Research Article

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Application of red-sand/chitosan hybrid filtration system for phosphate removal from agricultural wastewater

Abstract

Point sources of phosphate used in this study were from a livestock transport truckwash station, and a vegetable wash operation. Two types of red sand/chitosan hybrid filtration systems were used:

a. wastewater from settling ponds were introduced to a red sand (actual term) bed (10ft x 20ft x 3ft) and water percolating to the surface of red sand was introduced to iron-chitosan filtration unit.

b. Second filtration setup consisted of two 55 gallon (208 litres) the first containing ~18L of red-sand and the eluate from which entered a second barrel containing iron-chitosan (3kg) suspension. With the red sand bed-chitosan system, the red sand component lowered phosphate levels from ~19µg/ml (inflow from pond) by 6 fold (~3µg/ml). The chitosan filter unit further reduced it to ~0.04 to 1.5µg/ml with flow rates of ~3.5L/min. At the vegetable wash station, a variant of the system setup that utilized double barrel hybrid filtration system was used. In this application, the pre-filter attenuated soluble phosphate levels from ~14µg/ml (inflow from washes) by ~30 fold (~0.5µg/ml) and the chitosan filter unit reduced it further ~0.2–0.4µg/ml with flow rates ~3.5L/min for every wash cycle. The red-sand/chitosan hybrid system presents a portable and cost effective means for reducing suspended solids and soluble phosphates from agricultural wastewater effluents. This system also provides a potential solution for recycling unused phosphates.

Keywords: chitosan, red sand, filtration, wastewater, phosphates, ion exchange

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Introduction

The accumulation of phosphates and nitrates in wastewater derived from various sources including, agricultural processes and livestock farming, is eventually discharged into oceans, lakes and rivers. A most common reason for this is usually due to a lack of infrastructure or cost aversion. This leads to algal blooms, and eventually to eutrophication, adversely affecting water quality and eco-systems.

In recent years, several techniques have been employed for the treatment of phosphates which includes chemical precipitation, biological treatment, as well as ion exchange.[1–7] The currently employed techniques are very effective at attenuating phosphates from wastewater effluents however, they require a significant investment of capital and space.[8,9] Constructing wetlands[10] and reed beds[11] were some alternative techniques employed for the treatment of phosphates which are relatively cheaper, when it is compared to conventional strategies. Ion exchange is an alternative option for wastewater treatment due its capacity to sorb ions of interest which can be desorbed at a later stage for applications in other aspects such as manure production.[12] Common ion exchangers include zeolites[13] and synthetic polymers[14] that contain modified functional groups to remove positively or negatively charged ions depending on the nature of the functional group. Chitosan, a biopolymer obtained by the deacetylation of chitin. It has applications in ion exchange due to its ability to selectively sorb transition metal ions.[15] Chitosan is structurally similar to cellulose except that it has primary amines present at the C-2 position.[16] This hetero-polymer's amines and

hydroxyl groups present on the polymer participate in the formation of dative bonds with transition metal ions.[16–19] Chitosan had mostly been used as a coagulant in wastewater treatment applications however, metal-complexed chitosan has been shown to act as an ion exchange medium for anionic contaminants like phosphates, and research on its application in wastewater treatment is currently underway.[20–22] Sand based filtration systems have been used for the tertiary treatment of water[23] and are usually used to remove organic matter and suspended solids from influent wastewater streams. This type filtration system has also been used in conjunction with UV irradiation in order to treat wastewater effluents to produce potable water.[24] Red sand is a mixture of sand and red sandstone which is rich in hydrated iron oxide which is responsible for its red color. It is commonly found in areas containing red sandstone.

The present study is aimed at studying the effectiveness of a hybrid sand/chitosan filtration system for treating wastewater from agricultural sources that is focused on attenuating soluble phosphate content as well as suspended solids in the filtrate.

Materials and methods

Ascorbic acid (Sigma), Ammonium molybdate tetrahydrate (Sigma), Chitosan flakes (Dungeness environmental), Dipotassium phosphate (Fisher Scientific), Iron-complexed chitosan flakes (Chemfil Canada Ltd), Malachite Green Carbinol hydrochloride (Sigma), Iron (II) sulfate (Sigma), Polyvinyl alcohol (Sigma), Red sand (Hutcheson Sand & Gravel), Sulfuric acid (Sigma), Whatman filter paper (Fisher).

Preparation of iron-complexed chitosan flakes

Chitosan (DOD% 85) was mixed with 0.1M iron sulfate solution. The flakes were mixed at 350rpm in the iron sulfate solution incubated for 3 hours after which, the flakes, were washed with distilled H$_2$O, three times,10X chitosan volume, were dried in an oven at 50°C for 3 hours.

Study sites and experimental design

Filtration apparatus was tested at livestock transport truckwash station located in Sebringville, Ontario and a vegetable wash station located in Ansnorveldt, Ontario. Locations were chosen by local conservation authorities based on the urgency for phosphate treatment as both sites exhibited a high concentration of phosphate and suspended solids content.

Sampling

Wastewater samples were dependent on the wash cycles at both locations. The "initial" readings were taken during the beginning of every wash cycle. Wastewater was grab sampled from the artificial wetlands constructed at both sites as well as from the post treatment effluent at 8 hour intervals over 3 weeks. The samples (50mL) were then acidified with sulfuric acid and stored in polyethylene bottles, which were transported in iced cooler boxes. Samples were analyzed within 24 hours of collection.

Chemical methods

i. Water samples were analyzed using standard methods. Colorimetric techniques were used to determine total phosphate content (molybdenum blue method & malachite green phosphate assay). Total suspended solids were quantified by weighing the dry weight of particles trapped after filtration (Whatman filter paper).

ii. Red sand samples were homogenized using mortar and pestle. The samples were then loaded into the XRD machine (Rigaku Miniflex+). The X-ray tube used is a Copper-Kα tube with a wavelength of 1.541Å. The tube voltage is 30kV and the tube current is 15mA. The samples are analyzed at a rate of 1 degree/minute with a sampling rate of every 0.1 degree.
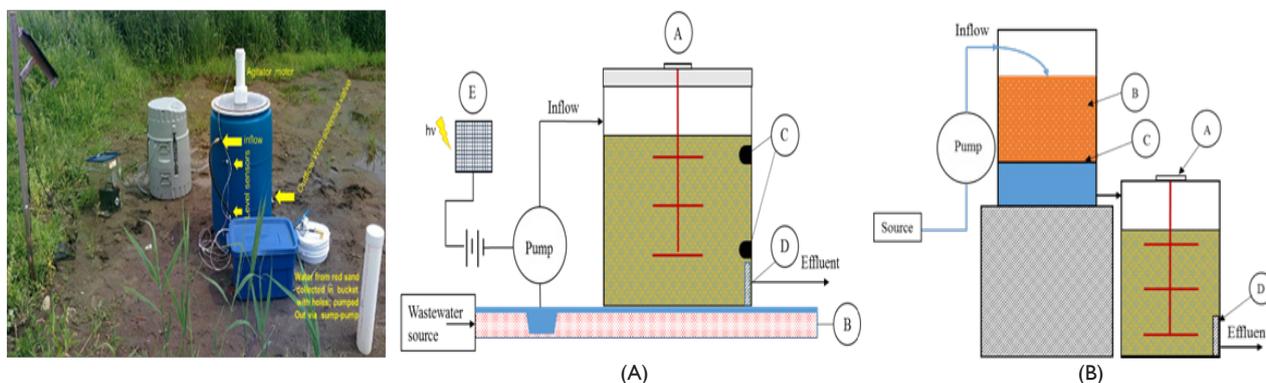

Figure 1 A) Schematics for the new chitosan filter unit prototype setup are similar to that of a continuous stirred tank reactor (CSTR). The unit is equipped with a motor attached to a 3 ft. paint mixer (A) with paddles 8.5cm wide. The water source was passively passed through (B) red sand. A well was manually dug out in order to make a crude well and with the help of a pump, the water was drawn into the reactor. The water level was controlled with the help of solenoid sensors and valves(C). The filtration unit's electronics were connected to portable process control system (PCS) which controlled the pump as well as the solenoid valves for intake of wastewater and release of treated effluent. The filter unit was used a 55 gallon water storage barrel equipped with a 0.5mm mesh filter (D) that would prevents the iron chitosan from leaving the filtration unit. Filtration unit was powered by a 12 V battery power source and was recharged using a solar panel (E).

B) Second filtration unit was designed to allow the post-sand filtrate to gravitationally enter the chitosan filter unit. The wastewater is pumped with the help of a sump-pump into pre-filter unit containing red sand (B), the sand is separated from the filtrate by a fine metallic mesh (C). The post-sand filtrate is then transferred to the chitosan filter unit where it is stirred continuously with the help of a motorized stirrer (A) and the effluent is passed through a metallic mesh (D).

Results and discussion

Phosphate desorption studies for iron-complexed chitosan and red sand

Saturating chitosan flakes with metals significantly improved its phosphate sorption capacity. In these field tests, chitosan was saturated with iron and its phosphate binding capacity based on desorption studies are shown in Table 1. In addition to this, it was observed Table 1 that red sand was not a very effective adsorbent for phosphates. The adsorption of phosphates could be due to the presence of aluminosilicates in the mixture, which are usually the main components of zeolite matrices.

Truckwash station

The hybrid red-sand/chitosan filtration system was first applied at this site, and during the sampling periods May–July 2015, the filtration system had demonstrated its effectiveness in attenuating a significant amount of phosphates from the truck wash effluents shown in Figure 2A & 2B. The pre-filter, red sand effectively removed ~99% of TSS from wastewater in the effluent as shown in Figure 5 and along with reducing the soluble phosphates from the settling pond by about 6–30 fold (~500µg/L) prior to the introduction into the chitosan filtration unit. This suggested that the red sand pre-filter was either adsorbing or precipitating all the soluble phosphates after the effluent had passed through it. Subsequently, the chitosan filtration unit was able to lower it further to ~200µg/L.

Vegetable wash station

The hybrid filtration system was used to treat a similar type of wastewater at this site. This site introduced the sloughs of sediment

and organic matter from the vegetable wash effluents after every vegetable wash into the waste streams. A similar trend was noticed when compared to the results observed at the truck wash station during the sampling periods of October to November 2014 Figure 3 and April to May 2015 Figure 4, where the wastewater source was high in phosphate content and after it allowed to flow through red sand, sediment-free wastewater was subsequently introduced into the chitosan filtration unit where there was a further reduction in the phosphate concentration. The gravity filtration of the wash effluents was able to reduce phosphate in wash effluents from ~14μg/mL to ~1 to 2μg/mL after passing through red sand as shown in Figure 3A & 4A. The chitosan filter unit connected in tandem, further lowered phosphate levels to ~ 0.5μg/mL.

Table 1 Comparison of chitosan flakes with iron chitosan flakes and 'red sand' indicates the adsorption capacity of iron-complexed chitosan is higher than the other filters are being used for water treatment. All experiments were performed in triplicates and values are the average concentration of phosphate from 3 separate experiments. The error bars represent standard error (n=3)

Filter	Phosphate recovered (mM)	Phosphates recovered (mg PO_4^{3-} /g Chitosan)
Native chitosan flakes	5.59±0.57	10.84±1.07
Iron-complexed chitosan flakes	8.79±0.23	17.05±0.44
Red sand	0.11±0.01	0.28±0.02

At both sites, it was observed that the red sand pre-filter had removed almost all suspended solid content and the result was reflected in the sharp decrease in soluble phosphates in the effluent samples. The particulate size of the filter made it ideal for the separation of suspended solids from the influent wastewater stream. This sharp decrease in phosphate concentration was most likely due to the filtration of soil-bound phosphates by red sand as the effluent stream passed through it.[25,26] In addition to this, an attempt to regenerant the spent red sand, regeneration studies were performed with 1M ammonium acetate and 1M sodium chloride. These results, as shown in Table 2 suggest that red sand had also contributed to the adsorption of soluble phosphates from the influent wastewater. However, the amount adsorbed suggests it cannot be used for ion exchange applications for phosphate contaminated wastewater. A similar setup has been used in other studies where sand was used for a similar purpose and was very effective in removing phosphorous[10] however, the additional chitosan filtration unit connected in sequence with the red-sand filter makes it possible to adsorb soluble phosphates in the effluents. The result would ensure that the water quality meets the standards for the region (PWQO Ontario).

Chemical composition of red sand (pXRD data)

The composition of the sand would give an insight on the processes that make red sand such a potent phosphate adsorbent. Upon analysis by XRD, the sand being used was comprised of various minerals and the peaks of interest matched closely with lithium aluminosilicate with an FOM of 0.83,[27] and other minerals such as $CsCu_2I_3$[28] and Tin (II) pyrophosphate.[29] This investigation suggested that adsorption played a small role in the removal of phosphates. In addition to this,

the mixture did not contain any iron salts and so, it must be removing phosphates using a different process when compared to iron-chitosan flakes.
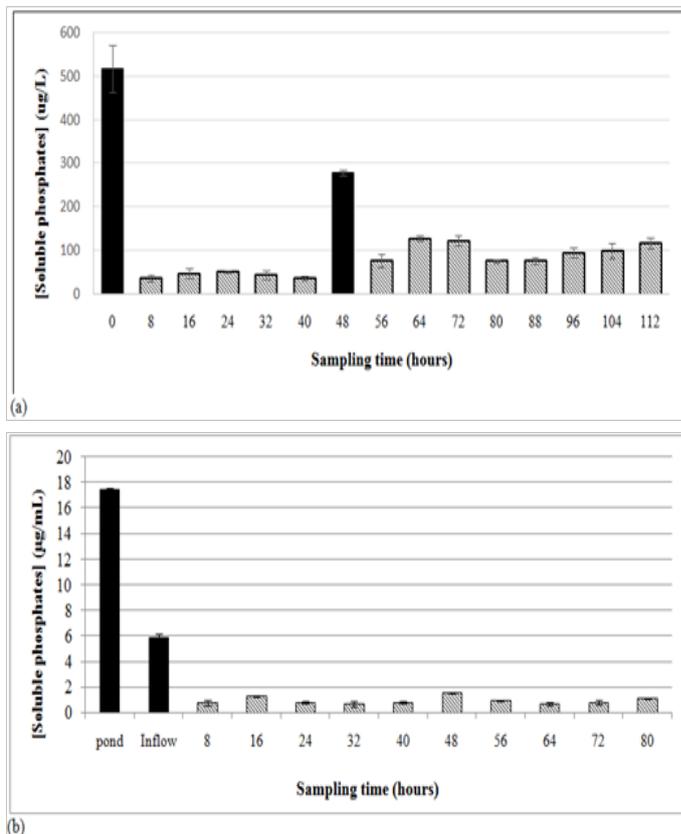

Figure 2 Phosphate concentration for samples (50ml) that were taken from the settling pond were drastically lower in value compared to post-red sand effluents. The "pond" indicates the average soluble phosphate concentration from the wastewater source and "inflow" indicates the soluble phosphate concentration of post-red sand effluents. The "patched" columns represents the average phosphate concentration of post-chitosan filter effluents. The black sample bars at times t = 0,48 hours indicate the post-red sand effluents from fresh input of wastewater. The sampling for A) was conducted during the period of June 2015-July 2015 and B) during the months of May and June 2015. All values were average phosphate concentration of 3 separate sampling events. The error bars represent standard error (n=3).

Regenerative studies of red sand

The results from the treatment of red sand with regenerant solution suggested that red sand adsorbed a small amount of soluble phosphates when compared to iron-chitosan flakes. The average soluble phosphates recovered from in the spent regeneration solution are shown in Table 2.

Table 2 Red sand (55kg) was treated with regeneration solution (500ml) (1M ammonium acetate or 1M sodium chloride). All values represented here were average phosphate concentration of 3 separate sampling events. The error bars represent standard error (n=3)

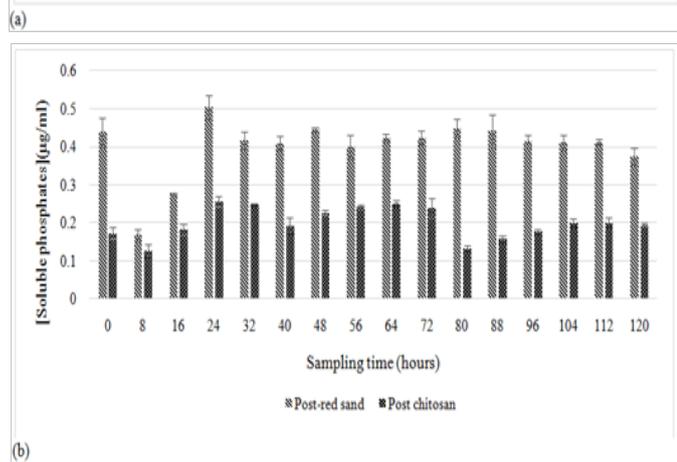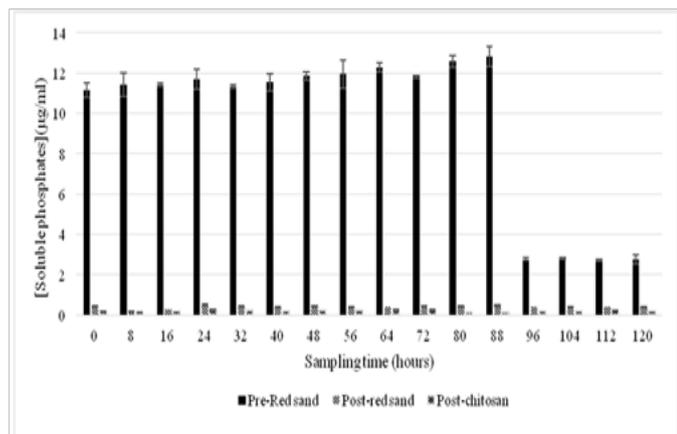| Regenerant	Phosphates recovered (μg/ml)
NaCl	4.51±0.03
CH_3COONH_4	3.56±0.02

(a)

(a)

(b)

(b)

Figure 3 Hybrid filtration system was used to treat vegetable wash effluents during the sampling period of May 2016 –June 2016. The phosphate concentration the wastewater samples (50ml) gathered from the source of wastewater (initial/pre-red sand), after pre-treatment with red sand (post-red sand) and after passing through chitosan filter (post-chitosan), respectively. A) The pre-red sand samples exhibited high phosphate levels and underwent a drastic decrease after passing through the red-sand. The graph shown in B) are the phosphate values in the post-red sand and post-chitosan samples that were analyzed by malachite green phosphate assay showing the efficacy of the hybrid system in removing phosphate from agricultural wastewater effluents. All values represented here were average phosphate concentration of 3 separate sampling events. The error bars represent standard error (n=3).
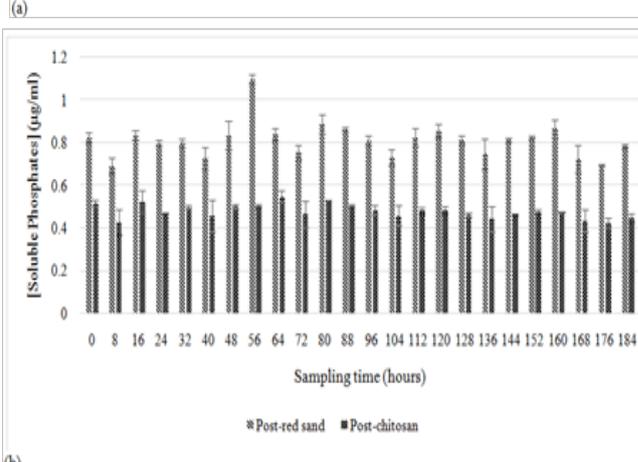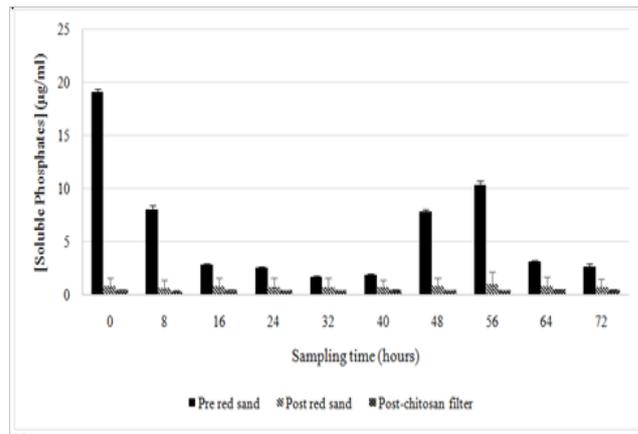
Figure 4 Hybrid filtration system was used to treat vegetable wash wastewater during the sampling period of May 2016–June 2016. As shown in figure A), the solid black bars, the dashed bars and dotted bars represent the phosphate concentrations in the wastewater samples (50ml) gathered from the source of wastewater (initial/pre-red sand), after pre-treatment with red sand (post-red sand) and after passing through chitosan filter (post-chitosan), respectively. The graph shown in B) indicate phosphate values in the post-red sand and post-chitosan samples that were analyzed by malachite green phosphate assay. All values represented here were average phosphate concentration of 3 separate sampling events. The error bars represent standard error (n=3).

(A)
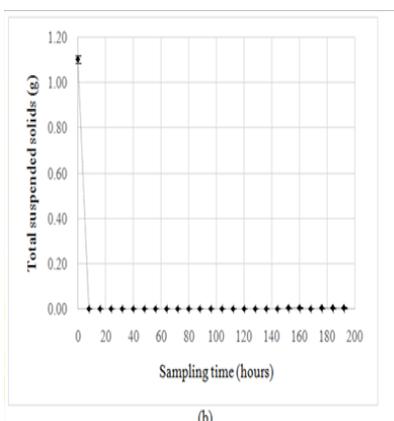
(B)

Figure 5 A) From left to right: Wastewater samples from the vegetable wash station (Pre-red sand effluent), after passing through red sand (Post-red sand) and the chitosan treated effluent (Post-chitosan filter). Similar results were noted at the truckwash station. Suspended solids in the wastewater is greatly reduced after it passes through red sand. B) TSS measurements for samples (5ml) acquired during the sampling period of May 2016–June 2016. TSS at time t = 0 hours represents the average TSS in wastewater samples before treatment of red sand at both sites. All values represented here were average phosphate concentration of 3 separate sampling events. The error bars represent standard error (n=3).
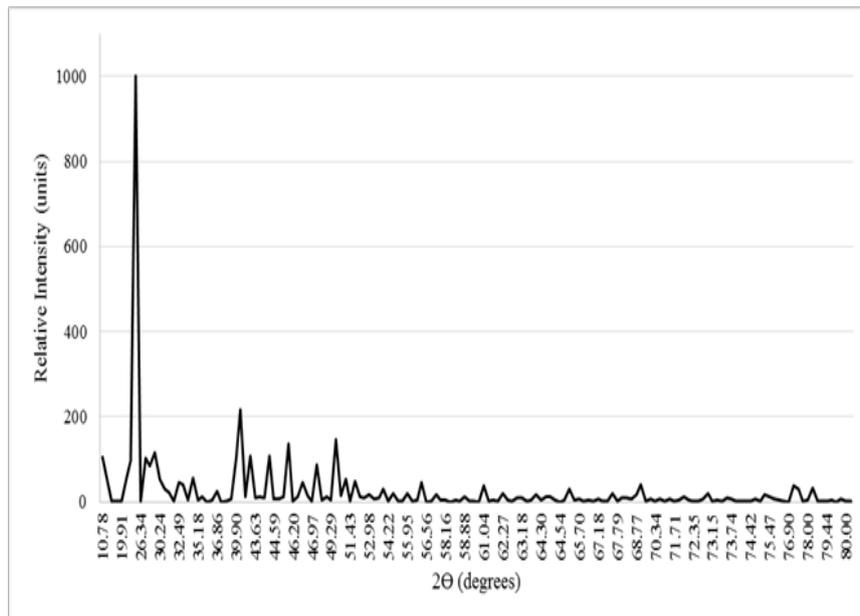
Figure 6: Red sand pXRD spectrum analyzed with the help of a Cu-Kα lamp (λ=1.54 Å) at a tube current of 15mA and voltage of 30kV. The major peaks match closely to Lithium aluminosilicate (LiAlSiO$_4$), Copper iodide salt with traces of Cesium (CsCu$_2$I$_3$) and phosphate salts such as tin (II) pyrophosphate (Sn$_2$P$_2$O$_7$). Spectrum analysis was provided courtesy of Melissa Price from Earth Sciences department, University of Windsor.

Conclusion

The hybrid red-sand/chitosan filtration system is a cost effective method to treat agricultural wastewater containing high TSS and phosphate content. The TSS content can be removed from the pre-filter unit and be reused for agricultural purposes as it will still contain high concentration of soil bound phosphates. Spent chitosan can be treated with ammonium acetate to elute the bound phosphates from the column and by precipitating it as struvite, it has a potential application in fertilizer production.

Acknowledgements

Conflict of interest

The author declares no conflict of interest.

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