Assessment of the Performance of Nutrient Reduction Treatments for the Rotorua Lakes

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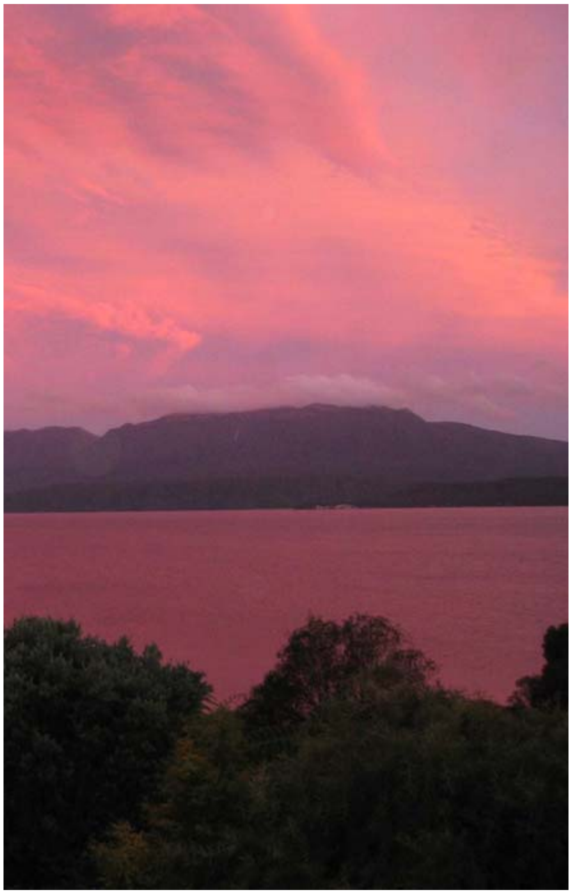

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Executive Summary

Eutrophication is a condition in an aquatic ecosystem where high nutrient concentrations stimulate blooms of phytoplankton. The deterioration of the Rotorua Lakes has focussed attention on potential remedial technologies to reverse lake eutrophication. One such option is the chemical treatment of lakes in order to remove nutrients and/or remediate sediments that are an internal source of such nutrients.

A nutrient stripping media based on the chemical modification of two abundant and indigenous New Zealand natural minerals, zeolite and pumice, was developed in this study. Modified zeolite and pumice were investigated for their ability to adsorb phosphorus and /or nitrogen from aqueous solutions. Batch incubation studies with nutrients were performed at laboratory scale with artificial and natural lake waters. Modified zeolite and pumice samples with different treatment processes and conditions were employed to understand the effect of various factors on phosphorus removal capacity. Results showed that modified zeolite and pumice exhibited substantially higher phosphorus removal capability than that of natural zeolite and pumice. Trials were conducted to compare modified media and two commercial remediation products: *Phoslock*™ and *Baraclear*™. Modified zeolite and *Baraclear* showed the best performance for nutrient reduction in water, though all media have the ability to achieve greater than 95% phosphate removal if sufficient dose is applied. The binding of phosphate appears to be largely irreversible under natural pH and temperature conditions for all media tested. Unexpectedly, all media tested also had the ability to remove more than half of the nitrate present.

The media developed in this study, and commercially available media, all have potential as remedial tools for the Rotorua Lakes. In this first step, the ability to removed dissolved nutrients was established. It was concluded that, to be successful, such treatments should have the ability to limit nutrient release from sediment. Thus, it is recommended that this be the next objective for study. In parallel with this, studies should examine the relative risks associated with the materials including toxicity and turbidity in local lake systems.

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1.0 Background

Eutrophication represents a serious problem for many water bodies around the world and the eutrophication of the Rotorua lakes has recently received considerable attention. Phosphorus and nitrogen serve as the key nutrients, affecting the amount of algal and weed growth. A difficulty associated with the treatment of phosphorus in water is that the majority of the phosphorus (50-90%) is concentrated at the sediment-water interface. Current application techniques involving alum, primarily treat the phosphorus closer to the surface of the body of water, and rarely reach the targeted problem areas in need of treatment (Griffith, et al. 1973). The success of alum treatment is dependent on nearly instantaneous adsorption of phosphorus. As a result, this technique may not perform as effectively in a number of water systems, especially high energy and deep systems, or in systems that require more than just instantaneous phosphorus adsorption. In the former case, alum is flushed from the target waters before it can perform; in the later case, the alum is poorly utilised in application. The alum can also leave an unwanted white cloud in the water for an extended period of time. There are also toxicity and human health concerns with regard to dissolved aluminium in water. In response to the need for nutrient removal and sediment remediation, several patented modifications of clay-based minerals have been developed including *Phoslock*^{TM} based on lanthanum and *Baraclear*^{TM} based on aluminium.

In addition to testing commercially available media for nutrient removal, this study was focussed on developing a remediation material from zeolite/pumice which will assist in reducing internal recycling of sediment nutrient stores in estuarine and freshwater systems. Zeolite and pumice are abundant New Zealand minerals. Natural pumice possesses a porous structure, which contributes to its large specific surface area. The large proportion of free silica sites at the grain surface results in a negatively-charged surface. Zeolite has a skeleton structure that allows ions and molecules to reside and move within the overall framework. The structure contains open channels that allow water and ions to travel into and out of the crystal structure. Due to these properties, zeolite is widely used in water and sewage purification, ammonia and heavy metals removal, ion exchange in radioactive wastewater treatment, removal of oil pollution from water, and adsorption of other components from liquid and gaseous phases (Colella, 1999; Piaskowski et al., 2000). However, the removal of anionic nutrients by use of natural zeolite or pumice has not been reported, possibly due to the limitation of the negatively charged surface. The present study was carried out to evaluate the enhanced phosphate removal capability of natural zeolite and pumice modified with aluminium-based substances. Due to the higher isoelectric point (net positive charge) of the modified surfaces, the treated zeolite and pumice can also play a role in coagulating and settling suspended dirt particles, bacteria and many microorganisms that possess negatively-charged surfaces in natural water.

2.0 Objectives of the study

- Develop a rapid laboratory method to assess the efficacy of mineral-based nutrient removal media
- Compare the performance of commercially available nutrient removal media with that of modified zeolite and pumice for the removal of dissolved reactive phosphorus
- Examine the ability of media to remove nitrate
- Compare relative dose, reaction time and pH sensitivity of the media tested
- Test nutrient removal in a nutrient rich sample of surface water from the Rotorua Lakes area

3.0 Materials and Methods

3.1 Materials

Zeolite used in this study was supplied by New Zealand Natural Zeolite Ltd. The chemical compositions and some important physical characteristics are summarised in Table 1.

Table 1. Chemical composition and physical characteristics of zeolite

Component	SiO_2	Al_2O_3	K_2O	CaO	Na_2O
Weight %	71.54	18.44	2.66	1.75	1.74
Exchange capacity	Slurry conductivity	Slurry pH	Absorbencies		
			Water	Oil	Ammonia gas
80-100 meq/100g	233 S/cm	5-6 for 20 % w/v	60-90% by weight	75% by weight	50-130 meq/100g

**Data provide by NZ Natural Zeolite Ltd.*

Pumice used in this study was supplied by Works Filter Systems Ltd. The chemical compositions are summarised in Table 2. The fraction of particles passing a UK standard No. 24 sieve, was collected to obtain pumice particles in the size range of approximately 177 to 290 µm diameter (24 to 60 mesh). Two patented commercial products, *Phoslock* (Appendix 1) and *Baraclear* (Appendix 2) were chosen in this study to compare with modified media. *Phoslock* is a lanthanum amended bentonite clay, whereas *Baraclear* is aluminium amended clay. Both formulations are sold as pellets that rapidly swell and dissociate into a suspension when added to water. A photograph of the commercial products in comparison to zeolite is shown in Figure 1.

Figure 1. Media tested in this study, from left to right, treated zeolite, *Phoslock,* and *Baraclear*.

As natural raw zeolite and pumice contain various extractable materials, which can affect the adsorption, 0.1 M HCl was used to pre-treat the mineral substrate to remove these residual inorganic salts. The particle size distribution of *Phoslock*, *Baraclear* and acid washed zeolite are shown in Figure 2.

Table 2. Chemical composition of pumice

Composite	SiO_2	AlO_2	Na_2O	Fe_2O_3	K_2O	CaO	MgO	TiO_2	MnO
Weight (%)	71.02	12.83	4.02	2.88	2.67	1.56	0.32	0.27	0.11

Composite	Nb	Zr	Y	Sr	Rb	Ca	Cr	As	Ba	Pb	Th
(ppm)	7	183	29	137	106	15	10	21	682	17	13

**Data obtained from Geosicence Laboratory in Sudbury, Ontario, Canada. Oxide measured in weight %., Heavy metals measured in ppm.*

Potassium dihydrogen phosphate (KH_2PO_4) was used as the source of phosphorus, and potassium nitrate (KNO_3) was used as the source of nitrogen throughout the bench experiments. Stock solutions at various concentrations and pH were prepared by dissolving the desired amount of KH_2PO_4 and KNO_3 into distilled water. Dilutions were prepared by adding distilled water to the stock solution to achieve the required concentration. Lake Okaro water was used for the case study. The raw water was passed through a phytoplankton net (44 µm mesh) to remove all particles and suspended algae.

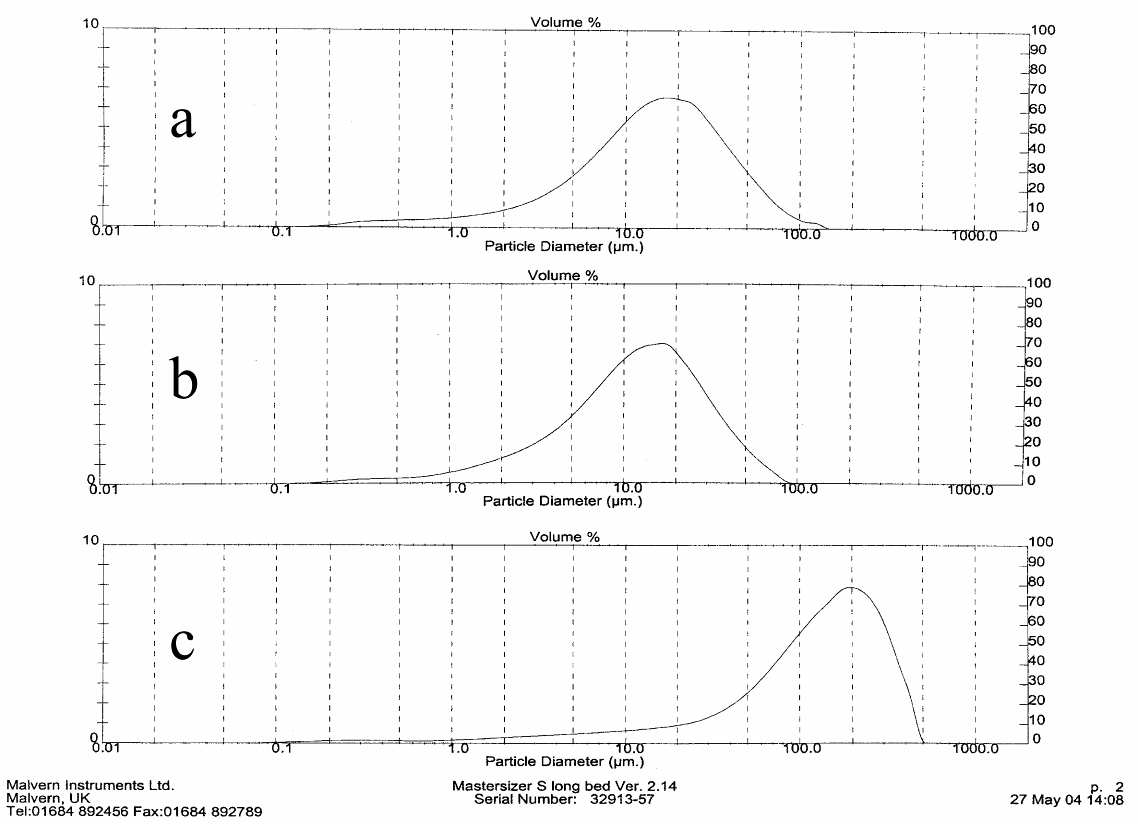

Figure 2. Particle size distribution of a) *Phoslock*, b) *Baraclear*, and c) Zeolite

3.2 Methods

A method was developed to rapidly measure the binding efficiency of mineral media at the laboratory scale. Adsorption experiments were carried out by shaking the media with 50 mL of known nutrients in solution. Measured quantities of media were added to the solutions in sealed tubes and the resultant suspensions were agitated for varying periods of time. A temperature-controlled shaker bath was used to keep the temperature at a constant 25°C. All adsorption experiments were performed at the natural pH of the phosphate solution, except those in which the effects of pH of the solution were investigated. The pH of these solutions was adjusted with 0.1 M HCl or 0.1 M NaOH using a pH meter.

At the end of the adsorption period, the supernatant was transferred to a 50 mL centrifuge tube and centrifuged at 2000 RCF for 10 minutes. The supernatant was aspirated out to determine the concentration of the residual nutrients.

Dissolved reactive phosphorus (DRP) and nitrate were measured with a Skalar autoanalyser. The amounts of phosphate/nitrate adsorbed were calculated from the concentrations in solution before and after adsorption.

Three modification processes were used to treat raw zeolite and pumice. Products are referred to as Z-1, Z-2, Z-3 and PM-1, PM-2, PM-3 (Z represents zeolite; PM represents pumice), respectively. A series of experiments were carried out with the commercially available media and the modified pumice and zeolite. The purpose of these experiments was to:

- Examine the phosphate binding potential of the modified zeolite and pumice in order to determine if these mineral treatments had potential for remedial tools
- Examine the nitrate removal potential of media that showed good phosphate removal ability
- Compare the ability of the commercial products and modified zeolite or pumice to remove DRP
- Study the rate of phosphate removal and the impacts of initial phosphate concentration on this rate
- Determine impacts of pH on phosphate removal
- Examine the ability of the various media to remove nutrients from water flowing into Lake Okaro

4.0 Results

4.1 Adsorption capacity of modified zeolite and pumice for DRP

In order to examine the adsorption capacity of modified and natural zeolite and pumice, media were incubated with high concentrations of phosphate. Concentrations used were in the order of 100 mg/L, 100-fold higher than would usually be found in surface waters. For all forms of modified zeolite and pumice, chemical modification led to increased binding of phosphate as compared to the unmodified material (Figure 3).

The Z-2 modification process produced the highest adsorption capacity with both pumice and zeolite. The adsorption ability for the modified zeolite was superior to that of pumice. However, as the pumice used in this study was coarser than zeolite, this was likely a function of increased surface area per unit weight of zeolite. Adsorption isotherms for experiments are shown in Appendix 3.

Experimental results indicated that both pumice and zeolite modified with the Z-2 process demonstrate very high capacity for phosphate, binding up to 90% of the phosphate ions at the highest concentration of media. As the Z-2 modified zeolite provided the best phosphate adsorption, this media was used for all subsequent experiments and comparisons.

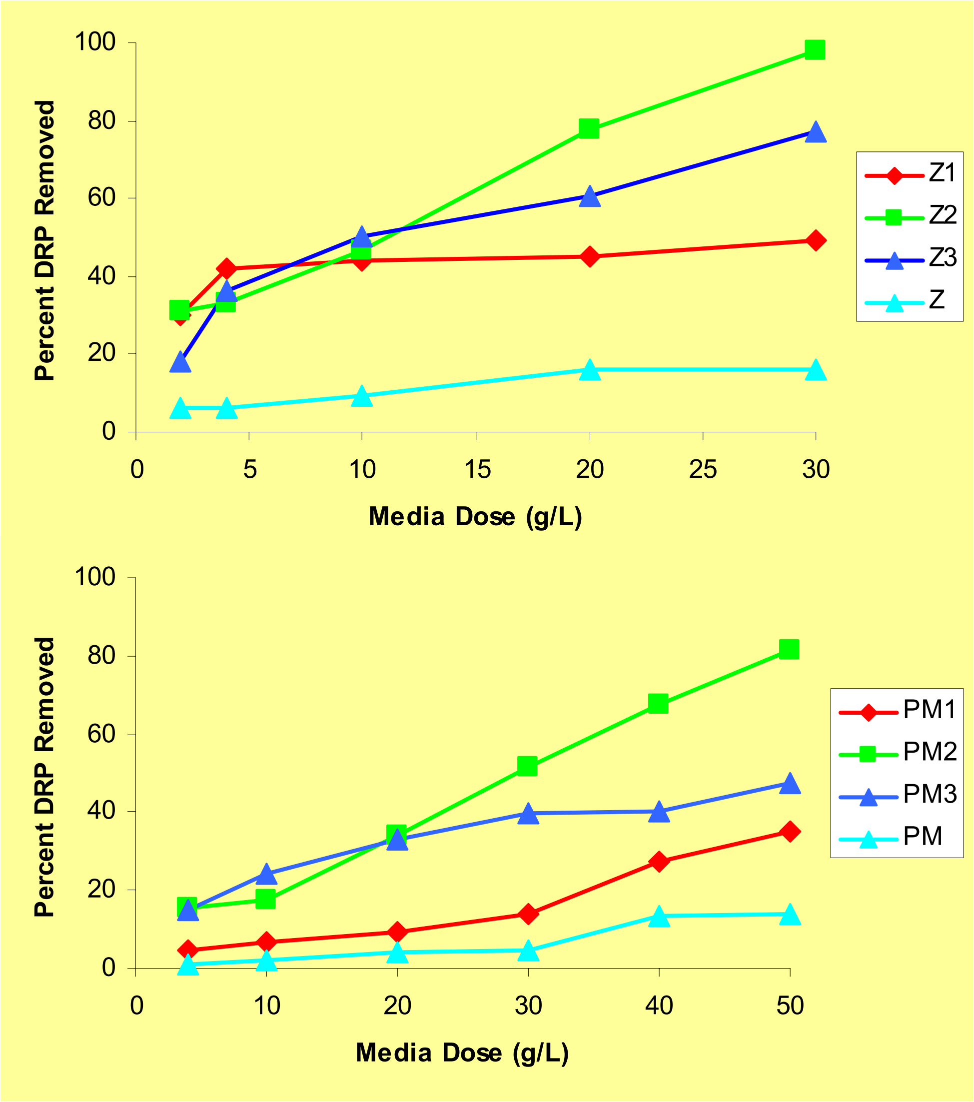

Figure 3. Binding capacity of modified zeolite (top) and pumice (bottom)

4.2 Adsorption capacity for oxidised nitrogen species (NO_x)

The Z-2 modified zeolite demonstrated high capacity to bind nitrate ions. Figure 4 shows adsorption of nitrate by the media at a range of nitrate concentrations. At the highest concentration of 1000 mg/L the media was still able to bind 98% of the nitrate in solution.

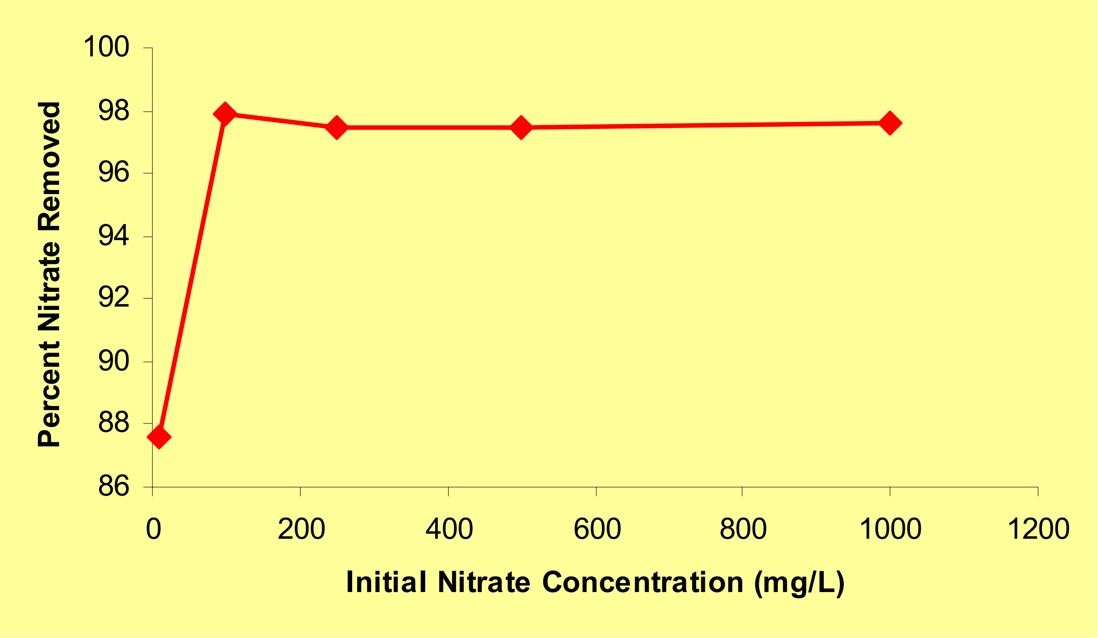

Figure 4. Binding of nitrate to Z-2 modified zeolite.

4.3 Adsorption rate of DRP on Z-2 modified zeolite and effect of pH

The binding of phosphate to Z-2 modified zeolite was rapid, with steady-state condition being reached in approximately two hours (Figure 5). The binding appeared to follow a first-order kinetic model (Appendix 3). There was a modest increase in binding with lower pH. The effect of initial phosphate concentration on adsorption was also examined using 5, 50, and 500 mg/L of DRP starting concentration (Figure 6). Kinetics experiments indicated that adsorption of the phosphate was rapid, and only minor differences in binding efficiency occurred with different starting concentrations. Phosphate removal was in excess of 84% for all concentrations tested.

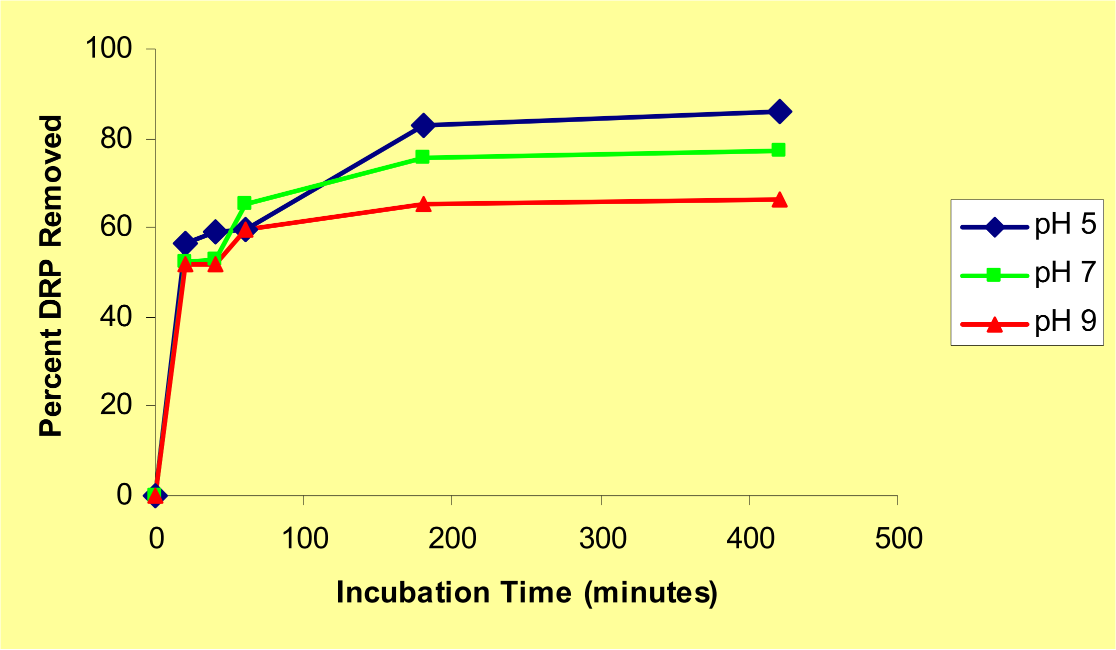

Figure 5. Binding kinetics of phosphate to Z-2 modified zeolite.

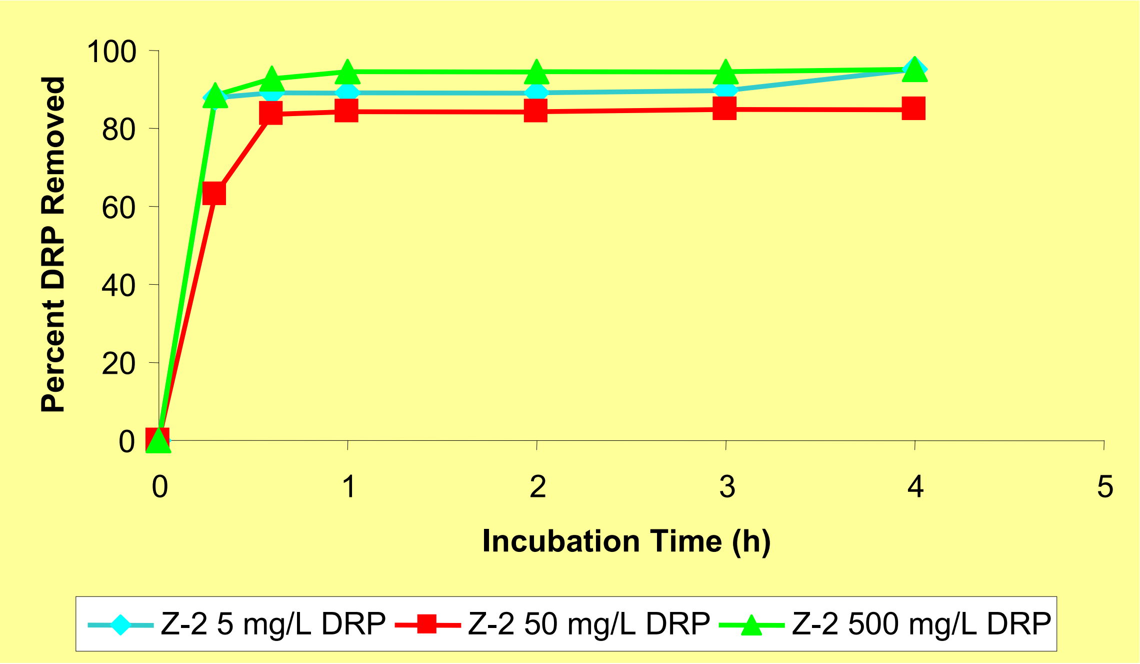

Figure 6. Adsorption kinetics of Z-2 with varying starting concentrations of phosphate.

4.4 Comparison of Z-2 zeolite with commercially available adsorbents

The Z-2 modified zeolite was compared directly with *Phoslock* at a variety of pH and incubation times. Initial phosphate concentrations were in the order of 50 mg/L. *Phoslock* demonstrated similar kinetics to Z-2 with maximum phosphate binding occurring within 1-2 hours. *Phoslock* was not as sensitive to pH as Z-2 with only a marginal increase in phosphate binding occurring at pH 5.0 (Table 3). Overall, Z-2 had a slightly improved efficiency for the binding of phosphate as compared to *Phoslock*, ranging from 6-10% higher binding efficiency. The greatest difference in binding occurred at pH 5.0. However, all treatments of both *Phoslock* and Z-2 performed very well and exceeded 83% phosphate binding.

Table 3. Comparison of the efficacy of Z-2 and Phoslock for the removal of DRP.

Media	Percentage of phosphorus removal		
	pH		
	5.01	7.05	9.72
Z-2	95.5	92.6	89.1
Phoslock	85.3	84.5	83.7

4.5 Phosphate binding reversal from Z-2 and *Phoslock*

This experiment was carried out in order to assess if phosphate could be re-released from the binding media. For the first stage, 1 g media was dispersed in a concentrated phosphorus solution, shaken for 6 hrs and settled for 12 hrs to reach equilibrium. As phosphate re-release was expected to be minor, very high phosphate concentrations (in excess of 1.5 g/L) were used so that the media would be saturated with phosphate and the phosphate released would be measurable. The sample was filtered through a 0.2 µm filter, the media added to 100 mL distilled water, shaken for a further 6 hr, and settled overnight (12 hrs). The residual in the solution represented the reversibly bound phosphorus. Table 4 shows the level of the reversed bound phosphate in *Phoslock,* and Z-2.

The Z-2 media showed the lowest rate of reversal, in the order of 1% whereas *Phoslock* had rates of reversal approaching 3%. Both media appear to bind phosphate irreversibly using the present methods. It is likely that the rates of reversal indicated are not representative of true reversal of binding. Due to the high levels of phosphate used in this experiment, it may have been difficult to rinse off all phosphate solution associated with the media, so these results may represent carry-over, not reversal of binding. However, the experiment demonstrates that significant re-release does not take place with either media.

Table 4. Percent of reversibly bound phosphorus

Percentage of reversal				
media	Initial concentration (mg/L)			
	6000	4500	3000	1500
Phoslock	2.26	2.79	2.94	3.29
Z-2	1.15	1.00	1.24	1.70

4.6 Lake Okaro Surface Water Case Study

Lake Okaro has the poorest water quality of the Rotorua lakes. The Trophic Level Index in 2003 was reported to be 5.61 and the average total phosphorus and nitrogen were 0.122 mg/L and 1.25 mg/L, respectively (Scholes 2004). In this study, a sample was taken from the inflow creek to the north-west of Lake Okaro, draining farmland. This sample had initial DRP and NO_x-N concentration of 0.185 mg/L and 1.520 mg/L, respectively. Modified zeolite Z-2, Z-3 and two commercial products, *Phoslock* and *Baraclear,* were selected as the adsorbents. All adsorbents were tested at media concentration of 1, 4, 10 and 20 g/L.

Both *Phoslock* and *Baraclear* are clay based pellets and disperse very quickly in water to form a suspension. Treated zeolite also forms a suspension upon agitation, but this suspension settles within minutes as opposed to hours for the clay-based particles (Figure 7). The relative charge, or isoelectric point, was also determined for the various media tested and is shown in Table 5.

Table 5. Isoelectric points of the media tested and untreated zeolite.

	Baraclear	*Phoslock*	Zeolite	Z-2	Z-3
Isoelectric Point	5.45	3.29	4.02	7.71	6.93

The Z-2 treated zeolite and *Baraclear* demonstrated the highest efficiency for DRP removal from Lake Okaro water as both were able to exceed 90% removal efficiency (Figure 8). This was followed by Z-3 treated zeolite then *Phoslock*. From the relationships obtained, *Phoslock* would require much higher doses to achieve the same removal efficiency as *Baraclear* and Z-2. The use of Lake Okaro water resulted in a reduction of phosphate removal efficiency as compared to that seen with lab water sample spiked with phosphate and the reasons for this loss of efficiency are unknown.

Figure 7. Treated zeolite, *Baraclear*, and *Phoslock* suspensions in water.

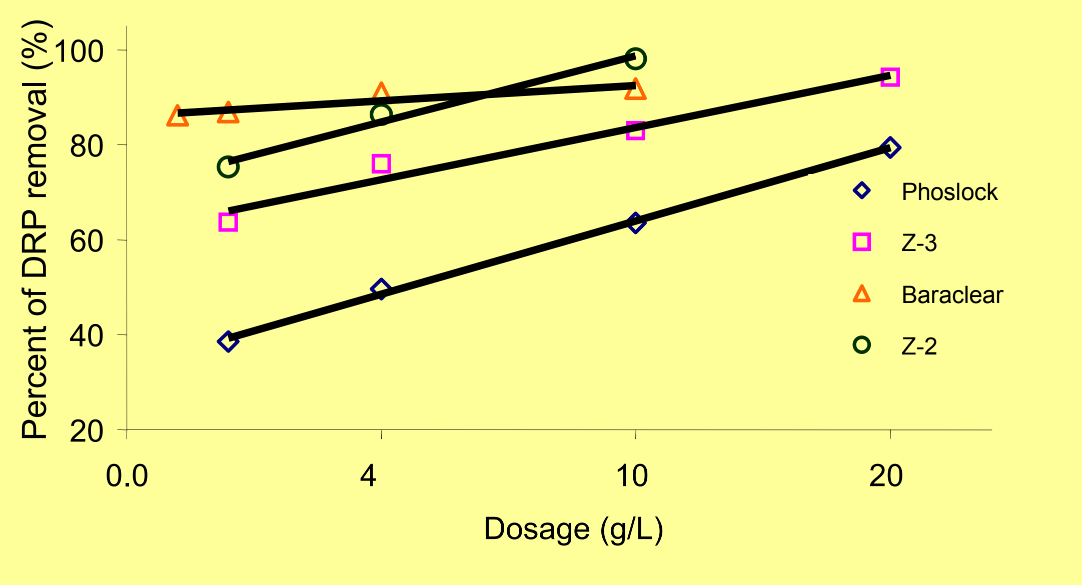

Figure 8. Removal of DRP from Lake Okaro water with treated zeolite and commercially available adsorbents.

Based on the binding data illustrated in Figure 7, the dosage of media required to remove 95% of DRP from Lake Okaro water was calculated and is shown in Table 6. The Z-2 treated media requires the lowest dose to obtain 95% DRP removal. However, due to differences in slope, *Baraclear* can obtain greater than 80% removal at lower doses than Z-2.

Table 6. Optimal dosage for 95% removal of DRP.

	Media			
	Z-2	Z-3	*Phoslock*	*Baraclear*
Dosage (g/L) (95% DRP removed)	17.4	30.4	40	27.6

The removal of nitrate/nitrite was also assessed for Lake Okaro water. All media tested had the ability to remove about half of the nitrite/nitrate nitrogen, irrespective of media dose (Table 7). It was not determined if the binding of these nitrogen species was irreversible.

Table 7. Removal of NOx species from Lake Okaro water.

	Percent of NOx removal (%)			
Dosage (g/L)	Z-3	Z-2	*Phoslock*	*Baraclear*
4	50.04	44.88	50.73	49.75
10	51.47	49.53	51.15	53.69
20	52.27	53.98	52.27	60.79

5.0 Discussion

This research demonstrated that a variety of nutrient adsorbing media have excellent potential for the removal of DRP from surface water. Those media using aluminium amendments of minerals, namely Z-2 treated zeolite and *Baraclear* showed the greatest performance for the removal of phosphate. Of the treated zeolite, Z-2 had the highest relative charge, explaining the superior performance for complexing phosphate. Unexpectedly, all media tested also showed the ability to complex a significant amount of the nitrate/nitrite nitrogen in surface water. *Phoslock* showed less affinity for phosphate as compared to the aluminium-based media tested. As lanthanum phosphate is even less soluble than aluminium phosphate, this was unexpected but may be related to the strong negative charge of *Phoslock* particles in solution. This discussion will focus specifically on the potential and strategies for remediation of the Rotorua Lakes, particularly the use of nutrient adsorbing material.

All aquatic plants require exogenous nitrogen and phosphate. As phytoplankton all fix carbon from the atmosphere, one or the other of these two macronutrients generally limit the growth of algal blooms. Each lake has a nitrogen to phosphorus ratio (N:P) that defines the relative abundance of these nutrients. There have been many substantial reviews discussing the impact of N:P ratios on phytoplankton populations (Smith, 1983; Aleya et at., 1994; Takamura et al., 1992; Zohary et al., 1992; Fujimoto et al., 1997) that suggest that bloom-forming cyanobacteria tended to dominate in lakes where the N:P mass ratio is low. Thus, when nitrogen is the limiting factor in growth, cyanobacteria may be favoured due to their ability to fix gaseous nitrogen from the atmosphere. This conclusion has led to the so-called "N:P rule" that increasing the mass ratios above 29 will reduce the proportion of cyanobacteria as a fraction of the total algal biomass. However, some researchers (Trimbee et al., 1987; Sheffer et al., 1997) hold the reverse view. They have recognised that even when such a response is observed, it may be due to the increasing P concentrations rather than a decrease in the N:P ratio. Paerl et al. (2001) suggested that the "N:P rule" is less applicable to highly eutrophic systems when both N and P loading are very large and N and P inputs may exceed the assimilative capacity of the phytoplankton. The understanding is further complicated by seasonal variation in N:P ratios and the availability of inorganic forms of N and P from the total nitrogen and phosphorus pool.

In the Rotorua Lakes Water Quality report (Scholes, 2004, Table 8), the majority of lakes in the Rotorua district have N:P ratios lower than 29, indicating that phosphorus is overabundant. Further analysis of these data show that, on the basis of N:P ratios, the five most eutrophic lakes cluster out from the five least eutrophic lakes, with the more eutrophic lakes having lower N:P ratios. However, there are also very tight correlations between both TP and TN and algal productivity as measured by Chlorophyll a. One striking observation is that those two lakes with the highest N:P ratio, Tikitapu and Rerewhakaaitu, are very dominated by green algae (Wilding, 2000) and are not known to demonstrate blue-green algae blooms. Rerewhakaaitu in particular is interesting due to the relatively high component of pastoral land surrounding the lake. It has been suggested that the alophanic soils surrounding the lake effectively complex phosphorus and prevent it from entering the lake (Fish, 1978). We have also noted that biota from these two very different lakes appear to be particularly depleted in the ^{15}N stable isotope of nitrogen as compared to the other lakes (C. McBride, unpublished data), further suggesting that phosphorus limitation is having significant effects on the ecology and fate of nutrients in those lakes.

Evidence from overseas, and from the Rotorua Lakes suggests that in the first instance, increasing the nitrogen to phosphorus ratio through intensive management of phosphorus inputs may be the best way to reduce harmful blue-green algae blooms in the lakes most affected. To force a reduction in overall productivity, more substantial phosphorus and nitrogen removal would have to be achieved. Sas et al. (1989) and Seip et al. (1992) suggested that if DRP was < 10 µg/L either on average over the entire growing season or absolutely during at least half of the growing season, then phytoplankton growth may be assumed to be P-limited during the growing season. Similarly, the threshold value below that where N-limitation occurred was assumed to be 100 µg/L inorganic nitrogen.

In some cases, nitrogen reduction will be more difficult to realise in the short term due to the high solubility of nitrate salts. For example, in the well-known case of Lake Taupo, ground water nitrogen inputs are significant, and due to the long groundwater residence time, these inputs will continue for decades regardless of any other measures taken. Work done on groundwater inputs into the Rotorua Lakes indicates that future nitrogen input may be substantial, particularly in Lake Rotorua given the large catchment size (Morganstern et al., 2004). Removing nitrogen will certainly reduce overall productivity, but low N:P ratio will continue to favour blue-green algal blooms.

Table 8. Nutrient and biological data for Rotorua lakes (from Scholes, 2004)

Lake	Chlorophyll a	Secchi Depth	TP	TN	TN:TP
Okaro	32.76	1.61	122.6	1250.5	10.2
Rotorua	14.77	2.48	43.8	426.2	9.7
Rotoehu	12.04	2.34	36.5	456.0	12.4
Rotoiti	7.27	4.96	23.1	276.8	11.9
Okareka	4.49	6.89	6.1	224.6	36.8
Rotomahana	5.08	4.24	24.8	221.9	8.9
Rerewhakaaitu	5.31	4.97	7.4	379.8	51.1
Rotoma	1.49	10.86	3.2	135.1	41.0
Okataina	2.13	9.2	6.1	123.1	20.0
Tarawera	1.58	7.98	7.0	112.9	15.9
Tikitapu	2.04	6.01	3.8	195.5	51.1

Some phosphate salts, unlike nitrate, are highly insoluble and phosphorus in unimpacted aquatic systems is naturally derived only from the weathering of minerals or internal recycling. As phosphate is rapidly tied up in soils, it generally does not enter groundwater via land-use practices in significant amounts (though there can be significant natural source in groundwater). The success of the Rotorua land application of municipal sewage scheme in removing phosphorus is an excellent example of this. For this reason, anthropogenic sources of phosphorus from agricultural activities and erosion, or enriched natural sources can more easily be limited in the short to medium term than nitrogen sources. One potential usage for phosphorus adsorbing media may be to treat surface water or effluent inputs where substantial phosphorus sources are known to exist.

As lakes become eutrophic, internal nutrient cycling from anaerobic sediments becomes more substantial. The total mass of phosphorus in a lake water column is relatively small as compared to the phosphorus stored in sediment. Thus, though removal of nutrients from the water column may have short-term benefits, longer-term benefits can only be realised through reduction of nutrient cycling from the sediments. A study with alum introduction in a lake in France demonstrated that removal of nutrients from the water column had limited benefits (Van Hullenbusch et al., 2002) and these results appeared to be mirrored by the Lake Okaro alum application trial.

Another method that has been tested for over 50 years for the reduction of trophic status has been lake aeration. Though many efforts have failed, the introduction of pure oxygen directly into the hypolimnion in a deep eutrophic lake resulted in a reduction of TP in the hypolimnion by 50% accompanied by a 55% drop in chlorophyll a. This caused the lake to revert from eutrophic to mesotropic (Prepas et al., 1997). Though such methods have the potential to reduce nutrient recycling, they are costly. Similarly, lake dredging approaches also have the potential for lake improvement, but are also very costly. Biomanipulation, or removal of biomass has been another means suggested of reducing overall nutrient loadings.

The greatest utility for nutrient adsorbing media in lake remediation is their ability to treat sediment and reduce nutrient release rather than just remove nutrients from the water column. In the case of *Phoslock*, bentonite clays form a nearly impermeable barrier over the sediment in combination with the ability to precipitate DRP. The treated zeolite tested in this report also has the potential to act in a similar fashion, though sediment capping would be expected to be more permeable as compared to *Phoslock*. Whereas clay particles are by definition colloidal, the zeolite can be obtained in any particle size. Different particle size may have different uses, for example larger particles may be more suitable to effluent treatment columns or batch removal of nutrients, whereas finer particles may be more suitable for nutrient removal from water bodies. Lake treatment with such media has the potential to provide a solution at a lower relative cost as compared to other methods of lake treatment. However, there are risks of such treatment including the release of metals into the environment, such as aluminium that is used for amendment of media. The re-suspension of fine particles during lake mixing, resulting in high turbidity on an ongoing basis is also a risk. This latter risk may be significant for a large shallow lake such as Lake Rotorua. The use of larger particle size may reduce this risk.

6.0 Conclusions and Recommendations

The modified zeolite and pumice have been demonstrated to substantially reduce phosphorus in both artificial and natural waters under batch-test conditions. The results indicate that the modified zeolite performed better than modified pumice, probably due to finer particle size. The adsorption capacity is pH dependent and increased with decreasing pH, but the modified media can still work very effectively over a wide pH range. The nutrients were strongly bound to the modified media, and phosphorus was mostly irreversibly bound under the test conditions used. The modified media were more effective in phosphorus removal than nitrogen removal in natural surface water. The modification process for zeolite and pumice is simple and economic and could be made locally. The reaction kinetics data presented could be used for designing substrates to treat natural water or effluents for the removal of phosphorus on a large scale.

During the progress of the work a number of aspects requiring further investigation were identified:

- The potential for the reduction in internal nutrient recycling through sediment remediation is the most critical question. In the first instance, this should be examined in water/sediment column experiments.
- Mesocosm (limnocorral) trials would be required to validate the performance of the various media in a site impacted by eutrophication. This should be performed in collaboration with limnologists in order to examine the impacts on productivity and pelagic algal and zooplankton communities.
- The environmental risk of the substances in question should be addressed with studies to examine the fate of metals on the media under various environmental conditions including pH. The use of a number of toxicity bioassays at different trophic levels should accompany examination of the fate of metals.

- An engineering model should be established to examine the relationship between particle size, depth of capping and lake energy in order to determine the risk of media re-suspension.
- As research proceeds, and effective doses for the different outcomes (nutrient removal from water vs. sediment capping) are determined, a cost model should be developed for fabrication of modified zeolite in comparison to commercially available adsorbents.

7.0 References

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Appendix 1

US Patent for Phoslock

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(12) **United States Patent**
Douglas

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(54) **REMEDIATION MATERIAL AND REMEDIATION PROCESS FOR SEDIMENTS**

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(57) **ABSTRACT**

A material and method for removal of environmental oxyanions (and especially phosphates), the material comprising a substrate such as a clay modified with complexing elements selected from Group IIIB, Group IVB, and lanthanide elements (or a mixture of such elements). The resultant modified substrate can bind oxyanions and make them unavailable for utilisation in the environment; in the case of phosphates, by algae and the like. The method includes forming a capping of material at the sediment/water interface, applying the material in the form of pellets at the sediment/water interface, or injecting the pellets into the sediment.

23 Claims, No Drawings

REMEDIATION MATERIAL AND REMEDIATION PROCESS FOR SEDIMENTS

The present invention relates to a sediment remediation process, together with a material for use in a sediment remediation process.

BACKGROUND OF THE INVENTION

The progressive eutrophication of estuarine and freshwater systems throughout Australia and overseas is often reflected in an increase in both phytoplankton bloom frequency and biomass, often with a shift to more nuisance species such as cyanobacteria. A significant proportion of the research into, and management of, estuarine and freshwater systems has focussed (with varying success) on reducing inputs of nutrients (in particular phosphorus) from the catchment.

However, the present invention has recognised that increased internal loadings derived from sedimentary nutrient stores accumulated over years to decades, constitute a major barrier to the effective management and restoration of estuarine and freshwater systems. Indeed, it is now apparent that if effective sediment-nutrient management strategies can be identified and adopted to modify internal nutrient (phosphorus) loadings, this will equip natural resource managers with a powerful tool for both short- and long-term estuarine and freshwater system management.

SUMMARY OF THE INVENTION

An aim of the present invention is to provide a sediment remediation process and a sediment remediation material which will assist in modifying, and in particular reducing, internal recycling sediment nutrient stores in estuarine and freshwater systems.

Broadly, the invention provides a method for remediating matter by removing oxyanion or phosphorus containing pollutants therefrom, the method comprising the step of contacting the matter with a substrate doped, cation-exchanged, or modified with, or otherwise having adsorbed complexing element(s) selected from Group IIIB and Group IVB elements.

The mechanism for reactions which occur in the substrate on addition of the complexing elements, and the chemical speciation of these elements are presently not well understood. By the term "modified" which term will be used hereafter, it is intended to cover whatever the reaction mechanism may be, which includes modification of the substrate by doping and/or cation exchange, and/or adsorption of the complexing element by the substrate. In addition, by the term "complexing element(s)", ionic moieties containing such complexing elements are included, in addition to complexing element(s) alone.

Typical matter may comprise sediments in waterways and catchments, effluent from sewage treatment plants (commercial and/or domestic), industry, aquaculture (commercial and/or domestic and/or agricultural), sediments in water supply impoundments (lakes, reserviors), sediments in constructed wetlands and stormwater detention basins or similar engineered or natural impoundments.

Typical pollutants envisaged include phosphorus containing compounds, anions generally which are capable of forming complexes, and in particular oxyanions such as in particular phosphates, but also arsenate, vanadate, chromate and selenate, tungstate, niobate, tantalate, and tellurate, amongst others, and peroxyanions inter-alia such as persulphate. It is also expected that the method may have application in removing pollutants such as organic chemical contaminants such as pesticides or herbicides or trace elements, although this is not the primary objective of the invention.

Generally, phosphorus will be removed as dissolved phosphates or orthophosphate. Phosphates exist as different species, depending upon pH and other solution physicochemical parameters. Phosphorus is often present in polluted aqueous environments in insoluble forms, and is transformed to soluble phosphate species by various processes that can occur within the environment. Examples of insoluble phosphorus include organically-bound phosphate which may become aqueously soluble due to biogeochemical processes, or phosphorus held in inorganic forms such as in mineral form as in mineral apatite or fertilizer, or that bound to crystalline and/or amorphous Fe-Mn-oxyhydroxide species all of which may be released due to various biogeochemical processes.

The method may include in addition, adding a water soluble salt of the complexing element selected from Group IIIB and Group IVB elements, along with the modified substrate. This would be expected to give rise to an immediate reduction in pollutant levels due to formation of complexes with the soluble salt, leaving the remediation material for more long term reduction in pollutants.

Preferably the salt is a chloride salt or a nitrate salt or a mixture of chloride and nitrate salts of the complexing element.

The present invention also provides a remediation material for use in reducing oxyanion or phosphorus pollutant loadings in matter, the remediation material comprising a substrate doped, cation-exchanged or modified with, or having adsorbed a complexing element(s) selected from the Group IIIB and Group IVB elements.

The substrate may be any suitable substrate having a moderate to high cation exchange capacity (CEC)—a substrate having a CEC of greater than about 30 milliequivalents per 100 grams (meq/100 g) having a 'moderate' CEC, while a 'high' CEC substrate may have a CEC of greater than about 100 meq/100 g and commonly about 150meq/100 g or greater.

It is preferred that the substrate is a mineral substrate due to these being in many instances relatively inert and/or harmonious in the environment.

In the most preferred form of the invention, the mineral substrate is an expandable clay such as saponite, bentonite or vermiculite. These materials are regarded as expandable clays due to their ability to absorb waters of hydration into their internal structure which may change the basal (d-) spacing.

Alternatively, the mineral substrate may be a fibrous, chain-like related clay mineral such as attapulgite, sepiolite, or palygorsite.

However, it will be appreciated that materials of a similar nature to clays, clay-like minerals, or expandable clays, may also be satisfactory. These may include materials both natural or synthetic. For instance, zeolites have also been investigated for use as the mineral substrate of the invention, both naturally occurring zeolites and artificially synthesised zeolites. Zeolites are also commonly a moderate to high cation exchange capacity material and although they are aluminosilicate minerals like clays, they have a different three dimensional framework structure with internal cavities.

The mineral substrate of the invention preferably has a high CEC in order to allow it to be modified to increase its pollutant or nutrient binding capacity, and in particular its phosphorous binding/absorbing/complexing capacity. Specifically, this involves the exchange of cations present in the mineral substrate with the nutrient complexing element or elements referred to above. This modification may be described as doping or cation exchange/ion exchange.

The mineral substrate may be pre-treated with a concentrated acid (e.g. HCl, H_2SO_4) to remove a large proportion of the interlayer and/or structural cations, before being treated with the complexing element. The pretreatment of clays with acid represents another pathway to prepare modified clays for phosphate adsorption. A potential advantage of this technique is that there may be a degree of modification to the underlying clay structure which enhances the uptake of the complexing element or other structural changes to the clay. These structural changes may make the clay more amenable to other modification steps which may improve the phosphate uptake capacity.

The complexing element is preferably an element capable of forming a complex with oxyanions. Most preferably the complexing element is capable of forming a complex with phosphorus containing compounds, as phosphorus is often the most common nutrient present in contaminated aquatic systems which may mean there is a high potential for algal bloom growth. Typically, the phosphorus will be present as phosphate anions in such aquatic systems.

The remediation material may be applied as a dry powder, as pellets, or as a wet slurry to the surface of a waterbody, or directly to the surface of bottom sediments, or injected into the bottom sediments. It is advantageous to form a capping layer of remediation material to the surface of bottom sediments, water conditions such as flow rates and turbulence permitting. The capping layer may be of any thickness, but a range between 0.5 mm and 5 mm should prove suitable, with an optimum range between 2 mm and 3 mm begin suitable for most conditions, without giving rise to undesirable side effects to the existing ecosystems. The layer thickness required will depend on factors such as rate, duration, and variability of phosphorus release, the rate and/or capacity of adsorption/binding/complexation of the remediation material, the desired phosphorus reduction and the influence of any other environmental and/or physicochemical conditions.

The remediation material may be sandwiched between geotextiles such as water permeable membranes or woven plastic cloth such as woven PVC (poly vinyl chloride) cloth. In the case of pelletised remediation material, a weave net having apertures smaller than the pellets may be used to sandwich the pellets, in order to accommodate a high solute flow while minimising loss of the remediation material.

The remediation material is believed to be particularly suitable for reducing internal phosphorus loadings in bottom sediments in estuarine or freshwater systems.

The element is preferably selected from the Group IIIB and IVB elements from the Periodic Table (CAS version). The Group IIIB elements comprise scandium, yttrium, lanthanum, and actinium, and for the purposes of this specification are deemed to include lanthanides. The Group IVB elements comprise titanium, zirconium, and hafnium. The lanthanides comprise lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thullum, ytterbium, and lutetium. A mixture of such elements may be used.

In particular, the element is most preferably selected from the group comprising lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu) and yttrium (Y) or the group comprising zirconium (Zr) and hafnium (Hf), with lanthanum being the element of choice. As discussed above, it will also be appreciated that some of the remaining elements referred to above will not be preferred due to toxicity problems. The most preferred elements are selected from Group IIIB, Group IVB, and lanthanides, and have an atomic number between 21 and 72 inclusive.

With particular reference to the use of lanthanum, it has been demonstrated that lanthanum forms an extremely stable, redox-insensitive complex with phosphorous under most common environmental conditions, making the phosphorous unavailable to phytoplankton in aquatic systems and thus, potentially reducing the magnitude and/or frequency of algal blooms. With the lanthanum bound in the substrate, the lanthanum phosphate complex is effectively immobilised. In addition zirconium also forms a useful cation-exchanged modified substrate. It is believed that a mixture of cations comprising lanthanum and/or zirconium, optionally with other rare earth elements may be used in the modified substrates.

The sediment remediation material of the present invention may be used as a reactive capping or layer on top of bottom sediments in estuarine or freshwater systems. Due to the high nutrient binding capacity of the sediment remediation material (and in the preferred form its phosphorus binding capacity), the layer of material binds and substantially reduces the availability of the internal store of nutrients in the sediment, thus reducing the waterway nutrient loading.

Thus, the present invention additionally provides a sediment remediation process, the process comprising placing a reactive capping or layer of a sediment remediation material on top of bottom sediments in estuarine or freshwater systems, the sediment remediation material comprising a mineral substrate doped, cation-exchanged, or modified with, or having adsorbed a nutrient complexing element(s) selected from the Group IIIB and Group IVB elements.

The sediment remediation material may also be altered by the addition of organic and/or inorganic ligands to the clay and/or to the interlayer ions thereof, to alter its chemical properties for a particular application. This can form complexes with the exchanged cation in the substrate, resulting in the modified behavior in the sediment remediation material.

The placement of the reactive capping or layer may be achieved using known equipment and apparatus. However, the form of the sediment remediation material may be physically and/or chemically altered to suit a particular application. For example, where the mineral substrate is an expandable clay, the clay may be heated for varying times and to varying temperatures (using a combination of temperature and time to achieve the desired effect) such that the clay is selectively and suitably dehydrated.

This dehydration step is believed to be beneficial because at various stages of hydration there may still be significant exchange (the magnitude of which may be controlled) of lanthanum (for instance) into solution. The release of lanthanum may also be modified either singly or in combination by changes in the physico-chemical conditions of the solution such as pH and/or ionic strength. This lanthanum, once released into solution, may then be available to bind phosphorous in the water mass, leaving remaining lanthanum in the clay to bind phosphorus from sediment or other sources. This form of the invention assists in binding phosphorous in both the water mass and the sediment, as the material settles down into the water to form the reactive capping.

This dehydration step may additionally be beneficial because at sufficiently high temperatures (ca.>900–1000 deg C.) the clay structures may decompose to form a variety of other mineral phases. These degradation products may also be useful but are yet to be evaluated.

Alternatively the sediment remediation material may be pelletised and the pellets injected, placed upon the bottom by mechanical or other means (e.g. settling through the water column), or otherwise mixed with the bottom sediments. In one such application, it is expected that the element may be substantially immobilised within the expandable clay by driving off any water of hydration.

Alternatively, the physical form of the sediment remediation material may be modified, such as by pelletisation, to not only modify the movement of the material under a range of hydrodynamic scenarios but also to influence the release rate and/or availability of lanthanum (for instance) due to changes in the surface area of the pellets.

In can thus be seen that in the preferred form of the invention, the lanthanum doped, cation-exchanged, or modified clay or other mineral substrate has the potential to be used in a variety of natural aquatic environments (for example—lake, river, estuarine), or artificial aquatic environments (for example farm dam, aquaculture and treated/untreated industrial and/or sewage effluent), to reduce the concentration of dissolved phosphorus and in turn algal growth and/or biomass and/or bacterial growth and/or biomass and/or biological oxygen demand (BOD). The sediment remediation material may also be used to adsorb/bind/complex a range of other anions/oxyanions in aquatic systems.

Extensive laboratory trials have been undertaken to evaluate a wide range of lanthanum doped, cation-exchanged, or modified materials under a wide range of physico-chemical conditions. Preliminary results suggest that a lanthanum modified saponite or a lanthanum modified bentonite (both commercially sourced expandable clays) are the most promising materials. These materials have been demonstrated in trials to reduce dissolved phosphorous concentrations by in excess of 90% under a range of salinities in small scale batch tests. Application of these materials to sediment cores obtained from the Swan River in Western Australian demonstrated a similar phosphorous reduction capacity relative to untreated sediment cores over a period of seven days.

DETAILED DESCRIPTION OF THE INVENTION

Aparticular preferred example of the method and material therefor will now be described.

Sediment remediation materials for laboratory evaluation purposes were generally prepared in batches of 1 g to 5 g. Although the modified clay was only prepared on a laboratory scale, the simple cation-exchange technique may easily be scaled-up to produce large quantities.

Generally the procedure involves the mixing of a solution of 0.1M $LaCl_3$ with high purity bentonite (e.g. Commercial Minerals CE150 —ca. 90% bentonite), in the ratio 100:1 solution: solid ratio (so that a large excess of La was available for ion-exchange), in an acid-washed plastic container. For laboratory scale production, the $LaCl_3$ solution and bentonite were mixed on a bottle roller for approximately 24 hours, although it will be understood that the mixing apparatus, solid/solution ratios and/or solute concentration and physico-chemical conditions may be varied to take into account requirements for scaling up.

On completion of the mixing, the product is centrifuged (10,000 rpm, 10 minutes) and the supernatant liquid decanted. A second eliquot of 0.1M $LaCl_3$ was added in the same solution: solid ratio and the mixing (ion-exchange) process repeated. The cation- exchanged sediment remediation material is then washed with distilled water and centrifuged. This process if repeated a minimum of three times to ensure removal of excess, unexchanged La. The washed cation-exchanged samples are then dried overnight in an oven at ca. 60° C. and stored under airtight conditions for later use.

In addition to the evaluation of clays substituted with lanthanide elements (principally lanthanum), a number of other clay derivatives are currently being prepared and evaluated. These clays include Zr-exchanged clays, pillared clays (using a variety of ions—Zr, La etc.) and clays using mixed ions (e.g. Zr and La). $ZrOCl_2$ has been used to successfully produce remediation materials with bentonite and saponite, in the same manner as set out in the first example. A mixed ion exchanged clay remediation material has been produced using a mixture of $ZrOCl_2$ and $LaCl_3$.

While bentonite has been used in this embodiment, many other types of clay are suitable but vary in their capacity to exchange La (or Zr) and hence their capacity to remove phosphorus.

The sediment remediation material produced as above may be applied by direct application to a waterbody, being spread in dry form as a powder or made up as a slurry, to the surface of a waterbody. Alternatively, the sediment remediation material may be pelletised and applied in a similar fashion. The former will result in a capping layer being produced which will overlie bottom sediment in the waterbody, subject to factors such as turbulence. The latter may be advantageous where it might be expected that environmental conditions might result in dispersal of finely divided sediment remediation material.

Pellets may be formed by binding the modified substrate. A variety of binders may potentially be used singly or in combination to manufacture a robust pellet which is resistant to dissolution and/or abrasion or has a controlled rate of decomposition. Binders that may be suitable include: Keggin (polyaluminuim) ions, starch, sodium silicate, portland cement (or combinations thereof). Calcination may also potentially be used to improve the properties of the pellets after the addition of the binder(s). The actual formation of the pellets may be achieved through a variety of processes (e.g. extrusion through dies or templates as a paste or viscous solid or rolling in mills or similar).

The sediment remediation material may also be directly applied to bottom sediments, directly at the sediment/water interface, or at various levels within the water column.

The sediment remediation material may also be applied in combination with solid or dissolved salts of lanthanum (for instance). This would allow a more rapid reduction of the free ion concentration of the (target) oxyanion(s) or anion(s) of interest followed by a more sustained reduction of the (target) oxyanion(s) or anion(s) of interest by the sediment remediation material. Additionally, the solid or disolved salts may include, or include in addition to group IIIB or IVB salts, a divalent or trivalent salt in addition, a suitable divalent salts being a calcium salt such as calcium nitrate, calcium chloride, or a mixture thereof. The effect of such salts is to form a liquid of the required density which will contain both dissolved lanthanum (for example) and the powdered sediment remediation material and deliver it to the desired depth within an aquatic system (e.g. sediment/water interface) and assist in preventing the resuspension of both the dissolved and solid sediment remediation agents. Hence, the material may be delivered to a depth in an aquatic system where it may have its desired optimal effect.

The sediment remediation material may be contained within semipermiable geotextiles, such as coarse weave PVC material, to allow flow of solute therethrough. The geotextiles with contained sediment remediation material may be suspended within a waterbody or placed on the bottom or sides of the waterbody, possibly in direct contact with the underlying sediment.

Any of the above arrangements may be utilised in an artificial/constructed or natural wetland, or a treatment pond, lake, reservior etc.

In the following example, a La exchanged saponite sediment remediation material was trialled with bottom sediments and river water. This remediation material was produced using the same method as described for the La exchanged bentonite sediment remediation material. The trials were conducted in the laboratory over 96 hours using 1.0 g of Swan River (Maylands, Western Australia) sediment and 0.1 g of modified clay or 30 mL of sample water and 0.1 g of modified clay (Ellen Brook, Avon River and Swan River, Western Australia), in the trials the sediment remediation material was mixed with the sample. The trials demonstrated that the sediment remediation material may efficiently remove phosphate from a variety of natural waters and wastewaters. A summary of the results of the trial is presented in the following table, which shows the reduction in dissolved phosphorus concentrations (as PO_4–P) released from the Swan River (Maylands, Western Australia) from bottom sediment over a range of salinities, and from Ellen Brook, Avon River, and Swan River waters (Western Australia) after the addition of La-saponite sediment remediation material.

Sample type (salinity)	PO_4—P (μg/L) in solution-no treatment	PO_4—P (μg/L) - modified clay treatment
Maylands sediment (0)	120	<5
Maylands sediment (5)	120	<5
Maylands sediment (30)	130	<5
Ellen Brook water (0)	450	9
Avon River water (4)	20	<5
Swan River water (25)	35	<5

A number of sewage effluents have also been tested. Samples of final effluent were collected from two sewage treatment plants (Denmark, Western Australia and Subiaco, Western Australia) and combined with La-exchanged bentonite sediment remediation material in the ratio 0.1 g La-bentonite/30 mL effluent and mixed for 24 hours. The results, which suggest that the sediment remediation material is able to remove dissolved phosphate from sewage effluent, are summarized in the following table:

Sample type (salinity)	PO_4—P (mg/L) final effluent-no treatment	PO_4—P (mg/L) - modified clay treatment
Denmark	3.49 ± 0.23	0.0025 ± 0.00
Subiaco	1.13 ± 0.04	0.0025 ± 0.00

Laboratory trials suggest that the two La-cation exchanged clays referred to above are able to reduce dissolved phosphorus concentrations present as either dissolved phosphate (in a range of natural waters) or released from bottom sediments by in excess of 90% under a range of salinities in small scale batch tests. The trials suggests that the two sediment remediation materials bind phosphorus rapidly and strongly. It is believed that the La-exchanged clay-P complexes formed in the sediment remediation materials are robust under a variety of environmental conditions commonly encountered in aquatic environments such as in the Swan-Canning River system. Specifically, the effectiveness of the modified clays in binding dissolved phosphorus appear to be:

unaffected by a range of salinities (0–35 parts per thousand),

unaffected by redox status (oxidising or reducing conditions) or dissolved oxygen levels (ie. anoxia to oversaturation)

able to bind phosphorus over a wide operational pH range (ca. 6–10 and probably ca. 5–11)

and believed to be unaffected by microbial action in the short-term.

Application of a sediment remediation material to sediment cores from the Swan River has also demonstrated a similar phosphorus reduction capacity to that demonstrated in in-vitro testing relative to untreated sediment cores over a period of seven days. Immediately after the application of the sediment remediation material as a capping over the core, there was a rapid decline in PO_4–P in solution to below detection limits which was sustained for approximately 150 hours. The robustness of the sediment remediation material in binding phosphorus was highlighted during the last stage of the experiment where induced anoxia did not result in the release of phosphorus bound to the modified clay in the experimental cores. Similar capacities to reduce phosphorus concentrations in waters overlying sediment cores due to the application of sediment remediation materials have also been demonstrated for Lake Monger (Perth, Western Australia) and the Canning River (Perth, Western Australia), the latter having phosphorus release suppressed for in excess of 400 hours.

There are a number of advantages of using the modified clay as a remediation material, over and above simple delivery of aqueous solutions of reactive compounds. The sediment remediation material was developed using a clay as the clay is a simple substrate to deliver the La (or other elements) in a solid form to the sediment-water interface, allow settling through the water column and allow bound oxyanions to be recovered in a solid form. As the clay is a natural material is likely to be harmonious with the environment to which it is introduced as the sediments of many aquatic systems are dominated by clays or have clay as a significant component.

It should be appreciated that the scope of the invention is not limited to the particular examples or applications described herein.

What is claimed is:

1. A method for remediating matter selected from sediments and effluent by removing phosphorus and oxyanion pollutants therefrom, the method including the step of contacting the matter with a substrate selected from one or more of an aluminosilicate clay and an aluminosilicate having a three dimensional framework structure with internal cavities, modified by cation exchange with an effective amount of complexing element(s) selected from Group IIIB, lanthanides, and Group IVB elements to remove said phosphorus and oxyanion pollutants.

2. A method as claimed in claim **1** wherein the substrate is selected from one or more of an expandable clay and a fibrous, chain like related clay mineral.

3. A method as claimed in claim **1** wherein-said substrate is selected from one or more of saponite, bentonite, vermiculite, attapulgite, sepiolite or palygorskite.

4. A method as claimed in claim **1** wherein the substrate includes zeolite.

5. A method as claimed in claim **1** wherein the substrate is pre-treated with a concentrated acid to remove a large proportion of the interlayer cations before being modified with said complexing element.

6. A method as claimed in claim **1** wherein the complexing element is selected from one of more of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, yttrium, ytterbium, lutetium, zirconium, and hafnium.

7. A method as claimed in claim **6** wherein the complexing element comprises lanthanum.

8. A method as claimed in claim **6** wherein the complexing element comprises zirconium.

9. A method as claimed in claim **6** wherein the complexing element comprises a mixture of lanthanum and zirconium.

10. A method as claimed in claim **1** wherein the modified substrate is altered by the addition of at least one of organic and inorganic ligands to alter its chemical properties for a particular application.

11. A method as claimed in claim **1** wherein the modified substrate is applied as a dry powder, as pellets, or as a wet slurry to the surface of a waterbody.

12. A method as claimed in claim **1** wherein the modified substrate is applied directly to a surface of bottom sediments of a waterbody.

13. A method as claimed in claim **1** wherein the modified substrate is injected into bottom sediments of a waterbody.

14. A method as claimed in claim **1** wherein the modified substrate forms a capping layer over the surface of bottom sediments of the water body.

15. A method as claimed in claim **14** wherein the capping layer has a thickness between 0.5 mm and 5 mm.

16. A method as claimed in claim **1** wherein the modified substrate is sandwiched between geotextiles selected from water permeable membranes, woven plastic cloth, woven PVC cloth, and woven PVC textile.

17. A method as claimed in claim **1** wherein the modified substrate is pelletised and sandwiched between woven net surfaces having apertures smaller than the pellets in order to accommodate a high solute flow while retaining the remediation material therein.

18. A method for remediating matter selected from sediments and effluent by removing phosphorus and oxyanion pollutants therefrom, the method including the step of contacting the matter with a substrate selected from one or more of an aluminosilicate clay and an aluminosilicate having a three dimensional framework structure with internal cavities, modified by cation exchange with an effective amount of at least one complexing element selected from Group IIIB, lanthanides, and Group IVB elements, and including adding a soluble salt of the complexing element selected from group IIIB and Group IVB elements to remove said phosphorus and oxyanion pollutants.

19. A method as claimed in claim **18** wherein the salt is a chloride salt, a nitrate salt or a mixture of chloride and nitrate salts of the complexing element.

20. A method as claimed in claim **19** further including the addition of a divalent salt, a calcium salt, or a trivalent salt.

21. A method for remediating matter selected from sediments and effluent by removing phosphorus and oxyanion pollutants therefrom, the method including the step of contacting the matter with a substrate selected from one or more of an aluminosilicate clay and an aluminosilicate having a three dimensional framework structure with internal cavities, modified by cation exchange with an effective amount of at least one complexing element selected from Group IIIB, lanthanides, and Group IVB elements, to remove said phosphorus and oxyanion pollutants, and wherein the substrate has a cation exchange capacity (CEC) of greater than about 30 milliequivalents per 100 grams (Meq/100 g).

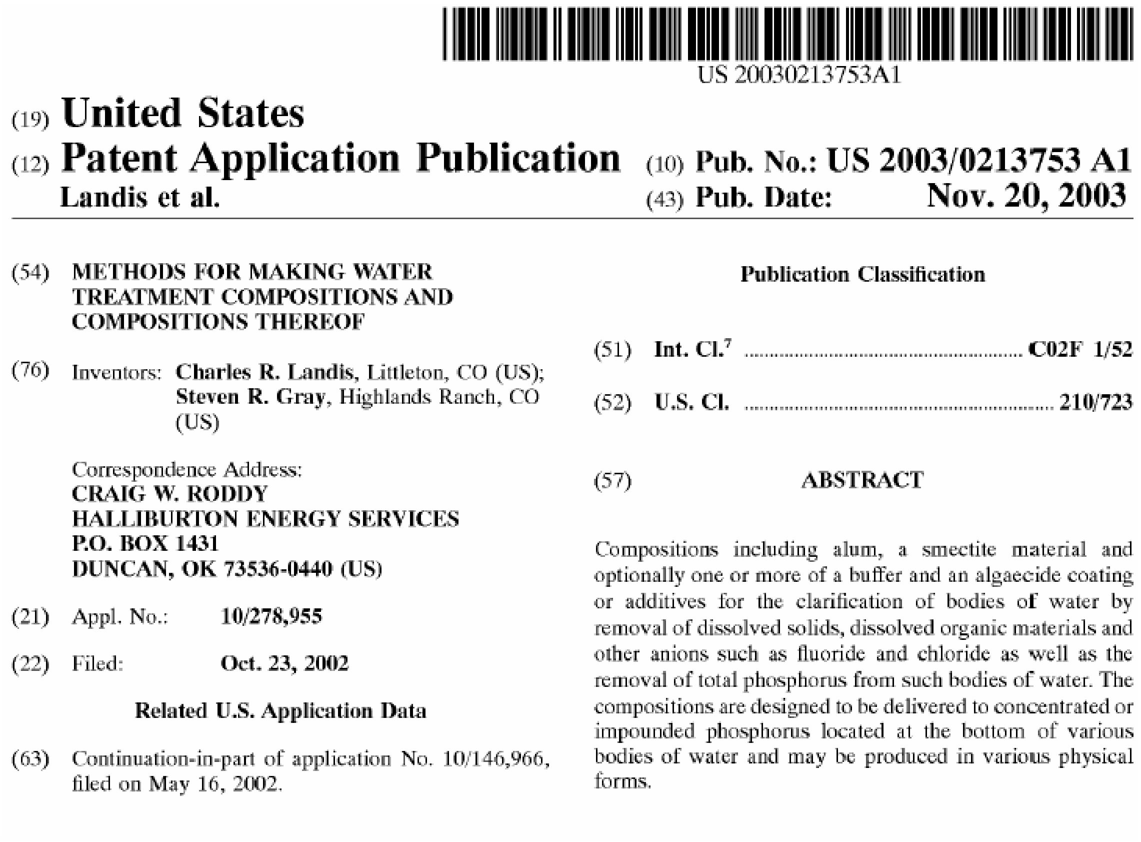
22. A method as claimed in claim **21** wherein the substrate has a cation exchange capacity (CEC) of greater than about 100 meq/100 g.

23. A method as claimed in claim **22** wherein the substrate has a cation exchange capacity (CEC) of greater than about 150 meq/100 g.

* * * * *

Appendix 2

US Patent for Baraclear



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(54) **METHODS FOR MAKING WATER TREATMENT COMPOSITIONS AND COMPOSITIONS THEREOF**

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(57) **ABSTRACT**

Compositions including alum, a smectite material and optionally one or more of a buffer and an algaecide coating or additives for the clarification of bodies of water by removal of dissolved solids, dissolved organic materials and other anions such as fluoride and chloride as well as the removal of total phosphorus from such bodies of water. The compositions are designed to be delivered to concentrated or impounded phosphorus located at the bottom of various bodies of water and may be produced in various physical forms.

METHODS FOR MAKING WATER TREATMENT COMPOSITIONS AND COMPOSITIONS THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part of copending U.S. patent application Ser. No. 10/146,966 filed May 16, 2002, the entire disclosure of which is incorporated herein by reference.

BACKGROUND

[0002] The present embodiment relates generally to the production of water treatment compositions for the clarification of bodies of water by removal of dissolved solids, dissolved organic materials (i.e. natural pigments and humic acids) and other anions such as fluoride and chloride as well as the removal of total phosphorus from such bodies of water. More particularly, the compositions are designed to be delivered to concentrated or impounded total phosphorus located at the bottom of various bodies of water and may be produced in a variety of physical forms that are designed to enhance the delivery of the compositions to a desired location in a body of water such as pellets, tablets and extruded noodles, briquettes or ribbons. The compositions include alum and a smectite mineral-bearing industrial material such as bentonite (montmorillonite), attapulgite, saponite, hectorite, sepiolite and fullers earth. The compositions optionally include one or more of a buffer and algaecide coatings or additives. The compositions can be delivered to a wide range of locations in bodies of water including the "sediment water interface" which is an area that can be generally defined as the top six inches of sediment combined with the deepest six inches of water. Even more particularly, the compositions are designed so that when they are dropped through a body of water, the alum is released when the pellet reaches a desired location in the water, thereby treating the phosphorus more efficiently and using or consuming less alum.

[0003] Acidic metal salt and sulfate solutions, such as aluminum sulfate ($(Al_2SO_4)_3.14H_2O$) solutions, commonly known and referred to as "alum," have long been used to remove color and suspended particles, as well as organic and microbiological contaminants from water. Alum is readily available and when diluted with surface water, it can function as a coagulant, flocculent, precipitant and emulsion breaker. As a coagulant, alum removes the primary nutrient for blue-green algae in the water. This function is important because these algae remove oxygen from the water (known as biochemical oxygen demand or BOD) and thus pose a danger to fish. Alum also forms an insoluble precipitate or floccule, i.e., a floc, with the impurities in the water. The floc grows in size as it attracts suspended and colloidal particles and organic compounds present in the water. The floc settles out of the water over time and can be removed by techniques that are well known to those skilled in the art such as by decanting or filtration.

[0004] One of the most difficult problems in water pollution control is the growth of algae. As noted above, algal organisms exert a BOD on the water and the algal BOD can often exceed the oxygen resources of the water. Algal growths can also cause unpleasant tastes and odors in water supplies. Dissolved phosphorus provide algae with a necessary nutrient supply. If the phosphorus supply could be removed the algae would not survive or flourish in the water column and a water pollution control problem would be addressed. An additional difficulty associated with the treatment of phosphorus in water is that the majority of the phosphorus (50-90%) is concentrated at the sediment-water interface of an impoundment and current application techniques involving alum primarily treat the phosphorus closer to the surface of the body of water. In addition, current techniques have been focused on nearly instantaneous sorption of phosphorus. As a result, the body of existing products and techniques do not perform as effectively in a number of water systems, especially high energy and deep systems, and in systems that require more than just instantaneous phosphorus sorption. In the former case, alum is flushed from the target waters before it can perform. In the latter case, the alum is poorly utilized in application. Also, the alum can leave an unwanted white cloud in the water for an extended period of time.

[0005] Therefore, there is a need for simple compositions, forms and methods for treating phosphorus impoundments in bodies of water.

DETAILED DESCRIPTION

[0006] According to one embodiment, a phosphorus impoundment is treated with a composition that includes alum and a member of the smectite family of minerals as the two major components. As used herein the term "alum" shall refer to and be defined to mean aluminum sulfate ($(Al_2SO_4)_3.14H_2O$). Also, as used herein the term "smectite mineral material" shall refer to and be defined to mean bentonite, attapulgite, saponite, hectorite, sepiolite and fullers earth. Bentonite is a smectite bearing ore that is enriched in the smectite mineral known as montmorillonite. Preferably, the composition includes from about 30 to about 99 weight percent of alum and from about 1 to about 70 weight percent of a smectite mineral material.

[0007] According to a preferred embodiment, the composition includes a pH buffering agent which shall be referred to herein as a "buffer." Preferably, the buffer is a common, widely available pH buffering agent such as sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$), calcium hydroxide ($Ca(OH)_2$), magnesium hydroxide ($Mg(OH)_2$), sodium hydroxide (NaOH), magnesium oxide (MgO) and calcium oxide (lime) (CaO) According to this embodiment, the composition includes from 0 to about 30 weight percent of a buffer.

[0008] According to another preferred embodiment, the composition includes an algaecide. Preferably the algaecide includes a common, widely available copper based system such as copper sulfate ($CuSO_4$) or one of its various hydrous varieties such as copper sulfate pentahydrate ($CuSO_4.5H_2O$) In addition, the algaecide may include chelated copper-based systems such as alkylated amines, preferably having an alkyl chain of from 6 to 30 carbon atoms, especially di-tallo di-bromo copper amines, preferably having from 14 to 18 carbon atoms, as well as, sodium and potassium salts of such alkylated amines. According to this embodiment, the composition includes from 0 to about 20 weight percent of an algaecide.

[0009] According to another preferred embodiment, the composition includes alum, a smectite mineral material, a buffer and an algaecide. According to this embodiment the components of the composition are present at the weight percentages noted above.

[0010] According to another preferred embodiment, the components of the composition (alum, a smectite mineral material, a buffer (if present) and an algaecide (if present)) are covered or coated by techniques well known to those skilled in the art, with one or more natural organic by-products such as corn starch, sugar-based resins, and various natural product derivatives such as chemical families of resins and starches. Suitable resins and coatings include guar gum, alginates, polyvinyl alcohol, partially hydrolyzed polyacrylamides and other similar polymers well known to those skilled in the art. According to this embodiment, the composition includes from 0 to about 5 weight percent of natural water soluble resins and by-products as a coating.

[0011] According to another preferred embodiment, the components of the composition (alum, a smectite mineral material and a buffer (if present)) are covered or coated by techniques well known to those skilled in the art, with an algaecide. Suitable algaecide materials and the preferred concentrations thereof are noted above.

[0012] The compositions of these embodiments selectively remove phosphorus from natural and man-made water systems. Phosphorus is a primary nutrient for aquatic flora/fauna such as blue-green algae which produce unsightly green slimes and clouds, and undesirable odors in waters. By removing the phosphorus, the algae are deprived of nourishment and therefore do not proliferate in the water column.

[0013] Each component of the compositions of the present embodiments, serves a function in the product towards the goal of optimal sorption and thus removal of phosphorus. Alum is a water treatment product that is used to remove phosphorus and other compounds such as dissolved organics, suspended sediment, and metals from a body of water. The primary purpose of the alum is to sorb the phosphorus from the water or sediments. Alum is generally commercially available from General Chemical Corporation.

[0014] The smectite mineral material, preferably bentonite, functions to 1) optimize the timing of the dissolution of the composition in the water column, 2) buffer the pH of the water that is being treated to a neutral pH level, and 3) optimize or control the density of the composition to more precisely estimate the residence time in the water column. Bentonite is generally commercially available from Bentonite Performance Minerals.

[0015] In addition to buffering the pH of the body of water, the buffer also enhances the density of the compositions for use in higher energy—higher flow—water systems. The buffers are generally commercially available from The General Chemical Group, Inc., Vulcan Materials Company, Franklin Limestone, Imerys, S. A. and Omya AG.

[0016] The algaecides are generally commercially available from Earth Tech, Inc. and Applied Biochemists.

[0017] The compositions of the embodiments discussed above generally retain approximately 90% of their integrity or shape for up to approximately 2 minutes. The compositions of the embodiments discussed above that have been coated with the materials discussed above, dissolve in water at a much slower rate than uncoated compositions. Specifically, the coated compositions generally retain approximately 90% of their integrity or shape for up to approximately 24 hours.

[0018] The compositions of the present embodiments are manufactured and produced according to techniques well known to those skilled in the art. Preferably, the compositions of the present embodiments are produced in a variety of physical forms that are designed to enhance delivery of the compositions to a desired location in a body of water such as spheres to oblate spheroids, cylinders to cubes and three-dimensional rectangles ranging in size from ¼" to 24" in diameter. More preferably, the compositions of the present embodiments are produced in the form of tablets, pellets, extruded noodles, briquettes or ribbons by equipment well known to those skilled in the art such as extruders, tabletizers, briquetters or agglomerators. In the process of forming such tablets, extruded noodles, briquettes or ribbons, each component of the compositions are provided in powdered or granular form and the components are blended. Preferably, the raw material components are blended in the proportions noted above and are physically mixed at the desired levels in tanks or similar units of 20 to 200 ton capacity, by augers and paddles for a prescribed amount of time, preferably from 5 minutes to up to 6 hours in batch mode, or by continuous metered feed onto a common belt or in a common continuously producing extruder, pelletizer, tabletizer, or agglomerator. For instance, a typical extruder is in the form of an elongated rectangular tub with at least one and optionally two augers oriented parallel to the ground that physically mixes the materials into a uniform mixture of the composition and then passes the composition through a restricted opening to form elongated noodles or cylindrical pellets. Conventional tabletizers and pelletizers take the mixed materials from a storage tank and compress the mixture via converging die plates into forms on the order of ¼" to 1" diameter spheres and spheroids. Commercial agglomerators take the mixtures as a powder (having a particle size ranging from 44 μm to 100 μm) and non-compressively combines the mixture into spheroids. Preferably, the composition has a moisture content of from 1 to 15 percent by weight. Preferably, the compositions manufactured according to the above mentioned processes may be coated with the materials discussed above according to techniques well known to those skilled in the art. Those skilled in the art will also recognize that other well known techniques may also be utilized to manufacture the compositions of the present embodiment.

[0019] The compositions of the present embodiments have utility in the following water treatment markets: municipal water treatment polishing agent, commercial construction/engineering, agricultural feedstock (such as in piggeries, cattle, sheep and ostrich farms), aquaculture (fish farms and hatcheries, such as for shrimp, salmon and trout), natural lake and river systems and watersheds, recreational and leisure (golf course ponds, amusement parks and aquatic centers), industrial effluent management, and mining and exploration (tailings ponds and discharge systems).

[0020] The compositions of the present embodiments, are time release alum-based sorbents of phosphorus in water. The vast majority of phosphorus-laden water systems contain a minority of suspended or dissolved phosphorus in the water column as compared to the sediment water interface. As used herein, the term "sediment water interface" shall refer and be defined to mean an area in a body of water that generally includes the top six inches of sediment combined with the deepest six inches of water. In the vast majority of water systems such as lakes, rivers, ponds or trenches, the majority of the total phosphorus is located at the sediment water interface. Powdered alum tends to remain in suspension removing the suspended phosphorus, organic matter, and other sediment but rarely reaches the targeted problem area in need of such treatment. Preferably the density of individual forms of the compositions of the present embodiment ranges from about 1.0 to about 2.0 gm/cm^3. It is also preferred that the individual forms of the compositions of the present embodiments have a diameter or major axis that ranges from ¼" to 24". Most preferably, the compositions of the present embodiments have a density and size such that the compositions settle quickly through the water column arriving where they are needed most at the sediment water interface.

[0021] The calculation for settling in water systems is based upon Stokes Settling Law which describes the rate of settling of a particle based upon the density of the particle and the density of the water. Stokes Settling Law is an accepted scientific principle used in a number of industries and can be used to estimate settling distances and time parameters for the compositions of the present embodiments. As noted above, the uncoated compositions according to the present embodiments will retain approximately 90% of their particle integrity for about 2 minutes which translates to a minimum of 50 feet of water column at the percentages of alum and smectite mineral material indicated above.

[0022] In commercial terms, the average depth of the water columns needing to be cleaned up is about 6', so according to Stokes Law, the uncoated product will reach the sediment water interface well in advance of the onset of significant dissolution.

Variations and Equivalents

[0023] Although only a few exemplary embodiments have been described in detail above, those skilled in the art will readily appreciate that many other modifications are possible in the exemplary embodiments without materially departing from the novel teachings and advantages described herein. Accordingly, all such modifications are intended to be included within the scope of the following claims.

What is claimed is:

1. A method of treating a phosphorus impoundment in a body of water comprising:

adding to the body of water a composition comprising alum and a smectite mineral material; and

releasing alum from the composition as the composition passes through the body of water.

2. A method according to claim 1, wherein the smectite mineral material is selected from the group consisting of: bentonite, attapulgite, saponite, hectorite, sepiolite and fullers earth.

3. A method according to claim 1, wherein the composition is in a form that enhances delivery of the composition to a desired location in the body of water.

4. A method according to claim 3, wherein the composition is in a form selected from the group consisting of a tablet, extruded noodle, pellet, briquette or ribbon.

5. A method according to claim 1, wherein the composition retains about 90 percent of the integrity of its form for about 2 minutes.

6. A method according to claim 1, wherein the composition further comprises a buffer.

7. A method according to claim 6, wherein the buffer is selected from the group consisting of sodium carbonate, sodium bicarbonate, calcium carbonate, magnesium carbonate, calcium hydroxide, magnesium hydroxide, sodium hydroxide, magnesium oxide and calcium oxide.

8. A method according to claim 1, wherein the composition further comprises an algaecide.

9. A method according to claim 8, wherein the composition comprising alum and smectite material is coated with an algaecide.

10. A method according to claim 8, wherein the algaecide is selected from the group consisting of a copper based system, a chelated copper-based system, an alkylated amine and sodium and potassium salts thereof.

11. A method according to claim 10, wherein the copper based system includes copper sulfate or a hydrous derivative thereof.

12. A method according to claim 11, wherein the copper based system includes copper sulfate pentahydrate.

13. A method according to claim 10, wherein the chelated copper-based system comprises di-tallo di-bromo copper amine.

14. A method according to claim 6, wherein the composition further comprises an algaecide.

15. A method according to claim 14, wherein the composition comprising alum, smectite material and a buffer is coated with an algaecide.

16. A method according to claim 1, wherein the composition comprising alum and smectite material is coated with a water soluble resin material selected from corn starch, guar gum, alginates, polyvinyl alcohol and partially hydrolyzed polyacrylamides.

17. A method according to claim 6, wherein the composition comprising alum, smectite material and a buffer is coated with a water soluble resin material selected from corn starch, guar gum, alginates, polyvinyl alcohol and partially hydrolyzed polyacrylamides.

18. A method according to claim 8, wherein the composition comprising alum, smectite material and an algaecide is coated with a water soluble resin material selected from corn starch, guar gum, alginates, polyvinyl alcohol and partially hydrolyzed polyacrylamides.

19. A method according to claim 14, wherein the composition comprising alum, smectite material, a buffer and an algaecide is coated with a water soluble resin material selected from corn starch, guar gum, alginates, polyvinyl alcohol and partially hydrolyzed polyacrylamides.

20. A method according to claim 16, wherein the composition retains about 90 percent of the integrity of its form for about 24 hours.

21. A method according to claim 1, wherein the composition in the form of a tablet, extruded noodle, pellet, briquette or ribbon, has a diameter or major axis of from ¼ to 24 inches.

22. A method according to claim 1, wherein the composition in the form of a tablet, extruded noodle, pellet, briquette or ribbon, has a density of from 1.0 to 2.0 gm/cm^3.

23. A method of treating a phosphorus impoundment in a body of water comprising:

adding to the body of water a composition comprising alum and a smectite mineral material; and

delivering the composition to the sediment water interface whereby alum is released from the composition at the sediment water interface.

24. A method according to claim 23, wherein the smectite mineral material is selected from the group consisting of: bentonite, attapulgite, saponite, hectorite, sepiolite and fullers earth.

25. A method according to claim 23, wherein the composition is in a form that enhances delivery of the composition to a desired location in the body of water.

26. A method according to claim 25, wherein the composition is in a form selected from the group consisting of a tablet, extruded noodle, pellet, briquette or ribbon.

27. A method according to claim 23, wherein the composition retains about 90 percent of the integrity of its form for about 2 minutes.

28. A method according to claim 23, wherein the composition further comprises a buffer.

29. A method according to claim 27, wherein the buffer is selected from the group consisting of sodium carbonate, sodium bicarbonate, calcium carbonate, magnesium carbonate, calcium hydroxide, magnesium hydroxide, sodium hydroxide, magnesium oxide and calcium oxide.

30. A method according to claim 23, wherein the composition further comprises an algaecide.

31. A method according to claim 30, wherein the composition comprising alum and smectite material is coated with an algaecide.

32. A method according to claim 30, wherein the algaecide is selected from the group consisting of a copper based system, a chelated copper-based system, an alkylated amine and sodium and potassium salts thereof.

33. A method according to claim 32, wherein the copper based system includes copper sulfate or a hydrous derivative thereof.

34. A method according to claim 33, wherein the copper based system includes copper sulfate pentahydrate.

35. A method according to claim 32, wherein the chelated copper-based system comprises di-tallo di-bromo copper amine.

36. A method according to claim 28, wherein the composition further comprises an algaecide.

37. A method according to claim 36, wherein the composition comprising alum, smectite material and a buffer is coated with an algaecide.

38. A method according to claim 23, wherein the composition comprising alum and smectite material is coated with a water soluble resin material selected from corn starch, guar gum, alginates, polyvinyl alcohol and partially hydrolyzed polyacrylamides.

39. A composition for treating a phosphorus impoundment in a body of water comprising:

a) alum; and

b) a smectite mineral material.

40. A composition according to claim 39, wherein the smectite mineral material is selected from the group consisting of: bentonite, attapulgite, saponite, hectorite, sepiolite and fullers earth.

41. A composition according to claim 39, wherein the composition further comprises a buffer.

42. A composition according to claim 41, wherein the buffer is selected from the group consisting of sodium carbonate, sodium bicarbonate, calcium carbonate, magnesium carbonate, calcium hydroxide, magnesium hydroxide, sodium hydroxide, magnesium oxide and calcium oxide.

43. A composition according to claim 39, wherein the composition further comprises an algaecide.

44. A composition according to claim 43, wherein the algaecide is selected from the group consisting of a copper based system, a chelated copper-based system, an alkylated amine and sodium and potassium salts thereof.

45. A composition according to claim 44, wherein the copper based system includes copper sulfate or a hydrous derivative thereof.

46. A composition according to claim 45, wherein the copper based system includes copper sulfate pentahydrate.

47. A composition according to claim 44, wherein the chelated copper-based system comprises di-tallo di-bromo copper amine.

48. A composition according to claim 41, wherein the composition further comprises an algaecide.

49. A composition according to claim 39, further comprising a water soluble resin material selected from corn starch, guar gum, alginates, polyvinyl alcohol and partially hydrolyzed polyacrylamides.

50. A composition according to claim 41, further comprising a water soluble resin material selected from corn starch, guar gum, alginates, polyvinyl alcohol and partially hydrolyzed polyacrylamides.

51. A composition according to claim 43, further comprising a water soluble resin material selected from corn starch, guar gum, alginates, polyvinyl alcohol and partially hydrolyzed polyacrylamides.

52. A composition according to claim 39, where the composition comprises from about 30 to about 99 percent by weight of alum and from about 1 to about 70 percent by weight of the smectite mineral material.

53. A composition according to claim 41, wherein the composition further comprises from 0 to about 30 percent by weight of the buffer.

54. A composition according to claim 43, wherein the composition further comprises from 0 to about 20 weight percent of an algaecide.

55. A composition according to claim 49, wherein the composition further comprises from 0 to about 5 percent by weight of the water soluble resin.

* * * * *

Appendix 3

Quantitative models for nutrient binding

Adsorption Isotherms

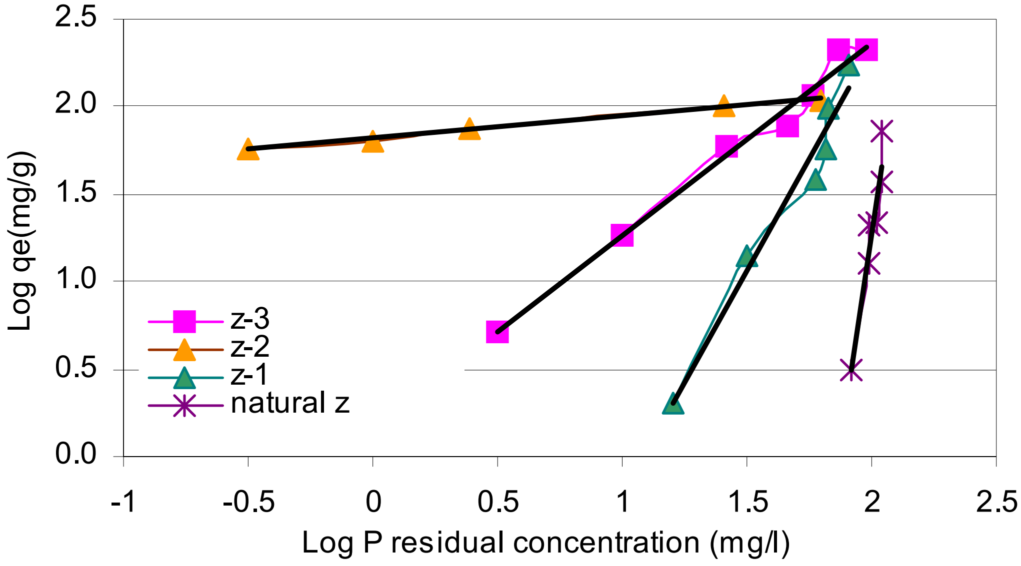
Adsorption isotherms were used to predict the relationship between equilibrium phosphorus concentrations and the quantity of the adsorbing media necessary to achieve those concentrations. High adsorbent dosages, up to 1.5 g, were used in the isotherm tests to determine whether the residual concentration could be reduced to the desired level. Tables give the experimentally obtained adsorption data of DRP as the pH values measured for the final slurries/solutions. The data fitted the Freundlich equation:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e$$

where q_e is the equilibrium phosphate concentration on adsorbent (mg/g), C_e is the equilibrium phosphate concentration in solution (mg/l), K_F (mg/g) and n (dimensionless) are the Freundlich adsorption isotherm constants. A larger K_F value represents a larger adsorption capacity while a larger $1/n$ value represents a more homogeneous adsorbent with a narrower site energy distribution. The values for n and K_F are given in tables; the related correlation coefficients (r-values) are given in the same table.

DRP adsorption data for zeolite

Zeolite dosage (g)	P residual concentration (mg/l)				P removed/zeolite (mg/g)			
	Z-1	Z-2	Z-3	Natural zeolite	Z-1	Z-2	Z-3	Natural zeolite
0.1	81.61	80.50	95.37	109.17	17.42	17.97	10.54	7.28
0.2	67.41	77.94	74.42	108.90	12.26	9.63	10.51	7.54
0.5	65.16	62.01	57.95	105.54	5.13	5.44	5.85	10.91
1.0	63.74	25.81	45.67	97.71	2.93	5.04	3.93	18.73
1.5	59.22	2.46	26.51	97.47	1.91	3.80	3.00	18.97
pH of slurries/solutions	4.06	5.31	5.63	4.70	Initial P concentration		116.44 (mg/l)	

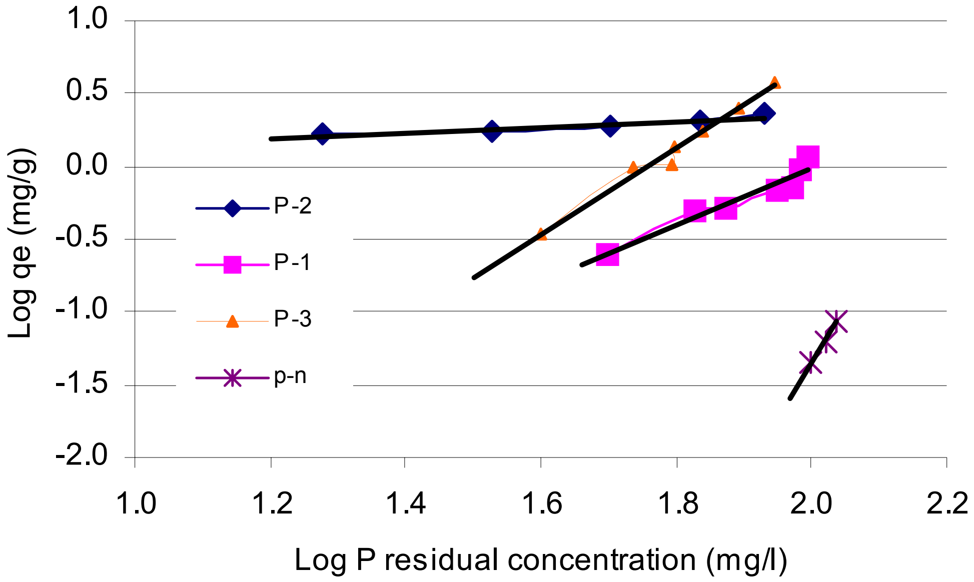


Freundlich isotherm constants for adsorption of DRP by modified and natural zeolite

	Adsorbents			
	Z-1	Z-2	Z-3	Natural zeolite
logK_F	-3.0505	1.8216	0.1602	-18.5430
1/n	2.7974	0.1237	1.1023	9.9144
r^2	0.8067	0.9921	0.9892	0.9065

DRP adsorption data for Pumice

Pumice dosage (g)	P residual concentration (mg/l)				P removed/pumice (mg/g)			
	PM-1	PM-2	PM-3	Natural pumice	PM-1	PM-2	PM-3	Natural pumice
0.2	98.84	87.39	88.20	102.21	1.16	4.02	3.82	0.32
0.5	96.32	85.37	78.37	101.14	0.72	1.81	2.51	0.23
1.0	93.92	68.41	69.09	99.31	0.48	1.75	1.72	0.21
1.5	88.82	50.22	62.50	98.78	0.49	1.78	1.37	0.16
2.0	75.02	33.73	61.99	89.53	0.71	1.74	1.04	0.35
2.5	67.35	18.96	54.63	89.06	0.72	1.69	0.98	0.29

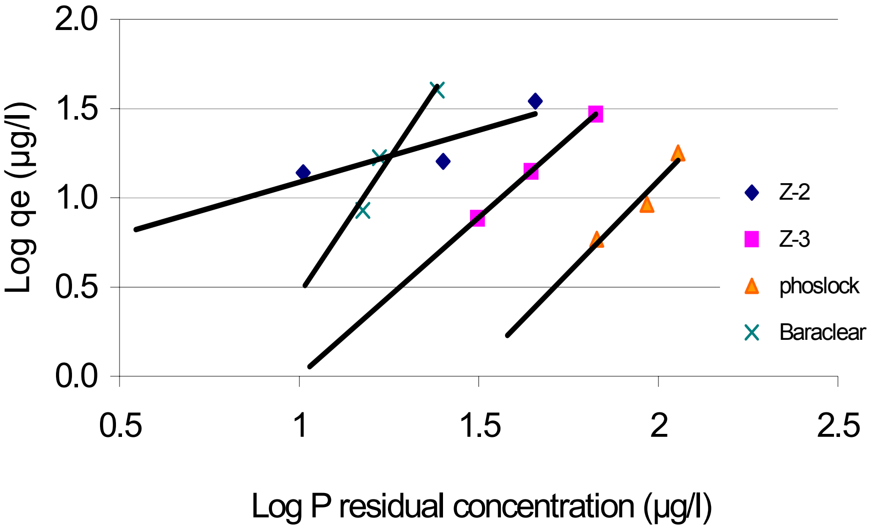


Freundlich isotherm constants for adsorption of DRP by modified and natural pumice

	Adsorbents			
	PM-1	PM-2	PM-3	Natural Pumice
$\log K_F$	-3.9032	-0.0359	-5.2333	-17.278
1/n	1.9436	0.1933	2.9768	7.9624
r^2	0.9346	0.8796	0.9835	0.9985

DRP adsorption data for Lake Okaro water

dosage (g)	P residual concentration (µg/l)				P removed/pumice (µg/g)			
	Z-3	Z-2	Phos-lock	Bara-clear	Z-3	Z-2	Phos-lock	Bara-clear
0.2	66.99	45.48	113.46	24.22	26.45	34.82	17.83	40.14
0.5	44.25	25.16	93.01	16.74	14.05	15.96	9.18	16.80
1.0	31.37	3.51	67.41	15.06	7.67	9.06	5.87	8.49



Freundlich isotherm constants for adsorption of DRP by modified and natural pumice

	Adsorbents			
	Z-3	Z-2	Phos-lock	Bara-clear
$\log K_F$	-1.7693	0.5036	-3.0297	-2.5737
1/n	1.7731	0.5835	2.0628	3.0323
r^2	1.0000	0.7735	0.9396	0.9435

Rate of Phosphorus Removal

The kinetics of adsorption for phosphorus in the media was studied using the Lagergren equation:

$$\log(q_e - q) = \log q_e - \frac{k_{ad}}{2.303} t$$

where q_e and q are the amounts of phosphate adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_{ad} is the rate constant of adsorption (1/min). A straight line of $log(q_e-q)$ vs t supported the applicability of this kinetic model, and indicated the adsorption processes followed first-order rate kinetics. The figure shows the adsorption rates of DRP on Z-2 at various pH conditions. The K_{ad} values were calculated from the slopes of these plots and are given in the table.

Table 8. Lagergren rate constants for adsorption of DRP on Z-2 at various pH.

PH*	**Z-2**	
	K_{ad} (1/min)	r^2
5.01	0.8846	0.9724
7.05	1.3823	0.9278
9.72	0.6704	0.9864

* *pH at initial DRP concentration 48.9 (mg/l)*