anoxic conditions may create.
Total Nitrogen is an essential nutrient for living life forms. However, an excess proportion of nitrogen in a conduit may incite low levels of broke up oxygen and adversely change the environment and the different lives that rely upon it. Wastewater treatment plants, spill over from prepared yards and croplands, overflow from animal waste and storage areas, and industrial discharges that contain consumption inhibitors are cases of nitrogen sources.
When there is substantial grouping of living beings, there will be enormous competition for resources. This abnormal state of rivalry and competition makes survival for living beings hard in such eutrophic frameworks. Along these lines, the decent variety of creatures and plants in eutrophic frameworks will be lower than ordinary frameworks. The addition in nutrient levels can have an effect on human activities. The foremost occurring issues can be summarized as follows: - The water might be not appropriate for drinking; expanded centralization of vegetation may square water stream and route, local types of amphibian living beings may vanish, treatment of drinking water might be hard and water supply can have an unsatisfactory taste or scent.
Pellet composition is important to this project's research. Zeolite is created from polycrystalline powders, inside a particle size estimated range of 1-10 µm. Thusly, it must be shaped into granules, circles, or expels before adsorption applications. This lessens the probability of a weight drop and grows mechanically solid particles. Pelletization is accomplished by utilizing regular clay, for example, bentonite, attapulgite, and kaolin. These clays are considered as inorganic covers, consolidated at 15-20% of the zeolite pellet [15]. Seidel also supports Jasra's claim, expressing that a by mass proportion of 80% zeolite precious stones to 20% fastener material was perfect. This is additionally streamlined with a cover structure as 80% kaolinite and 20% bentonite clays (similar to natural clay material) [16].
These pellets are exposed to high-temperature treatment to cease the clay's surface area and movement; produce appropriate mechanical stability and keep up high sorption properties. This development of zeolite pellets produces meso/macro-pores within the pellet; converting the absorbent elements of the reactant molecules[15]. It is basic to choose the suitable fastener, acquire ap-

propriate mixing and granulation conditions, and know the covers' effect on zeolite pellets' sorption and catalytic properties [15]. The binder material incredibly impacts the mechanical properties and adsorption capacities of the last molecular sieve item. The goal was to build up the subsequent qualities of the final optimized pellets [16]: zeolite-binder mixture flexibility, high mechanical stability, insignificant static and dynamic adsorption impacts of zeolite properties, and adequate binder thermal, hydrothermal, and chemical steadiness during sorption process, and low reactant movement.



Fig2.2: Zeolite used for TP and TN treatment



Fig 2.3: Soil (Bentonite+Kaolin) used for TP and TN treatment

3. Experimental Design

Parameters

Based on extensive study of literature review, many key factors were analysed in this research to determine the optimal pellet composition and removal rate [17]. These parameters are included in below.

Table 1: Experimental Parameters

	parameters	characteristic
1	Pellet composition	Clay+zeolite Clay only
2	Contact time (minutes)	15min 45min 90min 120min 150min 180min
3	Influent concentration	5mg/l for both phosphorus and nitrogen (synthetic solution)
4	Effluent concentration	Less than influent concentration
5	Furnace exposure (degree)	100 for 24hours 400 for 1hour 600 for 24hours
6	Removal efficiency	Contact time to Removal concentration (minutes:mg/l)

3.1. Pellet Formation

The following outlines the procedure used to form a different pellet, based on various clay types and ratios, as well as zeolite gradations and ratios [17]. This formation of pellet is taken from previous study but with little modified such as using different ratio of mixing clay.

1) In a medium steel bowl, 43.8 g of zeolite and 35 g of clay were added. These bowl contents were mixed to become evenly distributed.
2) Beginning with a clay:water ratio of 1:4, DDW was added to the bowl at 2 to 4 increments until measurable workability was achieved into paste consistency.
3) The paste was kneaded and formed into a 1-2 inch diameter cylinder.
4) Using a melon baller of interior volume of a ¾ inch sphere, the clay was extracted. The paste was removed from the melon baller. The paste mass was reshaped to form a sphere of ¾ inch diameter.
5) The pellets were air dried for 24 hours.
6) The pellets were placed on the furnace tray and inserted into the preheated furnace at approximately 100ºC (LOW Setting), dehydrated for 24 hours.
7) The furnace was increased to approximately 400ºC (2 Setting), and one hour later to approximately 600ºC (3.5 Setting), allowing for calcination for 24 hours.
8) The furnace was turned off and allowed to come to room temperature before removal, and stored in open sealable plastic bags.



Fig 3.1: Sample clay based pellet (zeolite+clay)

4. Result and Discussion

The experimentsl values of phosphorus, nitrogen and PH obtained after application of clay based zeolite pellet and clay pellet only.

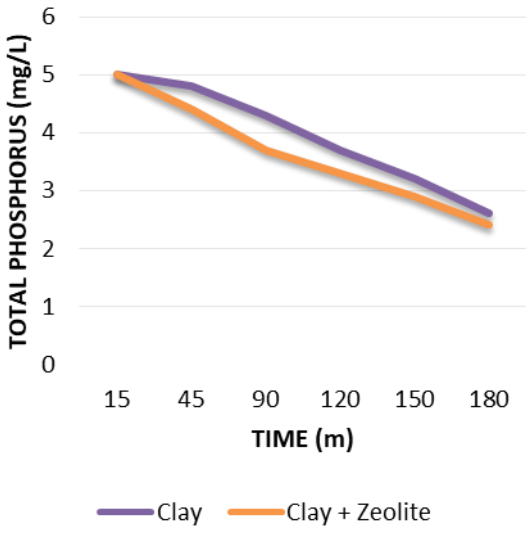


Fig 4.1: Total Phosphorus after treatment with time interval

Based on figure 4.1 shows that the result of the comparison of total phosphorus after treatment with time interval. The Total Phosphorus concentration starts to decrease after the 15 mins mark. As the time goes by, Total Phosphorus concentration gradually decreases at a steady pace. However, the clay only pellet takes longer time to absorb phosphorus compared to clay + zeolite pellet.

This shows that clay + zeolite pellet has better phosphorus absorbing capacity than clay only pellet.

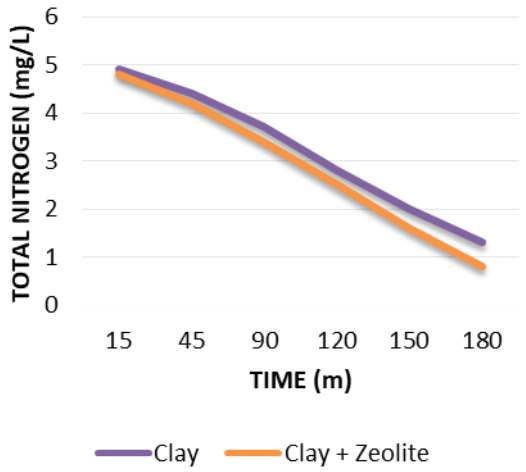


Fig 4.2: Total Nitrogen after treatment with time interval

Based on Figure 4.2 Result Comparison of Total Nitrogen After Treatment with Time Interval, we can see that both pellet types start off at 5 mg/L. At 15 mins, the Total Nitrogen concentration has reduced a little for both pellet types. However, clay + zeolite pellet has started to decrease the nitrogen more than clay only pellet. As the time goes by, Total Phosphorus concentration gradually decreases at a steady pace. However, the clay only pellet takes longer time to absorb nitrogen compared to clay + zeolite pellet. This shows that clay + zeolite pellet has better nitrogen absorbing capacity than clay only pellet.

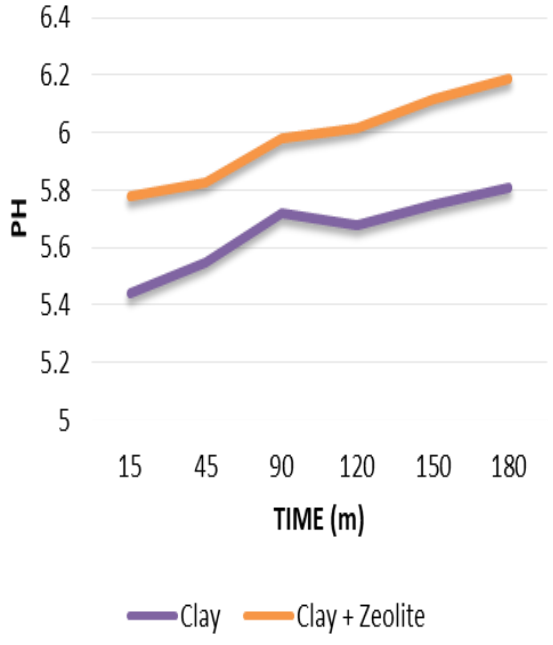


Fig 4.3: pH after treatment with time interval

Based on Figure 4.3 Result Comparison of PH after Treatment with Time Interval, we can observe that both pellet types are increasing the pH of the synthetic solution closer to 7 (neutral). As the time duration increases, the pH value also increases. However, there is a big difference between both the pellets. Clay + zeolite pellet increases the pH of the synthetic solution more dramatically than clay only pellet as shown in figure above. Consequently, this suggests that clay + zeolite pellet is more efficient in increasing the pH of a solution.

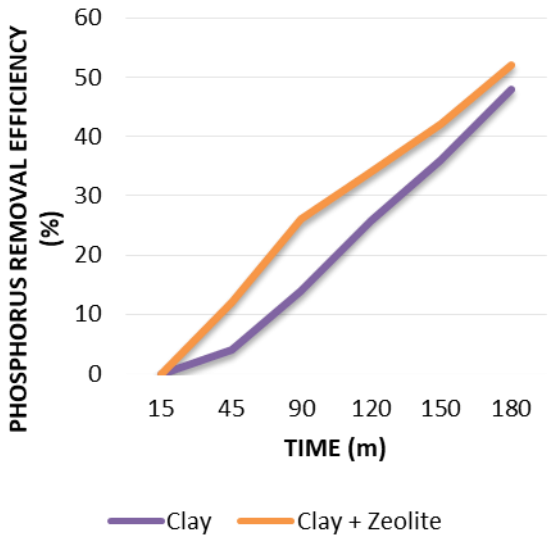


Fig 4.4: Phosphorus removal efficiency with time interval

Based on Figure 4.4 Result Comparison of Phosphorus Removal Efficiency with Time Interval, both pellet types start off at 0 % of removal efficiency. At 15 mins only, both pellet types start to remove some phosphorus. Both pellet types gradually remove phosphorus in the synthetic solution in a steady pace. Clay + zeolite pellet is obviously better than clay only pellet in terms of phosphorus removal efficiency. Thus, clay + zeolite pellet clearly is better at reducing the concentration of phosphorus about 53% in a water body affected by eutrophication.

This might be expected the way that zeolite has a particular limit of pores for the adsorption of substances, and when a more prominent measure of phosphorus is available, not all the phosphorus can be adsorbed also as nitrogen [18].

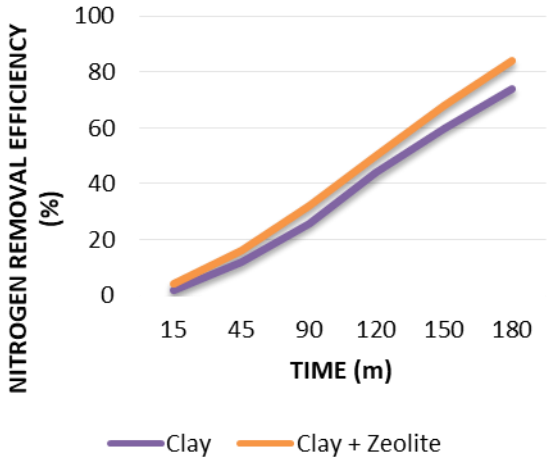


Fig 4.5: Nitrogen removal efficiency with time interval

Figure 4.5 shows the result comparison of nitrogen removal efficiency with time interval. Both pellet types gradually remove nitrogen in the synthetic solution in a steady pace. Clay + zeolite pellet is obviously better than clay only pellet in terms of nitrogen removal efficiency. Thus, clay + zeolite pellet clearly is better at reducing the concentration of nitrogen about 67% in a water body affected by eutrophication.

This might be because of the way that the bigger the amount of ammonium particles in the medium, the more troublesome it is that they all frame some portion of the ionic trade, on the grounds that lone a specific amount of negative burdens exists and is accessible as a component of the oxygen show in the zeolite structure [18]. In the meantime, just certain amounts of pores exist in

the mineral, which it makes conceivable to harbor a littler level of atoms in a profluent that contains a higher ammonium fixation.
Comparable conduct was seen by Rozic et al. [19] who found the most elevated N-NH+4 expulsion efficiencies (61.1 %) at an underlying ammonium convergence of 100 mg/L. With the expansion of the underlying convergence of ammoniacal nitrogen, the evacuation proficiency immediately diminished. This was normal as zeolites and different muds have restricted adsorption capacity which is critical from a down to earth purpose of see. Likewise, for metropolitan wastewater, the ammonium evacuation proficiency was improved by more than 27 % when the influent ammonium focus was somewhere in the range of 24.7 and 50.5 mg/L. [20]

5. Conclusion

From the result analysis, we have found that as the contact time increases, the removal efficiency of the pellets also increases. It is clear that pellet with clay and zeolite composition has a better adsorption rate on removal efficiency 53% for TP and 82% for TN rather than clay only pellet about 48% TP and 67% TN. Since the synthetic solution has a concentration of 5mg/L for both phosphorus and nitrogen, the only variables are pellet composition, pH, temperature and contact time. Both pellets have their pH increasing as the contact time increases.
However, clay + zeolite pellet was closing to 7 faster than clay only pellet. So, the clay + zeolite pellet can be used to reduce the concentration of phosphorus and nitrogen as proven. The best part is it's a simple and cost effective on-site Total Phosphorus and Total Nitrate removal unit. It can be used worldwide and will make a huge difference in reducing eutrophication problem

6. Recommendation

This research uses zeolite + clay and clay only as the treatment reagent. Other alternative materials shall be discovered in the future to improve the existing one. Zeolite can be paired with other materials to improve efficiency. Water hyacinth is a good pair up for zeolite and can be a replacement for clay. Activated carbon is also a good chemical adsorbing agent. There are many materials out there yet to be discovered for its water treatment abilities. So, this research will definitely open up the possibility for new materials with better efficiency to be used in the future.

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