Simple Method For Control of Phosphate Level of Manure Using Magnesium Oxide

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ABSTRACT:
A simple method is described for the reduction of available phosphate released from soaking manure in water. The method involves the indirect contact of magnesium oxide, MgO, with manure soaked in water for pre-specified time. Preliminary study indicated that phosphate could be removed effectively by MgO addition and the precipitation is accelerated by NH₄Cl addition. Thus, and for economic reasons, the study was continued using only MgO. Two sets of experiments were carried out. Water was used for the extraction of manure by shaking for 2 h followed by press filtration. The aqueous phase was used for phosphate removal experiments. The weighed amount of MgO was placed in a cotton bag fixed to the stirring bar of a jar tester. The concentration of phosphate was monitored after equilibration for 0, 7, 30, 50, 89, 100, 120, 150 and 192 hours. In the other set of experiments, weighed amount of manure powder (Less than 2 mm diameter particles) was placed in 50-mL capacity capped plastic bottles (50 bottles) with various amounts of MgO: 0, 0.4, 0.8, 1.4 and 2.0% (by weight MgO:Manure) in 9 bottles each. Water was added to the bottles to make 40 mL. The bottles were shaken on a rotary shaker at 250 rpm. One set of bottles containing the different amounts of MgO was removed from the shaker after 2 hours. The other sets were removed after 7, 10, 25, 24, 36, 48, 72 and 120 hours. Phosphate was determined in the filtered aqueous samples. The first seven hours was enough to cause a removal of 65-70% of phosphate from solution. The removal of the remaining part of phosphate required as long as 9 days. It was concluded that MgO in clothing bags may be suspended and moved inside manure-water suspension for 10 hours to extract the majority of the phosphate. The remaining manure may be used for fertilization with harmless phosphate content that may not result in the growth of undesirable water environment plants. The reacted oxide in the bags can then be used later as a slowly released phosphate source (Struvite) for plant application a matter that increase the economy of the method.

Keywords: phosphate control, manure, struvite, kinetics, magnesium oxide
INTRODUCTION:

The international concern with environmental pollution is increasing and is considered a multi discipline task. Chemists, biologists, and engineers are working in teams for the monitoring, removal of contaminants and remediation of the polluted lands. The valid methodologies of the water treatment are subjected to continual evaluation to improve the performance and establishment of the optimum operating conditions of the process [1]. Phosphorus is an essential nutrient for the plant growth and identified as the most important rate-limiting factor for algal growth in freshwater systems. Soils are treated with phosphorus containing materials in large quantities to enhance their productivity. Animal excreta, which is rich in nutrients and organic matter are recommended for sustainable animal agricultural practices and has been the traditional approach for many centuries. Manure is considered as a rich material in organic and inorganic phosphates [2]. The phosphate in manure ranges from (2.3 g/kg) for beef cattle to (9.2 g/kg) for swine manure and its release depends on the method of application [3].

Manures organic phosphate is in the form of phytate coming from different components of feed. Phytate is the salt of phytic acid, dihydrogen phosphate, and consists of sugar molecule with six phosphate groups [4]. The relatively high phosphate content of manure results in relatively high doses than necessary for crop plantation. The excess phosphate takes its way for the surface waters from the run-off
from soils and to ground water through the infiltration of irrigation water in the soil. As a result a state of eutrophication occurs in lakes and streams leading to decreased population of planktons and eventually low fish population [5].

Liquid manure systems involve collection of manure by flushing it from the barns and thoroughly agitated to remix settled solids, accumulation of manure in the form of storage/treatment, utilization by applying the manure to land as fertilizer. Animal manure is applied in large quantities in the animal agriculture practice due to the simplicity, economy and the trend to recycle the wastes of farms. Thus, simple land spreading of manure becomes increasingly less acceptable as a utilization method. Manure must be pretreated to adjust levels of organic carbon, nitrogen, and phosphorus [6].

The technologies employed for the removal of phosphate from water and manure were summarized in a recent report [7] with a large focus on the utilization of inorganic precipitation by aluminum salts and struvite formation. The chemical methods are considered better for the phosphate removal in comparison with the various methods, regarding the effluent quality and the saving in size requirements required for the biological methods [8]. Chemical methods produce 25% more sludge and need less energy than required than biological methods. However, chemical methods require chemicals for the processing.

Hydrated lime, Ca(OH)$_2$, was used to aid phosphate removal by precipitation after buffering to facilitate the process [9]. Both mineral and organic phosphates can be removed by the use of aluminum compounds. The removal involves sorption and not AlPO$_4$ precipitation [10]. The process could be improved by the addition of tannin from valonia as coagulant [11]. Water treatment product, Al-bas, was utilized for the removal of phosphate from wastewater, as a cost effective means for the chemical amendment for phosphorus treatment in poultry litter [12].

Struvite precipitation has proved effective in removal of ammonium and phosphate from various types of wastewaters [13, 14]. Struvite (MgNH$_4$PO$_4$·6H$_2$O) is a white crystalline compound consisting of magnesium, phosphorus, and ammonium in equal molar concentrations [15]. It has very low solubility in water, 23 mg/L, [16] which becomes lower in alkaline conditions [17]. With struvite precipitation technology, phosphorus is recovered and may be used to replace phosphate rock for the production of white phosphorus [18].

A by-product of a magnesium oxide production was used for phosphorus removal from wastewater as struvite and a model was proposed for the performance of the process [19]. The pH of the solution is the most important parameter in the removal process [20].

**Aim of the study**

The aim of the present work is at establishing optimum conditions for the removal of phosphate from treated sewage water and manure as struvite to aid environmental and economic purposes by adding magnesium oxide. Magnesium oxide, however, was used for the removal of heavy metals from water [21] and to separate chromium from waste tanning liquor [22]. The established conditions will be used to aid the design of a large scale process which is applicable in the farms during liquid manure processing.
Materials and Methods

Apparatus: spectrophotometer was used for the determination of phosphate in water. Jar tester was used for bench scale experiments. Equilibration experiments were performed with the aid of rotary shaker.

Materials and Chemicals:

Most parts of this work were carried out in New Jersey, United States of America, and thus, the manure samples were obtained from a research station in Rutgers University (1560 mg PO\textsubscript{4}/g dry weight) and from a farm (1090 mg PO\textsubscript{4}/g dry weight) in south New Jersey. Rutgers manure was freshly collected in wet state which necessitated drying in open air prior to any measurement or treatment. The manure samples from the farm were typically packed in air dried state in plastic clear bags and no further drying was necessary. The phosphate contents are the average of the results of five replicates.

Jar Test experiments

a. Manure samples (10-25 g) were placed in the Jar tester beakers with the calculated amounts of MgO and ammonium chloride. Aliquots of 10 mL were drawn from the beakers after: 5, 30 min, 1h and 2 h and the pH values were immediately measured. The samples were stored at 4\textdegree C for phosphate determination.

b. To plan for a pilot study, 50 g of manure (less than 2 mm particle size) were placed in a 1-L capacity plastic bottle with 50 mL of deionized water, capped and placed on a magnetic stirrer for 2 hours. The extract was filtered through a clothing material with some pressing to get the maximum amount of manure extract. Aliquots of 100 ml of the extract were placed in the Jar tester beakers and the volume was made up to 1.0 L with deionized water. Three cotton fabric bags (5x3cm) containing different amounts of MgO where suspended in the stirrers of the jar tester and one of the beakers was left without MgO to stand as a blank. Samples were withdrawn from the beakers after 0, 7, 30, 50, 89, 100, 120, 150 and 192 hours and stored at 4\textdegree C for phosphate determination.

Equilibration Experiments:

Manure was freed from reed pieces and ground to a maximum particle size of 2- mm. In 100 mL bottles, 2.5 g of Manure is placed with: 0.0, 0.015, 0.025, 0.030, 0.040 and 0.050 g of MgO and 100-mL of water were added in four sets. The bottles are placed on a rotary shaker and shaken at a speed of 100 rpm. After 48 hrs, the first set is removed from the shaker, centrifuged and filtered into 40 mL tubes and stored for analysis. The second batch is removed after 72 hrs. The third batch is removed after 120 hrs. The fourth batch is allowed to equilibrate for 192 hours. Water samples are filtered with the aid of syringe filter equipped with 0.2 µ filter and stored at 4\textdegree C for analysis.

Analytical method

The malachite green (MG) method of Van Veldhoven and Mannaerts [23] was used for soluble phosphate analysis with modifications provided by D’Angelo et al. [24]. A 200-µL sample was mixed with 40µL of Reagent 1 in a disposable, 96-well polystyrene microplate for 10 min on a plate shaker. Subsequently, 40µL of Reagent 2 (Malachite Green) was added and the plate was shaken for mixing for 20 min. Both
mixing steps were conducted at room temperature (23°C). Reagent 1 was 14.2 mmol/L ammonium molybdate tetrahydrate in 3.1 M H$_2$SO$_4$. Reagent 2 was 3.5 g/L aqueous polyvinyl alcohol (MW 50,000 Da; Sigma Chemical Co., St. Louis, MO, USA), prepared by stirring with d-H$_2$O at 80°C. After cooling to room temperature, malachite green carbinol (Sigma) was added at 0.35 g/L. The two reagents were stable at room temperature for several months. The acidity of the solution was maintained at ~0.9 M H$^+$. Special care was taken to ensure complete mixing and to avoid formation of air bubbles in wells during sample and reagent addition/mixing. The method is linear between 0.01 mg/L up to 3 mg/L. Calibration standards should be prepared in this range. The final absorbance was measured at 630 nm.

Results and Discussion

The inorganic phosphate contents of the two manure samples were the average values of five replicates because of the nature of the manure. Manure sample of Rutgers University station showed an average content of 1560 mg PO$_4$/Kg dry weight, while that of the NJ farm gave average phosphate content of 1090 mg PO$_4$/Kg dry weight.

The suspension of 10 g of NJ farm manure of manure in 1.0 L resulted in the slight alkaline solution (pH 8.99-9.10) and immediate release of phosphate was noticed. Within two hours, the phosphate concentration of the solution increased from 9.12 after 5 min up to 11.85 mg.L$^{-1}$ that is 76.96% of inorganic phosphate is released in the first five minutes.

Manure in water showed a buffer action. The addition of 1-mL aliquot of 1.0 M HCl to a suspension of Rutgers manure in water (25 g.L$^{-1}$) brought the pH down to 7.84 which returned into the 8.56 within minutes (Fig. 1). Further, the addition of 1-mL aliquot of 1.0 M sodium hydroxide resulted in a temporary rise of pH to10.05 and a return to 9.5 within minutes (Fig. 2).

![Figure (1): The buffer action of manure in 0.1 M HCl.](image-url)
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The buffer action is a result of the relatively high phosphate content and also the alkali and ammonium concentration which released into the solution [25], and generally contain an excess of $\text{NH}_4^+$ over phosphate [26]. Both manure samples suspensions gave moderate alkaline pH (8.5-9.1).

The addition of 1% MgO by weight to 10g/L suspension of Farm manure resulted in instant reduction of phosphate released to 56% (Fig. 3). Afterwards, the phosphate increased in the solution to 7.8 and 11.6 after 1 and 2 h, respectively. This indicates that the MgO surface was totally covered with struvite and the newly released phosphate could not find enough MgO to react with (Fig. 4).
Figure (4): Results of preliminary experiments of phosphate control with 0.1 g MgO.

To show the dependence of the phosphate on the presence of struvite components, Rutgers manure was equilibrated with various amounts of MgO and NH₄Cl. When 0.4% MgO by weight was added together with 4.0% by weight NH₄Cl, the reduction in available phosphate was 83.8% indicating the dependence of the struvite formation on both constituents (Fig. 5).

Figure 5: Results of preliminary experiments of phosphate control with 0.1 g MgO and 0.4 g of NH₄Cl.

However the action of MgO is more significant as reflected by the action of 2% MgO by weight and 4% by weight NH₄Cl causing a reduction of available phosphate from manure suspension by 96.46% (Table 1). This is in agreement with a report by Burns and Moody, [27], who found that magnesium, is the limiting ion for struvite formation and has to be added to manure slurries to force its precipitation. MgO can also furnish the alkaline environment necessary for the struvite precipitation [26]. Following on from this the study focused on the equilibration of manure suspension with MgO alone.
Equilibrium Studies:
NJ farm manure was equilibrated with MgO at 1:250 to 1 to 50 (MgO:Manure) ratios with a blank samples for relatively longer periods than those used in the jar test experiments. The results are graphically shown in Figs. 6. Magnesium oxide at a ratio of 1:250 to manure content resulted in a slow reduction in the phosphate concentration down to 23.2% within seven days. Doubling the MgO content (1:125) resulted in a reduction of phosphate to only 7.3% of the original value. The increase of MgO ratio up to 1:70 by weight of manure reduces the time requirements of removing more than 90% of phosphate down to four days. However for economic reasons the ratio of 1:125 may be the optimum value to keep a slight amount of phosphate content in the manure suspension.

It appears that 82.3-84.9% of the total change in the phosphate concentration occurs within the first 7 hours of the contact and a rate of reduction of about 12%/hour. Similarly, Huang et al [28] utilizing magnesite as a low-cost magnesium source to precipitate struvite, reported that for a reaction time of 6 h, phosphorus concentrations fell steeply from the initial 9105 mg/L to a range of 198.8–29.8 mg.L⁻¹.

After 7 h, the phosphate precipitation follows a linear pattern with an average rate of reduction of 0.08%/h. Thus, most of the solid MgO sites will be occupied by the struvite formed in the first 7 hours and only diffusion will govern the movement of the rest of phosphate ions towards the reaction sites.

For engineering purposes we need to make sure for the preferred design whether to use large amount of MgO in a single bag or several bags with small amounts of MgO. Fig. 7 shows the variation of the phosphate removal capacities with various amounts of MgO with equilibration time. The removal capacity increases linearly over the equilibration time at a relatively slow rate that decreases with the increase of MgO content. The lowest MgO content (0.4 g/L) exhibited the highest removal capacity of 18.75 and 21.75 mg.
PO4/g MgO for time durations of 7 hours and 8 days. Thus, for a better removal capacity it is a preferable design to use several cotton bags with relatively small amounts of MgO to ensure higher surface area for the reaction between hydrated MgO and phosphate and more chance for the hydration of MgO which is essential for the furnishing of the alkaline medium necessary for struvite precipitation.

![Figure (7): Change of Removal Capacity with Time, using 0.4g/L MgO, ●; 0.8 g/L, ♦; 1.4g/L, ▲ and 2.0 g/L MgO, ■](image)

However, the addition of soluble magnesium compounds like MgCl₂, as a source for Mg may have some advantages regarding the rate of phosphate removal over MgO [29], but the process must be supported by pH adjustment using NaOH additions [27]. Meanwhile, MgO as alkaline oxide will serve both as a reactant and pH raising aid. In addition it may also serve as a sorbent for phosphate [30, 31].

**Kinetics of the process:**

**The pseudo first-order equation**

The pseudo first-order equation [32] is generally expressed as follows:

\[
\log (q_e - q_t) = \log q_e - \left(K_1/2.303\right)t
\]

where

- \(q_e\) and \(q_t\) are the adsorption capacity at equilibrium and at time, \(t\), respectively (mg.g⁻¹);
- \(K_1\) is the rate constant of pseudo first-order adsorption (L.min⁻¹).

The values of \(\log (q_e - q_t)\) were plotted versus \(t\) to give a linear correlation. The reaction rate constant, \(k_1\), and the \(q_e\) can be determined from the slope and the intercept of the plot, respectively. The results are graphically shown in Fig.8. It is clear that at the MgO: Manure rations employed, the pseudo-order kinetic model give linear correlation. The calculated values of the equilibrium solid MgO capacity for phosphate and the reaction/removal rate constant are listed in Table 2.
The pseudo second-order equation

The pseudo second-order adsorption kinetic rate equation [33] is expressed as:

\[ \frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k \cdot t \]  \hspace{1cm} \text{(2)}

Figure 8: pseudo first-order plots.

The results of the kinetic study are shown in Fig. 9. The equilibration data were fitted with the pseudo first-order equation (1) and pseudo second-order equation (2) above. The calculated values of the equilibrium solid MgO capacity for phosphate and the reaction/removal rate constant are listed in Table 2.

From the table it can be concluded that, pseudo first order model fits very well with experimental results, where the values of the correlation coefficient, \( R^2 \), was range between 0.9339 and 0.9836. First order kinetic model often is used to describe adsorption and reaction processes, [32], whilst the removal of phosphate by adsorption, on chemically modified sugarcane bagasse, follows pseudo-second-order kinetic equation [34]. The process is capable to give an adsorption capacity value of 21.3 mg/g at natural pH.

Proposed Method:

The possibility of reducing the phosphate content of manure extract by more than 70% noticed above may give the basis of designing a simple process for the removal of large percentage of phosphate. The method may be summarized as follows:

1. Prepare cotton bags and place fine MgO particles as a thin layer in the bags;
2. Place the bags on the stirring bar or any stirring aid which is usually turning slowly inside the manure preparation tank for 8-10 hours.
3. Liquid manure is then tapped out of the tank for drying by the normal method.
4. A new manure batch may then be introduced to the tank for phosphate reduction.
5. The bags, contain MgO coated with a layer of struvite that can be used as a slow release resource of phosphate.
6. Manure may then be used directly or after drying for spraying on agricultural lands, being holding 25-30% of its original phosphate content.

CONCLUSION:
The following conclusions can be drawn:
1- A practical method was established for the control of the available phosphate from manure and not for complete phosphate removal.
2- The overall method involves the hanging cotton bags containing MgO with the stirring mechanism of the manure preparation tank.
3- The phosphate from the manure will react with MgO to form struvite on the surface of the MgO particles.
4- The process may be performed within 6-10 hours.
5- The manure may then dried by the normal methods.
6- The MgO bags afterwards will contain struvite on MgO and can be stored as a slow release phosphate resource.

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Table (1): Action of MgO and NH4Cl on the phosphate concentration in solution.

<table>
<thead>
<tr>
<th>Time, min</th>
<th>No addition</th>
<th>0.4% MgO</th>
<th>0.4% MgO* + 4% NH4Cl*</th>
<th>2% MgO* + 4% NH4Cl*</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>20.9</td>
<td>28.748</td>
<td>13.874</td>
<td>1.338</td>
</tr>
<tr>
<td>30</td>
<td>34.42</td>
<td>24.928</td>
<td>8.447</td>
<td>1.832</td>
</tr>
<tr>
<td>60</td>
<td>32.81</td>
<td>28.127</td>
<td>6.637</td>
<td>1.273</td>
</tr>
<tr>
<td>120</td>
<td>39.63</td>
<td>28.555</td>
<td>6.427</td>
<td>1.435</td>
</tr>
</tbody>
</table>

* All percentages are given with respect of the manure weight

Table (2): Results of the kinetic treatment of the manure equilibration MgO.

<table>
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<tr>
<th>Rate Equation</th>
<th>MgO content, g/L</th>
<th>Equilibrium solid content of PO4, qe, mg/g</th>
<th>k1 = 1·min⁻¹</th>
<th>Correlation Coefficient, R²</th>
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<tbody>
<tr>
<td>Pseudo First-Order</td>
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<td>3.693</td>
<td>0.0138</td>
<td>0.9836</td>
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<td></td>
<td>0.8</td>
<td>2.67</td>
<td>0.0108</td>
<td>0.9339</td>
</tr>
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<td></td>
<td>1.4</td>
<td>1.254</td>
<td>0.0131</td>
<td>0.9679</td>
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<tr>
<td>Pseudo second-Order</td>
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<td>0.015</td>
<td>0.8705</td>
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<td>0.8</td>
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REFERENCES


