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USE OF LANTHANUM -MODIFIED BENTONITE TO REMOVE PHOSPHORUS CAUSING THE EUTROPHICATION IN THE RESERVOIRS OF WASTEWATER TREATMENT PLANT

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Abstract

Phosphate (P) is one of the nutrients that contributed in the eutrophication especially in the reservoir of wastewater plant and lakes. The consequence of the increase of nutrients (phosphate and nitrogen) will cause algal blooms. Many methods have been used to remove and mitigate the eutrophication such as. Chemical methods are more effective, fast and low cost compared with other methods. The La- modified bentonite (LMB) was made from the prepared powders which consist of local bentonite, soluble starch and La $(NO_3)_3.6H_2O$, at 70%:20%:10% (in weight). LMB was tested to remove the (P) from standard solution with 0.5M concentration. A significant decrease of removal for (P) was 90%. Four concentration of LMB (25, 50, 75 and 100ppm) have been used to treat the samples collected from the reservoir of wastewater treatment plants that contain P. Removal percentage of phosphorous from the samples by using LMB compared with the control is 96%, for the four concentrations. The results revealed significant decrease of P level in the samples after treatment. So LMB could be used in the future as chemical compound for eutrophication treatment.

Key words: lanthanum modified bentonite, phosphate, eutrophication, algal bloom, wastewater.

Introduction

Most Reservoirs of wastewater plants are often exposed to the eutrophication due to the inputs of nutrients especially phosphorous (P) and nitrogen (N). Many studies relate cyanobacterial blooms to the increased internal phosphorus (P) loading (Nürnberg, 2017). The use of geo-engineering materials are increased to control of phosphorus (P) release from bed sediments (Mackay *et al*., 2014). This increase in the P can cause algal blooms, which are often cyanobacteria-dominated, that need to be removed (Waajen *et al*., 2015).

So, to mitigate the negative effects of eutrophication many of management interventions have been used such as flushing, mixing, the application of algaecides and biomanipulation (Waajen *et al*., 2015). Nowadays the interesting in P-sorbing materials is increased (Hickey and Gibbs, 2009; Spears *et al*., 2013). So a range of materials are recently available for use at the field scale and an increasing number of novel materials are being proposed for use (Hickey and Gibbs, 2009).

The techniques that have been developed to bind P in the sediment, like addition of iron Fe (Boers *et al*., 1992) and aluminum (Al) addition (Welch and Cooke, 1999; Lewandowski *et al*., 2003; Reitzel *et al*., 2005) for artificial oxygenation. Due to Al is insensitive to changing redox conditions, it is preferred to use more than Fe (Boers *et al*., 1992). However, using of Al in lake restoration has some limitations. Therefore, the application of Al can be a difficult method to in lakes with low alkalinity where the buffering capacity of the input water may be too low to prevent a decline in pH concentrations (Reitzel *et al*., 2012).

Lanthanum, also called Rare Earth Elements (REEs), has a unique physical and chemical characteristics that enabled it to use in many applications including chemical, military, aerospace, agricultural and other fields (Massari and Ruberti, 2013; Thomas *et al*., 2014).

REEs compromise 5.0 g and 18.0 g per metric ton of in the earth's crust and in igneous rocks respectively. It can be found in the form of the basic oxide in many ores such as cerite, parisite, allanite, orthite and monazite sand, binding with Cerium, in concentrations of about 25% (Venugopal and Luckey, 1978).

REE has been greatly used for many years as fertilizer to increase the crop production in China (Jin *et al*., 2009). Lanthanum, trivalent, react with phosphate in the molar ratio of lanthanum to phosphate is 1:1, (Haghseresht *et al*., 2009) as shown as shown in Eq. 1.

$$La^{3+} + PO3^{-4} \longrightarrow LaPO_4 \quad (1)$$

La^{3+} reacts *in-vitro* with various tissue components, e.g. proteins, enzymes and phosphates (Das *et al*., 1988). A group of clays that formed by crystallisation of vitreous volcanic ashes were composed what known 'Bentonite', that deposited in water. This material has many applications such as used as filler in crayons, a lubricant in oil well drilling, base in cosmetics and in the manufacture of concrete. Also Bentonite has been confirmed as a food additive in Australia (Chemicals Notification and Assessment, 2001).

Lanthanum ions La^{+3} (5%) is locked into a bentonite clay construct to form Lanthanum Modified Bentonite (LMB) or Phoslock (Dithmer *et al*., 2015). The ion-exchanged La in Phoslock captures and immobilizes P as an insoluble La phosphate phase (Douglas *et al.,* 1999; Robb *et al*., 2003; Dithmer *et al.,* 2015).

The biological actions of lanthanum ion (La^{+3}) is almost entirely depend on the use of this rare earth ion as a substitute or antagonist for Ca^{+2} in a variety of cellular and subcellular reactions (Weiss, 1974).

Materials and Methods

Preparation of lanthanum bentonite

Bentonite was provided locally from Karbala city which was purified in the laboratory of Ministry of Science and Technology by an ion exchange process. Based on Chen *et al.,* (2012), the La- modified bentonite was made from local bentonite, soluble starch and La $(NO_3)_3.6H_2O$, at 70%:20%:10% (in weight). Bentonite was used as both aggregates and binders of the ceramic; soluble starch was used as a porosifier to increase pores after the mixture fired at high temperature; $La(NO_3)_3.6H_2O$ was introduced as an additive to load La, that was expected to form a hydrous lanthanide oxide complex which would enhance the adsorption ability toward phosphorus. DDW was added to the prepared powder and mixed thoroughly. Then the mixture was dried at 105°C for 24 h in Memmert oven.

Finally, the dried mixture was sintered at 600°C for 1 h in a muffle furnace oven. After drying the mixture it was grinded by the mortar and sieved with 0.075mm sieve to obtain fine particles.

Stock solution preparation for LMB

The stock solution of LMB was prepared by dissolving 1g of the powdered in 100ml of D.W. to obtain concentration 1000 ppm. A serious of dilutions was prepared of the stock solution (25, 50, 75 and 100 ppm), as illustrate in table 1.

Table 1: Shows concentrations and volumes of stock for LMB based on 100 ml of reaction container.

Reaction	Lanthanum bentonite (ppm)	Volume
1	25	0.25 ml
2	50	0.50 ml
3	75	0.75 ml
4	100	1.00 ml

Preparation of standard curve for phosphate solution

Phosphate was measured by Murphy and Riley, (1962) method. Stock phosphate solution was prepared by dissolve 0.4394g of Potassium phosphate monobasic KH_2PO_4 (dried at 105°C for one hour) in 900 mL DDW. Two milliliter of concentrated H_2SO_4 was added and dilute to 1 L [1.0 mL = 0.100 mg P (100 mg P/L)]. The previous solution was diluted by adding 100 ml of it to 400 ml of DDW. Each 1ml contains 0.020 mg of P (20mg/l). For drawing standard curve a serial of standard phosphate concentrations (0.65, 1.95, 3.25, 4.87 &6.50 mgl^{-1}) was prepared. Ten ml of each concentration was diluted to 50 ml by DDW and then 8ml of the complex reagent was added to them. After 10 minutes they were measured by spectrophotometer at wavelength 820nm.

Treatment the samples with LMB

Twenty milliliter of the sample that collected from wastewater treatment plant was transferred to reaction vessel with 100ml volume. After LMB was added, to reaction vessel the volume was completed to 100 ml with BG11 media.

Samples were incubated in algal incubator (JSR) for three days. Water samples were filtered through Whatman filter paper 0.45mm pore size filters.

Some environmental parameters (phosphate, pH, turbidity, temperature, dissolved oxygen and biomass) of the collected samples were determined. In a separate experiment, we objected the standard sample treated with LMB, to 40°C for 1 hour and after treatment the P was measured.

Results and Dissection

Phoslock (LMB) has the ability to sequester P as orhabdophane, which has not previously been structural determined. Rhabdophane is the hydrous La orthophosphate formed at ambient conditions in an aqueous environment and exists in nature as a mineralogical phase, i.e., has very low solubility (Firsching, 1991; Lucas, 2004).

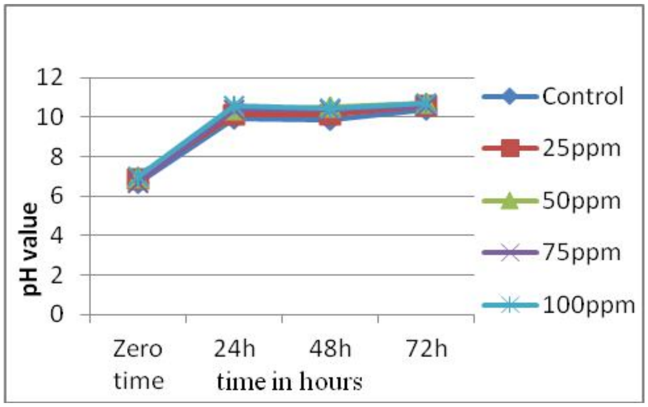

Fig. 1: Show the pH value of the samples through three days after treated with LMB.

When P is captured by Phoslock it is considered biounavailable and no longer a part of the phosphorus cycle in the wastewater treatment reservoir (Robb *et al*., 2003). La and thereby Phoslock, is not specifically selective toward binding P in forms of orthophosphate (Dithmer *et al*., 2015).

The pH was range between 6.9-7.2 at the zero time and it rose through three days of the experiment to be range between 10.1-10.7, this variations are associated with biological activity, in which photosynthesis causing pH to increase during the day and respiration causing pH to decrease at night (Roleda, 2018), as shown in fig. 1.

Turbidity was decreased during the three days of the treatment. However, it decreased after treatment, but it still high according to the WHO, (2011), that determined the turbidity value in drinking water by 5 NTU. Results of turbidity showed a significant decreased from 112 NTU to less than 40 NTU as show in fig. 2.

The external P-loading (0.28 ppm) was in the range of the critical loading (0.21-0.6ppm) above which cyanobacterial blooms were likely to occur (Waajen *et al.,* 2015).

The addition of the LMB caused significantly

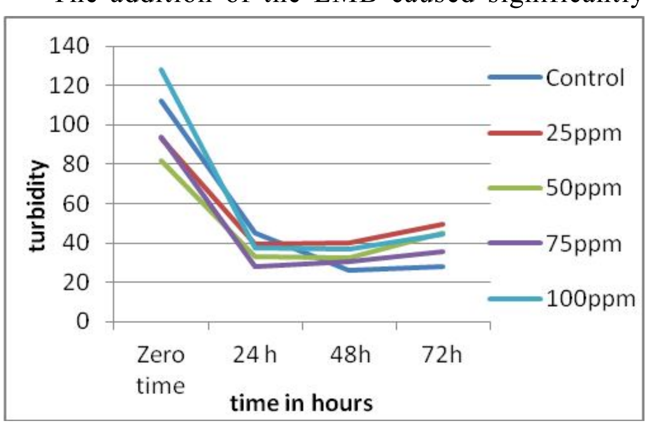

Fig. 2: Show the turbidity of the samples across three days of treatment.

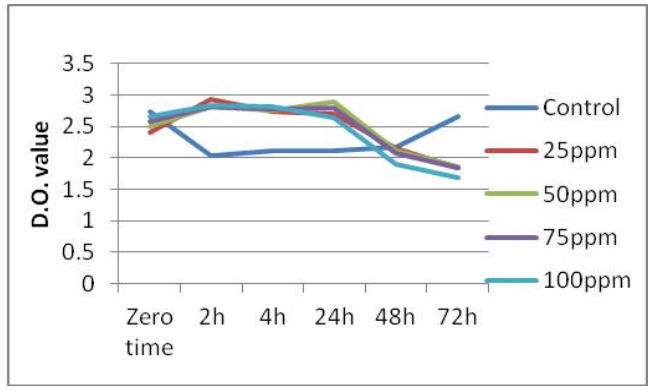

Fig. 3: Show the D.O. of the samples across three days of the treatment.

increased turbidity during the application as show in fig. 2. It took weeks after the addition until the samples became clear enough (Van Oosterhout and Lürling, 2011).

The dissolved oxygen values have shown decreased in their amount in the third day of the treatment, compared with the control which was variable in the first two days, to rise again in the third day as show in fig. 3.

This decreased in D.O. is due to the decreased of the biomass represented by algae that represent primary producers in water (Hao *et al*., 1997) as show in fig. 4.

This affect can be explained as being due to the ability of La^{+3} to link with certain negative groups in the porous phospholipid cholesterol in a strongest manner than Ca^{+2} in the cell membrane (Weiss, 1974).

Moreover La^{3+} affects Ca pumps and thus prevents phototaxis of *Chlamydomonas reinhardtii*. La 3+ turns off electrogenic Ca^{2+} transport while responding to light in blue green algae even at low concentrations (Donat-P., 1982). The application of Phoslock is developed for reparation the aquatic systems that distracted or eutrophied by immobilizing phosphate and thus reducing the annoying cyanobacteria (Lu¨rling and Tolman, 2009). Lanthanum phosphate complexes, which precipitate in

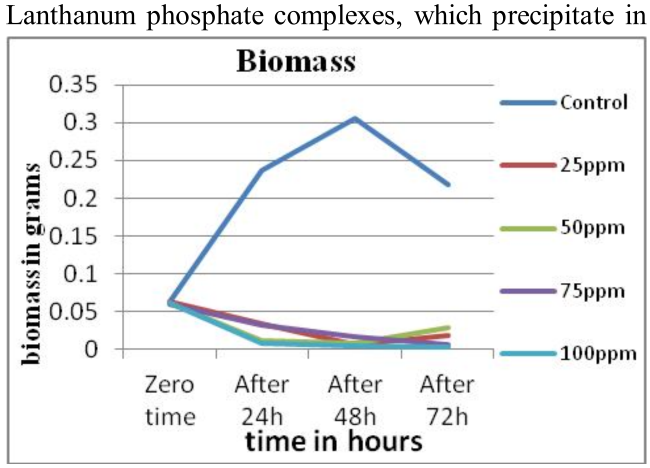

Fig. 4: Show the amount of biomass during three days after treatment.

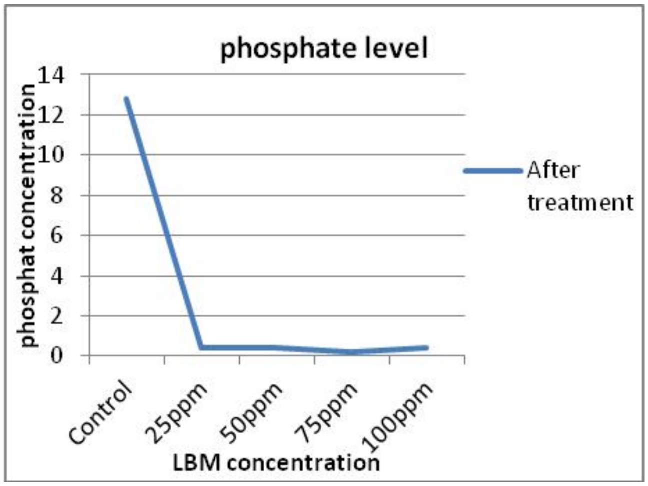

Fig. 5: Show the concentration of the phosphate in the samples after three days after treated with LMB.

the medium, has a high affinity to phosphate and creates insoluble (Petersen *et al*., 1974; Stauber and Binet, 2000 and Herrmann, 2015).

The experiment show decreased in the phosphate concentration according to the control. The experiment was conducted for three days.

Finally, the large differences in results between studies can be explained that it might be caused by factors affecting the availability of lanthanum. One of these factors is glass containers that might absorb up to 25% of the total La to the glass (Weltje *et al*., 2002).

Conclusion

From the results that shows decrease in the pH, D.O. and biomass, we conclude that the LMB could be used to mitigate the phosphate concentration in water which ultimately causes decreased in the biomass of algae. The increase in the turbidity due to suspended particles of LMB can be dissolved by settling down particles or this water could be used for irrigation, which can be around 1-30 NTU.

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