



Mitigation of eutrophication through phosphate removal by aluminium pillared bentonite from aquaculture discharge water

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ABSTRACT

Deterioration of aquatic ecosystem by accumulation of nutrients has increased due to anthropogenic activities, and adsorption is one of the efficient methods for removal of phosphate from discharge water. The present study investigated the efficiency of aluminum pillared bentonite in removing phosphate from aquaculture discharge water with high salinity. Adsorption capacity of pillared bentonite increased with increasing temperature from 11.85 (25 °C) to 13.81 (35 °C) and 15.85 (45 °C) mg/g. At 30 ppt salinity, there was 57.7% reduction in phosphate sorption capacity of the pillared bentonite from 0 ppt. The kinetic studies revealed that adsorption followed the pseudo second-order model. The free energy change of the phosphorous sorption by pillared bentonite was -4.19 , -5.87 and -6.24 kJ mol⁻¹ at 25 °C, 35 °C and 45 °C, respectively. The pillared bentonite reduced the phosphate level by 85.3–99.6% from eutrophic waters of shrimp farm, fish larval rearing tanks, algal culture system, discharge water treatment system, etc. The study revealed that aluminum pillared bentonite is efficient in reducing the phosphate level of aquaculture discharge water, and it could be used for the treatment of aquaculture discharge water before releasing into the environment.

1. Introduction

Eutrophication by nutrient enrichment is one of the most important water quality problems in marine ecosystems (Smith, 2003; Anshah et al., 2013). Even though phosphate is an essential nutrient for phytoplankton growth, its excess amount may result in plankton crash and water quality deterioration. Intensified aquaculture practices resulted in phosphate content in excess of prescribed limit and led to environmental degradation by eutrophication of water bodies (Cai et al., 2013; Luring et al., 2016). Aquaculture discharge water from Indian sub-continent are characterised by low nutrient load due to extensive farming practices (Muralidhar and Gupta, 2007; Vass et al., 2015; Priyadarsani and Abraham, 2016; Saraswathy et al., 2019). Existing aquaculture Discharge Water Treatment System (DWTS) in shrimp farms is effective in reducing the suspended solids only, but not the nutrients. Similar trend of eutrophication by excess release of phosphate may happen in India if the aquaculture becomes more intensive. Eutrophication may be manifested by the drivers of climate change such as temperature and rainfall, etc. To avoid the environmental degradation by excess phosphate, effective methods are needed to reduce the phosphate level of discharge water from aquaculture ponds (Boyd, 2003; Carpenter, 2008; Copetti et al., 2016).

Even low level of inorganic contaminants from the aqueous system

could be removed by the adsorption mechanism (Kumararaja and Manjaiah, 2014; Liu et al., 2017; Kumararaja et al., 2018). Phosphate has been successively removed from aqueous system with a number of adsorbents such as polymeric hydrogels, limestone, iron oxide, chitosan, (Kioussis et al., 1999; Chuang et al., 2006; Mortula et al., 2007). Clay minerals are the most commonly tested adsorbents for environmental remediation because of their higher adsorption capacity by virtue of its large specific surface area (Kumararaja et al., 2014). To enhance the anion adsorption capacity, clay minerals have been subjected to array of treatments (Tian et al., 2009; Zamparas et al., 2012; Moharami and Jalali, 2015; Ma et al., 2016). Pillaring with polyhydroxy aluminium is more effective due to the affinity of phosphate anion to the aluminium, improved surface area and porosity (Yan et al., 2010; Shanableh and Elsgany, 2013; Pawar et al., 2016; Kumararaja et al., 2017). Application of zeolite enhanced the production of *Onchorynchus Mykiss* by improving the water quality (Obradovic et al., 2006; Danabas and Altun, 2011). So far, the studies of phosphate sorption by pillared bentonite have been reported with discharge water of negligible salinity. Brackish water aquaculture discharge water is enriched with competing anions such as chlorides, carbonates and bicarbonates with. With the objective of reducing phosphate from high saline aquaculture discharge water, polyhydroxy aluminium pillared bentonite was evaluated as an adsorbent.

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2. Materials and reagents

2.1. Materials

By sedimentation procedure clay sized particles were obtained from bentonite supplied by Minerals Ltd, New Delhi. Analytical grade reagents were supplied by Sisco Research Laboratories Ltd (SRL), India. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and KH_2PO_4 were used without any further purification for the preparation of pillaring solution and phosphate stock solution, respectively. The eutrophic water samples were collected from Algal culture unit, larval rearing tanks of finfish hatchery, Discharge Water Treatment System (DWTS), Muttukkadu Experimental Station of Central Institute of Brackishwater Aquaculture (CIBA), Chennai, India, Muttukkadu estuary and low saline water from Shrimp farm in Nagapattinam, India. For field scale evaluation, pillared bentonite was applied to DWTS of Muttukkadu experimental station and phosphate concentration was measured at different time interval. The water samples were analysed for its chemical parameters by APHA, 2012.

2.2. Synthesis of pillared bentonite

Sodium hydroxide solution (0.2M) was added to the 0.2M aluminium chloride solution and kept in a magnetic stirrer to prepare poly-hydroxy aluminium pillaring solution with an OH/Al ratio of 2. Sodium saturated bentonite suspension (10% w/v) was equilibrated with the pillaring solution by delivering at a rate of 3–4 mL min⁻¹ under continuous stirring. Excess precipitate of the mixture was removed by washing with distilled water, dried at 80°C for 24 h and calcined at 300°C for 4 h. The dried product was grounded and kept in a desiccator (Kumararaja et al., 2017).

2.3. Characterisation of pillared bentonite

Calcium magnesium exchange method and ethylene glycol monoethyl ether (EGME) saturation method was employed to obtain cation exchange capacity and surface area of the pillared bentonite, respectively. Point of zero charge was determined by potentiometric titration method. To 1 g clay sample, 50 ml of sodium chloride differing ionic strength of (1, 0.1, 0.01M) was added separately and the pH of the suspension was measured. After each increment of 0.5 ml 0.1N HCl addition, pH was measured and continued till the three curves meet at a point which is the point of zero charge.

2.4. Phosphate adsorption

The adsorption study was conducted by batch method and the variables were pH (4–10), adsorbent dose (0.05, 0.1, 0.25, 0.5, 1 and 2 g), contact time (5, 10, 15, 30, 45 min, 1, 2, 3, 4, 5, 6, 12, 18 and 24 h), initial concentration (5, 10, 20, 30, 40, 50 and 100 ppm), temperature (25, 35, 45 °C) and salinity (0, 10, 20 and 30 ppt). In batch experiments, phosphate solution (100 ml) was equilibrated with the pillared bentonite (0.25 g) for 24 h. The clear filtrate was obtained by centrifugation at 8000 rpm for 15 min and phosphate was estimated by molybdenum blue color method of APHA, 2012 using UV/Vis spectrophotometer (SHIMADZU) at 880 nm.

The amount of phosphate adsorbed (mg/g) was calculated using mass balance equation: Eq. (1):

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where $C_0 - C_e$ are the initial and equilibrium concentrations (mg/L) of phosphate, respectively; V is the volume of the solution (L) and m is the mass (g) of pillared bentonite, Q_e is the amount of phosphate adsorbed per g of pillared bentonite (mg/g).

The removal efficiency of the pillared bentonite (%) was calculated by following equation:

$$\text{Removal Efficiency (\%)} = \frac{C_0 - C_e}{C_0} * 100 \quad (2)$$

2.5. Adsorption isotherms

To elucidate the mechanism of adsorption, the experimental data were fitted with common isotherm models (Langmuir, Freundlich and Dubinin-Radushkevich isotherms). The linear form of Langmuir equation given as Eq. 3

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot q_m} + \frac{C_e}{q_m} \quad (3)$$

The Freundlich isotherm describes the multilayer adsorption on the heterogeneous surface and linearized form is expressed as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

Dubinin-Radushkevich isotherm was applied to distinguish the physical and chemical adsorption process. The index of adsorption energy E is obtained from the parameters of linearized Dubinin-Radushkevich isotherm (Eqn (4) and Eqn 5

$$\ln q_e = \ln q_D - B_D \varepsilon^2 \quad (5)$$

where q_e is the amounts of phosphate adsorbed (mg g⁻¹) at equilibrium, B_D is isotherm constant.

$$E = \frac{1}{2B_D^{0.5}} \quad (6)$$

Value of E less than 1 to 8 kJ mol⁻¹ corresponds to the Physical while 8 to 16 kJ mol⁻¹ corresponds to chemisorption.

2.6. Adsorption kinetics

The most commonly kinetic models (pseudo-first order and second order models) were applied to the data to understand the phosphate adsorption process to the pillared bentonite. The linear forms are given in Eqs (6) and (7), respectively.

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (7)$$

$$\frac{t}{q_e} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

Slope of straight-line plot of $\ln(q_e - q_t)$ versus t gives pseudo-first order constant and intercept of the plot between t/q_t and time t gives the second-order rate constant (k_2).

2.7. Adsorption thermodynamics

Adsorption thermodynamic parameters such as changes in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were calculated from the following equations

$$\Delta G^0 = -RT \ln K_c \quad (9)$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (10)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (11)$$

where R is universal gas constant (8.3144 Jmol⁻¹K⁻¹), T is absolute temperature in Kelvin (K) and K_c is the thermodynamic equilibrium constant.

3. Results and discussion

3.1. Characterisation of pillared bentonite

The point of zero charge of pillared bentonite was 6.81 (Fig. 1).

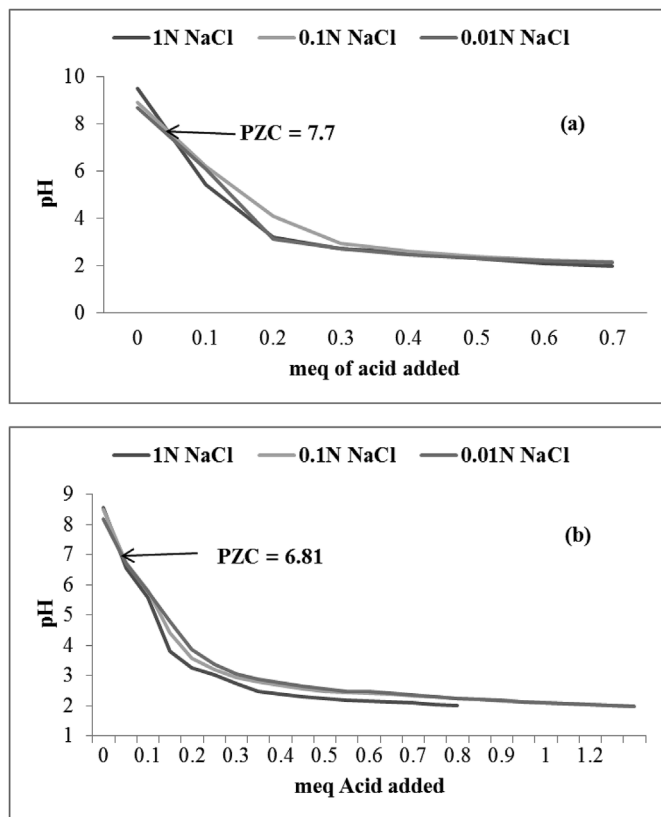


Fig. 1. Potentiometric titration curve showing the point of zero charge (PZC) of bentonite (a) and aluminium pillared bentonite (b).

Pillaring of bentonite with polyhydroxy aluminium shifted the point of zero charge towards acidic pH and the value is in good agreement with the previous reports (Avena et al., 1990; Mrad et al., 1997; Arfaoui et al., 2012; El Miz et al., 2014). Occupation of sorption sites by pillaring ions resulted in reduction of cation exchange capacity of the bentonite from 83.3 to 45.4 cmol (p^+) kg^{-1} . The specific surface area of the bentonite increased from 399 to 678 $m^2 g^{-1}$ upon pillaring due to increased interlayer spacing (Klopprogge et al., 2002; Zeng et al., 2013; Kumararaja and Manjaiah, 2015; Kumararaja et al., 2017).

3.2. Effect of pH

Solution pH is one of the important factor influences the phosphate adsorption process by affecting the speciation and surface charge of the clay. Phosphate adsorption capacity of pillared bentonite decreased with increasing pH (Fig. 2). The reduction in sorption at higher pH could be due to domination of highly negative species PO_4^{3-} , development of negative charges on the clay surface by deprotonation resulting in electrostatic repulsion between phosphate anion and negatively charged clay surface (Ma and Zhu, 2006; Tian et al., 2009; He et al., 2017). Enhanced competition between the hydroxyl (OH^-) and phosphate ions at higher pH also reduces the adsorption (Karimaian et al., 2013). At acidic pH protonation and release of Al from clay surface enhances sorption (Kasama et al., 2004; Guaya et al., 2015; Shanableh et al., 2016; Xie et al., 2015).

3.3. Effect of adsorbent dose

The effect of pillared bentonite dose on percentage removal and amount of phosphate adsorbed was studied. The phosphate removal percentage increased from 39.6 to 99.4 with the increasing dose from 0.5 to 20 $g L^{-1}$ (Fig. 3). Amount of phosphate adsorbed ($mg g^{-1}$) decreased with increasing dose from 9.9 to 0.61. Increased total available

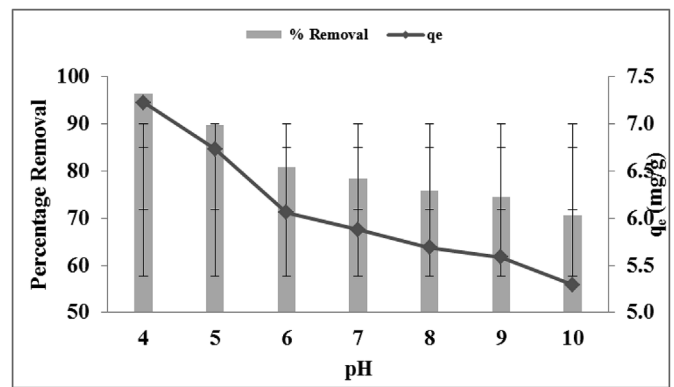


Fig. 2. Effect of pH on percentage removal and amount of phosphate adsorbed (mg/g) by aluminium pillared bentonite.

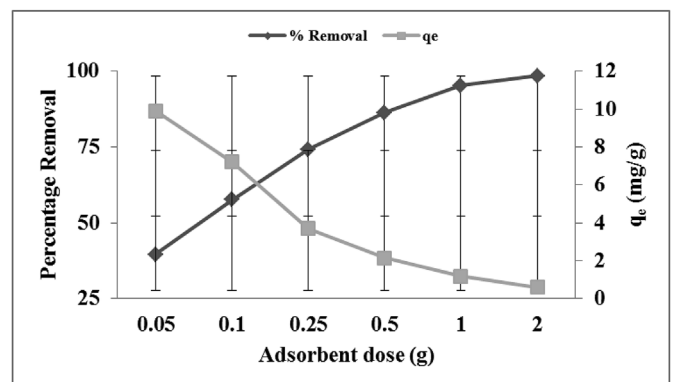


Fig. 3. Effect of adsorbent dose on percentage removal and amount of phosphate adsorbed (mg/g) by aluminium pillared bentonite.

surface area of pillared bentonite at higher dose resulted in enhanced removal percentage. The decrease in sorption capacity with increasing dose is attributed to limited availability of phosphate anion and with the increasing amount of unoccupied adsorption sites (Rahni et al., 2014; Ma et al., 2016).

3.4. Effect of salinity

The influence of salinity on phosphate adsorption by pillared clay was studied at 0, 10, 20 and 30 ppt salinities. As the results indicate (Fig. 4), the phosphate sorption capacity of the pillared bentonite decreased with increasing salinity. The q_e ($mg g^{-1}$) decreased from 11.85 at 0 ppt to 8.21, 6.26 and 5.01 at 10, 20 and 30 ppt, respectively (Table 1). The reduction in adsorption with salinity may arise from competition for the adsorption sites from the competing anions (CO_3^{2-} and HCO_3^-) (Huang et al., 2014; Guaya et al., 2015; Liu et al., 2016; He et al., 2017; Mitrogiannis et al., 2017). Neutralization of zeta potential by divalent cations (Ca^{2+} and Mg^{2+}) in high alkalinity might have resulted in less dispersion of pillared bentonite in water and less phosphate sorption (Zhu et al., 2009; Zamparas et al., 2013; Reitzel et al., 2013; Wang and Li, 2016).

3.5. Adsorption isotherm

Amount of phosphate adsorbed per unit amount of pillared bentonite increased with increasing initial phosphate concentration (Fig. 5). The amount adsorbed increased from 1.72 to 11.1 $mg g^{-1}$ with increasing initial concentration of 5–100 mg/L and this is attributed due to the increment in driving force to overcome the mass transfer resistance between the phosphate and clay surface at higher concentration (Ma et al., 2012; Zamparas et al., 2013; Pawar et al., 2016; Wang

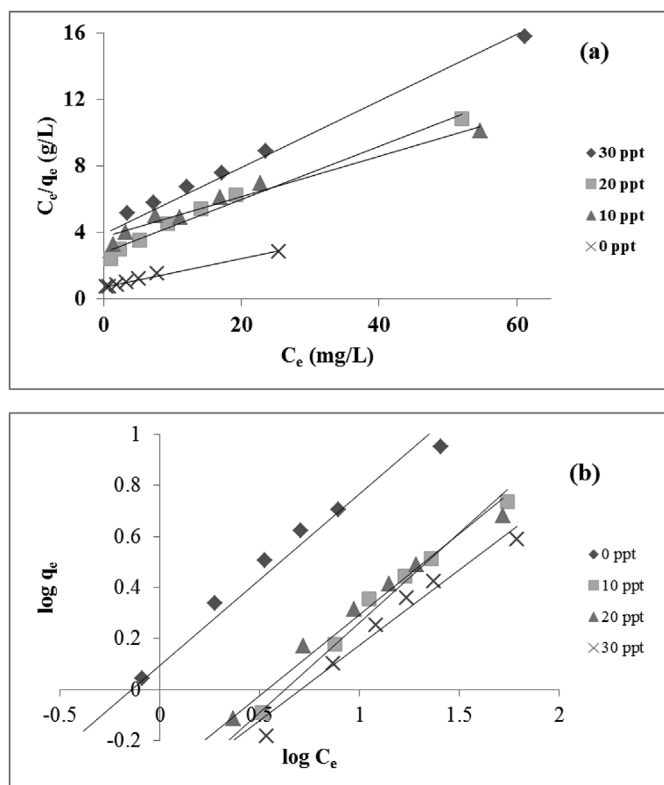


Fig. 4. The adsorption of P onto aluminium pillared bentonite at different salinity; the fitting of isotherm data of P sorption onto pillared bentonite using (a) Langmuir and (b) Freundlich isotherm models.

and Li, 2016). The Langmuir isotherm ($R^2 = 0.99$) fitted the phosphate sorption data better than Freundlich ($R^2 = 0.925$) and D-R ($R^2 = 0.895$) isotherms indicating the monolayer sorption of phosphate onto pillared bentonite (Table 1). The Langmuir dimensionless factor (R_L) value is less than unity which indicates favourable sorption of phosphate. Similar results of Langmuir isotherm fitted the phosphate sorption data better than other isotherms (Huang et al., 2014; Kumararaja et al., 2016; Mitrogiannis et al., 2017). The Freundlich constant $1/n$ value lies between 0 and 1 (0.28) indicating the favourable adsorption of phosphate by pillared bentonite under the studied condition. The D-R isotherm determines the nature of adsorption process (chemical or physical) based on the sorption energy, E . The sorption energy (9.72 kJ mol^{-1}) indicates the mechanism of phosphate sorption onto pillared bentonite is chemisorption and ligand exchange are the major mechanism. The ligand exchange mechanism of phosphate sorption is depicted below (Altunlu and Yapar, 2007; Shanableh et al., 2016; Cui et al., 2016). Phosphate replaces the present in the pillared bentonite. First phosphate is transferred to the site and ion exchange $-\text{OH}$ at the active site. After the adsorption process the

Table 1

Effect of salinity and temperature on parameters of Langmuir and Freundlich isotherm for phosphate adsorption onto pillared bentonite.

Model	Parameter	Salinity (ppt)				Temperature ($^{\circ}\text{C}$)			
		0	10	20	30	25	35	45	
Langmuir	q_m (mg g^{-1})	11.85	8.21	6.26	5.01	11.85	13.81	15.85	
	K_L (L mg^{-1})	0.11	0.03	0.09	0.13	0.11	0.47	0.18	
	R^2	0.990	0.907	0.885	0.967	0.99	0.998	0.973	
Freundlich	K_L (L g^{-1})	2.77	2.6	2.19	1.24	2.77	2.19	4.93	
	$1/n$	0.28	0.64	0.67	0.7	0.28	0.33	0.54	
	R^2	0.925	0.887	0.873	0.824	0.925	0.955	0.960	

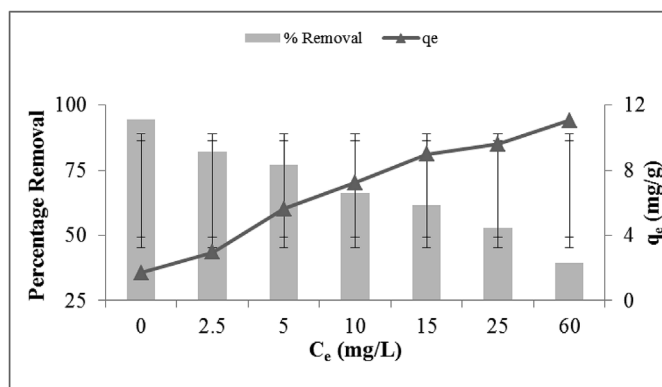


Fig. 5. Effect of initial concentration on percentage removal and amount of phosphate adsorbed (mg g^{-1}) by aluminium pillared bentonite.

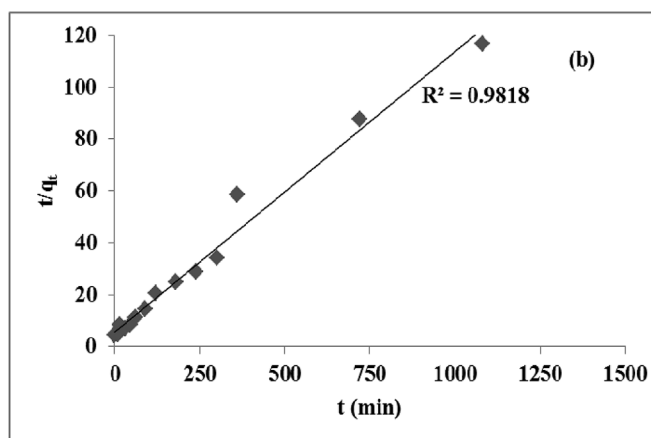
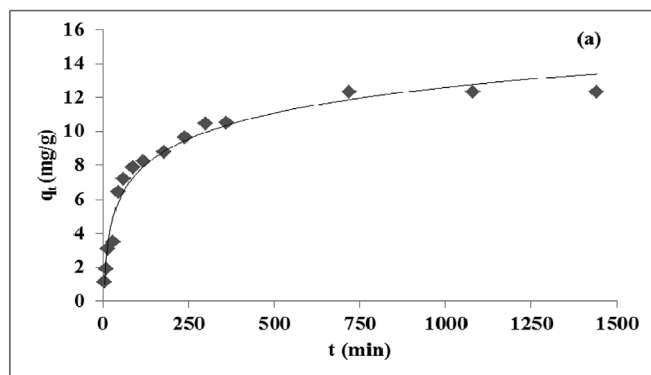


Fig. 6. Effect of contact time on phosphate uptake by aluminium pillared bentonite (a). The fitting of kinetic data using (b) pseudo-second order model.

Table 2
Pseudo-first and pseudo-second order kinetic parameters of phosphate adsorption onto pillared bentonite.

Pseudo-first order		Pseudo-second order	
q_e (mg g ⁻¹)	10.26	q_e (mg g ⁻¹)	9.34
K_1 (h ⁻¹)	0.41	K_2 (g mg ⁻¹ h ⁻¹)	0.14
R^2	0.961	R^2	0.982

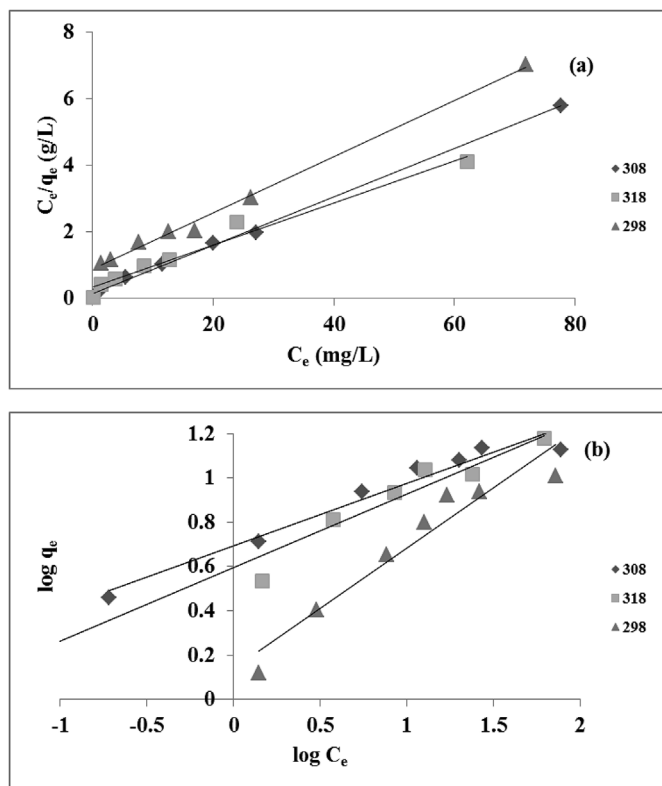


Fig. 7. The adsorption amounts of P onto aluminium pillared bentonite at different temperature; the fitting of isotherm data of P sorption onto pillared bentonite using (a) Langmuir and (b) Freundlich isotherm models.

Table 3
Thermodynamic parameters of phosphate adsorption onto pillared bentonite.

Temperature (°C)	K_L (L mg ⁻¹)	ΔG^0 (KJ mol ⁻¹)	ΔH^0 (KJ mol ⁻¹)	ΔS^0 (KJ mol ⁻¹ K ⁻¹)
25	0.11	-4.19	24.71	0.97
35	0.28	-5.87		
45	0.47	-6.24		

Table 4
Water quality parameters of natural eutrophic water.

Sample ID	Salinity (ppt)	pH	Phosphate (ppm)	Carbonate (ppm)	Bicarbonate (ppm)	Total Alkalinity (ppm as CaCO ₃)	Calcium (ppm)	Magnesium (ppm)	Total Hardness (ppm as CaCO ₃)
1	29	8.23	0.165	42	100	153	243	1156	5445
2	30	7.48	0.2097	27	139	160	86	569	2554
3	25	7.51	0.1689	12	126	123	283	921	4545
4	30	7.34	0.386	27	116	141	119	1048	4606
5	20	7.85	1.122	14	134	133	357	1132	5544
6	31	7.92	0.295	35	143	176	619	6489	1202
7	1	8.05	1.231	8	170	153	71	434	363

1- Muttukkadu Estuary; 2- *Rachycentroncanadum* tank; 3- *Lates calcarifer* tank; 4- *Chanos chanos* tank; 5- Chlorella culture; 6- *Liopenaeus vannamei* pond; 7- Discharge Water Treatment System.

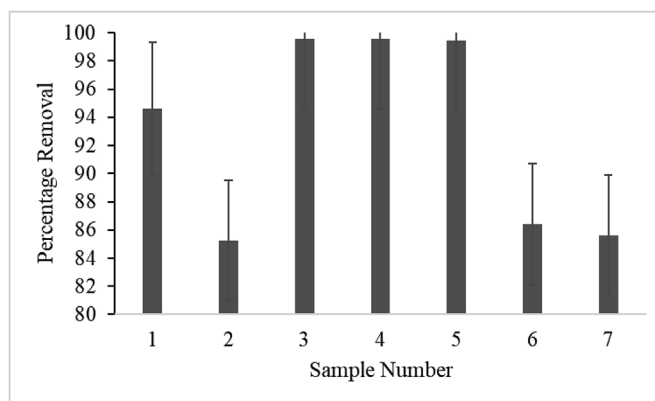


Fig. 8. Percentgae removal of phosphate from aquaculture water of varying salinity
1-Muttukkadu Estuary; 2- *Rachycentron canadum* tank; 3- *Lates calcarifer* tank; 4- *Chanos chanos* tank; 5- Algal culture; 6- *Liopenaeus vannamei* pond; 7- Discharge Water Treatment System.

Table 5
Phosphate adsorption capacity of the modified bentonites.

Adsorbent	Adsorption capacity (mg/g)	Reference
Al-bentonite	7.1	
Al-CTMAB-Bent	7.63	Ma and Zhu, 2006
HyAl-Mt	10.06	Zhu and Zhu, 2007
Al-bentonite	8.98	Tian et al., 2009
Fe-Al-Bent	10.5	Yan et al., 2010
Fe-Al-Bent	8.33	Rahni et al., 2016
Al-bentonite	11.85	This study

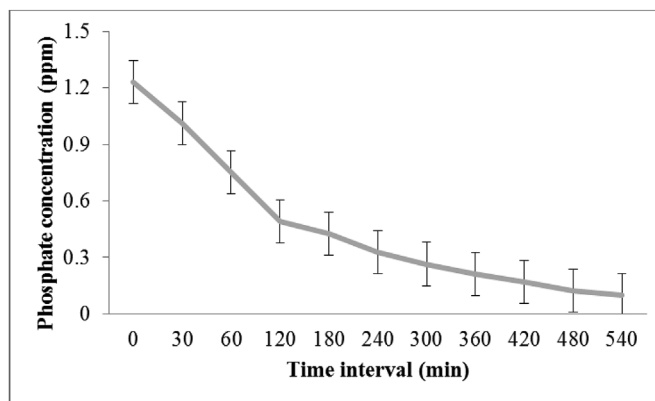
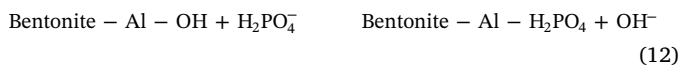


Fig. 9. Phosphate reduction in DWTS after application of aluminium pillared bentonite.

solution pH raised due to release of -OH ion by exchange with the phosphate ion.



3.6. Adsorption kinetics

Most phosphate is adsorbed during the first 60 min of adsorption (Fig. 6). As the contact time proceeds, the rate of phosphate removal decreased considerably due to decrease in number of free surfaces by filling with phosphorus and blockage of free path in adsorbent pore (Ho, 2006; Foo and Hameed, 2010). After 5 h of sorption, equilibrium was established. The steep slope indicates the fast adsorption rate at the beginning because the active sites are filled rapidly and the gradual decrease with time due to intraparticle diffusion processes (Yan et al., 2010; Ma et al., 2016). The mechanism of phosphate adsorption was evaluated by fitting the sorption data kinetic models. The rate constants are given in Table 2 and the kinetics of phosphate sorption indicated that pseudo-second order model fitted the data well ($R^2 = 0.982$) which implies the chemisorption or chemical bonding between pillared bentonite site and phosphate is the dominant process (Liu et al., 2017).

3.7. Adsorption thermodynamics

Phosphate sorption capacity of the pillared bentonite improved with the rising temperature from 11.85 at 25 °C to 13.81 and 15.85 mg g^{-1} at 35 °C and 45 °C, respectively (Fig. 7; Table 3). The result demonstrated that the phosphate removal process was endothermic. Higher phosphate adsorption at high temperature indicates that the adsorption reaction is of endothermic nature and the ion-exchange mechanism is favoured at higher temperatures (Zamparas et al., 2013; Kumararaja et al., 2016). Increased mobility of phosphate with the increasing kinetic energy at higher temperature may also result in higher adsorption (Zhu and Zhu, 2007; Ma et al., 2012). The negative values of ΔG^0 (-4.19 to $-6.24 \text{ kJ mol}^{-1}$) indicate the feasibility of phosphate adsorption and the process is spontaneous (Table 3). The increase in ΔG^0 with rise in temperature confirms that the process is more favourable at higher temperatures. The positive value of ΔH^0 ($24.71 \text{ kJ mol}^{-1}$) indicates that phosphate removal is an endothermic process as confirmed by increase in sorption capacity with the temperature. Endothermic nature of phosphate sorption by different adsorbents reported by number of researchers (Moharami and Jalali, 2015; Cui et al., 2016).

3.8. Phosphate removal from natural water

Water quality parameters of the natural water samples are highly variable. The salinity varied from 1 to 31 ppt and the phosphate concentration ranged between 0.65 and 1.23 ppm (Table 4). To 100 ml natural water 0.25 g of pillared bentonite was added and treated for 15 min. The percentage removal varied from 85.3 in Cobia tank estuary water to 99.6 in *Chanos chanos* larval rearing tank water (Fig. 8). The material developed in the present study is having higher phosphate adsorption capacity than the modified bentonites (Table 5). The results indicate that the pillared bentonite treatment resulted in more than 80% reduction in phosphate level of aquaculture water. Aluminium pillared bentonite was applied (500 g) to discharge water treatment system (1.5 m^3) of the Muttukkadu Finfish hatchery of ICAR-CIBA, Chennai. The phosphate concentration was measured at different time interval. The phosphate concentration reduced with the time interval (Fig. 9). The phosphate level was reduced by 60% within 120 min of application. The phosphate concentration was reduced below critical level of 0.2 ppm after 6 h of application. Phosphate concentration of fish pond effluent was reduced by 79% within 30 min of application of Phoslock at a dose of 400 mg/L (Kurzbaum et al., 2017). Application of Phoslock to a eutrophic lake reduced the phosphate concentration

(Nurnberg and LaZerte, 2016). Iron oxide based media in Recirculatory Aquaculture System enhanced the phosphate removal by 50–55% (Sibrell and Kehler, 2016). Hence the DWTS could be improved by the application of pillared bentonite for reducing phosphate level prior to discharge into the environment.

4. Conclusions

The present investigation was carried out with the objective of reducing the phosphorus level of aquaculture discharge water with the low cost available bentonite with improved efficiency by pillaring with polyhydroxy aluminium. The pillared bentonite was characterised for its properties and evaluated for the phosphorus removal efficiency by batch adsorption method. The Langmuir monolayer adsorption capacity of phosphate onto pillared bentonite was 11.85 mg g^{-1} . Treatment of aquaculture discharge water with the synthesised material showed a significant reduction in phosphorus level. The novel pillared bentonite could enhance the efficiency of the Discharge Water Treatment System (DWTS) of the aquaculture facility by removing the phosphate and thereby avoid eutrophication.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ocecoaman.2019.104951>.

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