



Research Article

Assessment of urban river water quality and developing strategies for phosphate removal from water and wastewaters: Integrated monitoring and mitigation studies



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Abstract

In this work, the water quality status of the surface water that lies around the Karamana River basin, Trivandrum urban area, was studied on the basis of the water quality index (WQI) method. The eutrophic condition of the basin is revealed, and proper mitigation strategy was adopted for the removal of phosphate species using pillared clay materials. Proper sampling was carried out in the urban rivers, and various physico-chemical parameters for evaluating the quality of water were analysed. WQI values obtained for these riverine systems are in the range 317.7–3005.1, indicating that the water is not suitable without treatment for any domestic activities. Also, phosphate ions in the range 1.98–20.52 mg/L reflect the dominance of phosphate species in surface water. A proper mitigation strategy was adopted for the selective removal of phosphate ions using adsorption technique by using zirconium-pillared bentonite clay (ZPBC) prepared by the stirring–ageing technique. The batch adsorption experiment performed on simulated phosphate solution shows that for 2.0 g/L of ZPBC a maximum phosphate adsorption capacity of 35.71 mg/g was achieved in 30 min at pH 3.0. The data obtained were used to study models in kinetics and isotherm. The reusability of spent ZPBC for five continuous cycles without major loss in adsorption capacity using 0.025 M Na₂CO₃ extractant was proved from the desorption study. A single-stage reactor was also designed from the isotherm data and proved to be effective. The applicability of the adsorbent towards phosphate anions was successfully checked in the laboratory using surface water collected and found that the complete removal of phosphate was achieved using 6.0, 8.0 and 10.0 g/L of ZPBC.

Keywords Urban area · Water quality index · Mitigation · Phosphate · Adsorption · Desorption

1 Introduction

Urban river water chemistry is a principal component of metropolitan areas as it maintains the survival of the urban ecosystem through receiving and flushing out mechanism. But the discharge of municipal sewage and industrial effluents beyond the controlling level cause harmful effects on the lives of city dwellers. The presence of pollutants in

the aquatic environment inhibits the penetration of light into the water bodies, creating an anoxic condition and destroying flora–fauna of the aquatic environment [1–3]. Thus, using water quality index (WQI) with international standard limits we can determine the water chemistry and hence the status of water pollution in these areas [4, 5]. WQI method based on different modes of calculations has been widely developed by many authors to assess water

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quality of rivers all around the world like Hooghly River in India, Yellow River in China, Suquia River in Argentina, Amazonian rivers in Brazil and Beheshtabad River in Iran [6–10]. Thus, from the outcome of WQI calculations, the public and government can easily understand the healthiness of the river and also can take suitable measures regarding human intervention and surface water preservation in the area, particularly in a developing country like India, where rivers are considered as sacred.

The occurrence of excessive nutrients (N and P) in rivers is mainly due to anthropogenic activities which may lead to eutrophication, causes uncontrolled algal growth, ineffective environment for fish and depletion of dissolved oxygen and affects the biodiversity; in overall, it may lead to the extinction of a variety of species [11, 12]. Phosphorus can be brought to minimal concentration than nitrogen, so in order to control eutrophication special emphasis is given to phosphorus than nitrogen [13, 14]. Phosphorus compounds such as inorganic phosphate, pyrophosphate, phosphodiester and organic phosphate esters are converted to orthophosphate chemically or enzymatically in an aqueous environment. So, orthophosphate is the only prominent form that could be utilized by prokaryotic and eukaryotic organisms [15, 16]. For the treatment of wastewater, various techniques are reported by researchers, such as adsorption, oxidation, flocculation–coagulation, membrane filtration and biological treatment [17, 18]. Among them, adsorption is an effective technique for the removal of pollutants because of low cost, minimal sludge production, recovery of adsorbent and high efficiency [1, 2, 19]. So we have opted for an adsorption technique for the complete removal of phosphate in river water [20]. Bentonite is an easily available 2:1 natural clay mineral with low cost and non-toxicity and is widely used for nutrient removal studies because of its high anion exchange capacity. It has an octahedral layer that is sandwiched between two tetrahedral layers with a negative charge on its surface which is mainly balanced by Na^+ and Ca^{2+} , which are exchangeable with pillared cations resulting in the increase in efficiency in phosphate removal [21, 22]. So by modifying the precursor bentonite, the efficiency of adsorption towards phosphate could be increased.

The systematic monitoring of water quality of an urban river basin followed by mitigation of a specific anion in the presence of other co-existing ions is not reported in any of the research work related to water chemistry. The aim of the present study is to explore the eutrophic condition of the surface water in the urban area of Trivandrum using the water quality index method followed by adsorption of phosphate anions present in the riverine system using pillared clay. The mitigation study for phosphate removal on these urban rivers was carried out using the adsorbent ZPBC. The preparation of the adsorbent ZPBC and its

characterization is reported by our group [23]. In this work, adsorption conditions for simulated phosphate solutions such as contact time with various concentrations 15, 25, 50 and 100 mg/L and with different temperatures 15, 25 and 35 °C were optimized to study various kinetic and isotherm models. The spontaneity of the adsorption process was investigated using thermodynamic studies. Finally, the adsorbent was effectively applied for the removal of phosphate in riverine samples collected during fieldwork.

2 Materials and methods

2.1 Monitoring studies

2.1.1 Study area and sampling locations

Trivandrum, the capital city of Kerala, situated between 8° 17' and 8° 54' N latitude and 76° 41' and 77° 17' E longitude is blessed with three major rivers. This study is mainly concentrated on the highly populated urban areas of this district, where the entire Karamana River basin lies. Karamana River (67 km), the major river in this basin, has its origin from Chemmunji Motta of Western Ghats, recognized as one among the world's eighth hottest spots by the UNESCO world heritage due to its rich biodiversity. This river is the major surface water source for the Trivandrum water supply scheme. The best-known tributary of Karamana River is Killiyar which is also part of the monitoring study. Another major canal residing in this basin is Parvathy Puthanar (part of Travancore–Shoranur Canal) having a length of 16.5 km stretching from Akkulam–Veli (N) to Kovalam (S) of the city. This canal is also taken for the water quality study as the sewage is dumped into this canal from various small drains present in the city. About 70% of the sewage from urban areas is conveyed to the sewage treatment plant at Muttathara, but the remaining part is dumped into this riverine system that causes severe problems for the flora and fauna of the aquatic system. The sampling sites were identified and recorded using a portable GPS (Make: Garmin, Model: Montana 650, USA), and the locations from which samples have been collected are shown in Fig. S1.

2.1.2 Field work details

The samples were collected during the post-monsoon season (November 2018) from two rivers each namely Karamana (stations 1, 2 and 3), Killiyar (stations 4, 5 and 6) and Parvathy Puthanar canal (stations 7, 8 and 9) from about 0.6 m below the water surface. The parameters such as water temperature (°C), pH, electrical conductivity (EC), total dissolved solids (TDS) and dissolved oxygen

(DO) were measured *in situ* without pretreatment using a calibrated transportable water quality equipment (Make: Eutech, Model: Aquaread 1000 D, Germany). Before the laboratory analysis of chloride (Cl^-), sulphate (SO_4^{2-}) and bicarbonate (HCO_3^-), phosphate $\text{PO}_4^{3-}\text{-P}$, ammonia ($\text{NH}_4^+\text{-N}$) and nitrate ($\text{NO}_3^-\text{-N}$) water samples were filtered using 0.45- μm Whatman TM uniflo PVDF sterile disposable syringe filters and preserved in an airtight 1-L acid-cleaned sealed polyethylene bottle (PE). Before the collection of water samples in PE bottles, they were thoroughly rinsed with distilled water. All the field samples were preserved in ice bags to maintain ambient conditions until they get analysed. The method adopted for the determination of chemical parameters of the samples is taken from procedures mentioned in American Public Health Association [24]. The chemicals required for the determination of chemical parameters were purchased from E. Merck, India. The experiments and calculations were completed within a week, and the entire analysis was carried out in triplicate.

2.1.3 Examination of the quality of water by WQI method

The physico-chemical parameters such as pH, EC, DO, TDS, Cl^- , SO_4^{2-} , $\text{NO}_3^-\text{-N}$, $\text{PO}_4^{3-}\text{-P}$ and $\text{NH}_4^+\text{-N}$ were used for the calculation of WQI. Each parameter was given the weightage (w_i) value from 1 to 5 depending upon their importance in the surface water (Table S1).

DO, EC and nutrient parameters such as $\text{PO}_4^{3-}\text{-P}$ and $\text{NO}_3^-\text{-N}$ were given weightage 5 ($w_i=5$). DO is needed for the survival of flora–fauna of the aquatic system. The decrease in DO value is an indication of polluted water, and there is a high possibility of eutrophication. The eutrophic condition of surface water mainly concentrates on the amount of $\text{PO}_4^{3-}\text{-P}$ and $\text{NO}_3^-\text{-N}$ present. These two anions from fertilizers and detergents when discharged into surface water cause the growth of aquatic plants and depletion of DO, finally affecting the water quality by causing eutrophication. EC is an indirect measure of total dissolved salts and also confirms the presence of inorganic pollutants (industrial effluents) present in surface water. Thus, EC indicates the state of surface water, i.e. whether the water system is suitable for the survival of aquatic life [25]. Hence, we assigned these three parameters a weightage 5.

The reason for assigning the weightage 4 for parameters pH, $\text{NH}_4^+\text{-N}$, TDS and SO_4^{2-} is as follows: the acidity or alkalinity of water can be understood by the measurement of pH. The flow of fertilizers that contain nutrients, mainly phosphate and nitrate, into the surface water results in higher pH and proliferation of algal growth. Conversely, the physiological functions of aquatic life are affected at low pH [26]. So pH indicates the state of water. The concentration of $\text{NH}_4^+\text{-N}$ in the surface water depends upon

pH and temperature. Although aquatic organisms excrete ammonia, the high concentration of $\text{NH}_4^+\text{-N}$ in the aquatic system occurs due to the discharge of domestic sewage and industrial effluents [27]. The source of SO_4^{2-} in urban surface water might be from sulphate-bearing fertilizers, sulphuric salts in domestic sewage and also by weathering of soils. Moreover, sulphates form strong acids that change the pH of water [28]. The high value of TDS causes an increase in salinity, changes the ionic composition of water, eliminates less tolerant aquatic species and thus overall affects the quality of surface water [29]. Chlorides (Cl^-) are usually combined with sodium and to a lesser extent with calcium, magnesium and potassium, making them a stable component in water. The increase in the content of Cl^- causes acidification of streams and affects the reproduction capability of aquatic plants and animals [30]. Thus, it affects the water quality and given a weightage 3. For the WQI calculation, the standard values of surface water were taken from various studies [31–33]. The relative weight (W_i), quality rating (q_i) and WQI are computed using the following equations [34]:

The relative weight and quality rating equation:

$$W_i = \frac{w_i}{\sum_{i=1}^n w_i} \quad (1)$$

and

$$q_i = \frac{C_i}{S_i} \times 100 \quad (2)$$

Sub-index equation:

$$SI_i = W_i \times q_i \quad (3)$$

Water quality index equation:

$$\text{WQI} = \sum_{i=1}^n SI_i \quad (4)$$

where n represents the number of parameters, w_i is the weight of each parameter, C_i is the concentration of the i th parameter for each sampling site, S_i (mg/L) is the standard for surface water, and SI_i is the sub-index of the i th parameter.

2.2 Mitigation studies

2.2.1 Materials

The adsorbent, bentonite clay (AR grade) was procured from Sigma-Aldrich, India, and for pillaring process Emsure-grade zirconium (IV) oxychloride was purchased from Merck, India. For the contact time and temperature studies, simulated stock solution of phosphate

(1000 mg/L) was prepared using KH_2PO_4 purchased from Merck, India. For the spectrometric determination of phosphate, E. Merck chemicals were used (ascorbic acid, ammonium heptamolybdate tetrahydrate, potassium antimony (III) oxide tartrate hemihydrates). The desorption studies were carried out using NaOH, Na_2CO_3 , HCl and NaHCO_3 supplied from Merck, India. All chemicals used were AR grade, and the reagents were prepared using Milli-Q water.

2.2.2 Procedure adopted for ZPBC—zirconium-pillared bentonite clay

The successful synthesis of ZPBC and the detailed procedure carried out using the stirring–ageing technique are reported in our previous work [23]. A brief description of the procedure adopted for pillared clay preparation is as follows: about 4 mL/min of 0.2 zirconium oxychloride (500 mL) is added dropwise to an RB flask containing the stirring solution of sodium bentonite (12 g) kept at room temperature. The process is continued for 10 min, and after that 40 mL of the remaining zirconium solution was added to the stirring mixture as described above and kept for ageing for another 10 min. The same slot addition of aliquot and ageing is continued until 6 h and 25 min is reached. Finally, the mixture is stirred vigorously for 2 h followed by 4-h ageing. After checking the pH, the solution was centrifuged and the residue part is washed with deionized water to free from chloride. The material is then dried at 80 °C, milled, labelled as ZPBC and kept in the bottle for further studies. The pillaring of Zr onto precursor clay is confirmed from various spectroscopic techniques that were reported in our work mentioned above.

2.2.3 Batch adsorption experiments

The effect of contact time (10, 20, 30, 40 and 50 min), initial phosphate concentrations (15, 25, 50 and 100 mg/L) and temperatures (15, 25 and 35 °C) for the adsorption of phosphate were studied by taking 2.0 g/L of ZPBC in Erlenmeyer flasks optimized at pH 3.0 using 0.1 M NaOH and 0.1 M HCl. Then, treated solutions with varying different concentrations of phosphate were analysed using ultraviolet–visible NIR spectrophotometer (Make: Shimadzu, Model: UV-3600 plus, Germany) measured at a wavelength of 880 nm by ammonium molybdate method [24]. The amount of phosphate adsorbed was calculated by using the following equation:

$$q = \frac{[(C_0 - C_A)]V}{m} \quad (5)$$

where C_0 is the initial phosphate concentration and C_A is the concentration of phosphate at equilibrium in mg/L, V

is the volume of phosphate solution in mL, and m is the mass of the adsorbent in grams.

The reusability of the adsorbent (ZPBC) was investigated by conducting desorption studies. The phosphate-loaded ZPBC was centrifuged and washed thoroughly with Milli-Q water to remove any unabsorbed phosphate ions. The desorption experiments were carried out using NaOH, Na_2CO_3 , HCl and NaHCO_3 as desorption agents. Among them, Na_2CO_3 was found to be more effective and was selected for further studies. The regenerated clay was used for adsorption, and the sorption experiment was continued for five cycles.

The effect of the adsorbent dosage (2.0, 4.0 6.0, 8.0 and 10.0 g/L) was carried out for the phosphate removal studies. The filtered riverine samples collected during the field work were used for the dosage experiment. The entire test was conducted in duplicate, and the mean values are reported.

3 Results and discussion

3.1 Monitoring studies

3.1.1 Hydrochemical characteristics

Physico-chemical parameters reflect the surface water quality, and the result obtained during analysis is shown in Table 1. The surface water temperature varied from 29.1 to 31.4 °C during the sampling period. The acidity and basicity of the water are well understood by pH studies. In the present study, it can be seen that pH values varied from 7.01 to 8.71 from stations 1 to 9. A wide variation for DO values was obtained for all the stations during in situ measurements. The lower DO was obtained for stations 7, 8 and 9 with values ranging from 3.01 to 3.32 mg/L. The DO concentration obtained for the canal is very much lower, i.e. below the standard limit (5 mg/L) of WHO (2011) for drinking purposes and also below the standard limit of surface water (6 mg/L). Sewage channel is joining this canal at different points leading to nutrient load, weed growth and a decrease in DO. Stations 7, 8 and 9 reported a high value of EC compared to all other stations and are found to be above the surface water standard limit (400 $\mu\text{S}/\text{cm}$). The high value of EC in the canal indicates a high degree of pollution due to the dumping of sewage waste. TDS values for Karamana River and Killiyar were within the permissible limit (500 mg/L) of WHO (2011), but in the case of Parvathy Puthanar, values are very high (1782.01 to 1987.30 mg/L). The values are higher than the surface water standard (1200 mg/L). The TDS level in Parvathy Puthanar is high due to septic and domestic sewage waste present in the water. The bicarbonate levels from stations 1–6 were

Table 1 Results of physico-chemical parameters of Karamana River basin

Stations	Temperature (°C)	pH	EC (µS/cm)	TDS (mg/L)	DO (mg/L)	HCO ₃ ⁻ (mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	NO ₃ ⁻ N (mg/L)	PO ₄ ³⁻ P (mg/L)	NH ₄ ⁺ -N (mg/L)
1	29.2	7.01	88.01	58.08	6.01	56.32	43.21	45.04	5.91	1.98	1.80
2	29.2	7.12	87.31	53.01	6.32	49.12	57.06	51.01	6.62	2.56	2.01
3	29.1	7.23	89.21	73.37	5.23	54.31	61.56	46.32	6.01	2.27	2.56
4	29.2	7.35	220.23	145.20	4.12	79.12	95.26	68.45	8.82	3.68	3.61
5	29.5	7.45	221.21	154.60	4.01	83.12	76.23	71.05	10.07	3.84	4.03
6	29.6	7.52	275.01	220.12	4.92	87.56	82.53	89.23	12.01	5.92	5.21
7	30.0	8.01	2156.7	1782.01	3.32	266.89	107.21	129.23	17.91	15.02	8.03
8	30.1	8.32	2341.2	1873.01	3.21	289.96	116.38	137.12	18.24	17.34	9.72
9	31.4	8.71	2483.0	1987.30	3.01	349.82	128.32	143.61	23.15	20.52	10.92
Mean	29.66	7.63	884.65	783.72	4.46	146.25	85.30	86.78	12.08	8.13	5.32
Standard deviation	0.62	0.58	1086.89	884.76	1.22	55.99	28.76	40.02	6.26	7.35	3.42

within the permissible limit of 120 mg/L of (WHO 2011) for drinking purposes but slightly high values for other stations. The concentrations of Cl⁻ and SO₄²⁻ varied from 43.21 to 128.32 mg/L and 45.04 to 143.61 mg/L, respectively, indicating that the values are within the standard limit (250 mg/L). The major nutrients such as ammonia (NH₄⁺-N), phosphate (PO₄³⁻-P) and nitrate (NO₃⁻-N) also affect the quality of water, and their limit beyond permissible limits causes serious health problems in rivers. Among the nutrient parameters, mainly phosphate is easily absorbed by plants, causing increased productivity of phytoplanktons resulting in eutrophication, and finally the entire area becomes deserted [35]. PO₄³⁻-P values for all the stations ranged from 1.98 to 20.52 mg/L with the maximum in stations 7, 8 and 9. In general, all the stations PO₄³⁻-P values were found to be exceeding the permissible limit (> 0.1 mg/L) prescribed by WHO (2011) and surface standard limit set by researchers. Moreover, it is reported that for phosphate values greater than 1.0 mg/L, there is a high risk of eutrophication. The values for NO₃⁻-N and NH₄⁺-N varied from 5.91 to 23.15 mg/L and 1.80 to 10.92 mg/L, respectively, having high values for Parvathy Puthanar. NO₃⁻-N values for stations 1–5 were within 10 mg/L as per surface water standards, whereas NH₄⁺-N was higher for all stations with values above the permissible limit (0.5 mg/L). Higher ammonia creates an oxygen demand in these stations and also releases nitrous oxide gas produced as a result of the denitrification process. The trend obtained from the nutrient analysis is as follows: PO₄³⁻-P > NH₄⁺-N > NO₃⁻-N. The level of nutrients, especially phosphate present in the riverine systems, is high due to the dumping of sewage wastes, both solid and liquid from small drainage channels or from people residing banks of rivers. The phosphate level is tremendously high in Parvathy Puthanar, indicating the disappearance of the canal in the nearby future due to eutrophication. So proper treatment strategies must be introduced for saving the rivers and canal from nutrient pollution, particularly from phosphate.

3.1.2 Interpretation of WQI

The WQI value obtained from the calculations for nine stations is presented in Table 2. The results showed that WQI values are varying for different sampling sites. WQI values calculated for the Karamana River and Killiyar are in the range 317.7–370.71 and 581.62–910.96, respectively. For Parvathy Puthanar, WQI values > 2200. The surface water standard was considered for the calculation of the water quality index method. In other studies, WQI is calculated on the basis of the drinking water standard. So the comparison of our results with them is not possible. In some places of urban areas, people use water directly for bathing

Table 2 WQI values obtained for post-monsoon season from rivers and canal

Stations	1	2	3	4	5	6	7	8	9
WQI values	317.70	326.84	370.71	581.62	613.91	910.96	2217.87	2558.82	3005.12

and domestic purposes. Even if we take the drinking water standard limit of WHO, WQI values obtained will be very higher indicating unsuitability in drinking purposes. Most of the areas' river water is used after pretreatment. However, the concentration of ions, especially nutrient anions, in all the stations obtained is very high when compared to the surface water standard limit and also the drinking water standard limit. The high phosphate level indicates a great threat to the current aquatic environment, and this will definitely affect the existence of the future riverine systems. So a proper mitigation method should be adopted at the earliest for the preservation of the aquatic system.

3.2 Mitigation studies

3.2.1 Effect of contact time and temperature

A maximum of 92.4% phosphate removal was achieved at pH 3.0 for 15 mg/L phosphate solution concentration using an adsorbent (ZPBC) dose of 2.0 g/L. Further increasing the pH, adsorption decreases appreciably. At pH 3.0, the surface of the pillared clay becomes more positive that tends to attract $H_2PO_4^-$ from phosphate solution resulting in effective adsorption. Figure 1a represents the contact time required for various concentrations 15, 25, 50 and 100 mg/L to reach equilibrium using the above-optimized condition. As contact time proceeds, the amount

of phosphate adsorbed increases and reaches equilibrium within 30 min. The maximum q_e values obtained are 6.97, 11.30, 19.22 and 19.32 mg/g for various concentrations 15, 25, 50 and 100 mg/L within 30 min. As contact time proceeds further, there is no appreciable change in phosphate adsorption from the solution by the adsorbent due to the unavailability of the bare clay surface for the uptake of phosphate molecules. The fast adsorption rate is very crucial and important for the practical application of the adsorbent [36]. The influence of temperature on the interaction between ZPBC and phosphate was studied using three different temperatures 15, 25 and 35 °C under the optimized condition (Fig. 1b). It can be seen that as the temperature rises the amount of phosphate adsorption reached 34.83 mg/g at 35 °C. A possible explanation for the increase in the amount of adsorption at higher temperatures can be due to the increase in active sites on the adsorbent surface for adsorption and also rise in the temperature increases the mobility rate of phosphate species onto the surface of the adsorbent. Hence, it is assumed that adsorption is an endothermic one [37].

3.2.2 Adsorption kinetics, isotherm and thermodynamic studies

To predict the adsorption chemistry of ZPBC with phosphate (physisorption or chemisorption), the

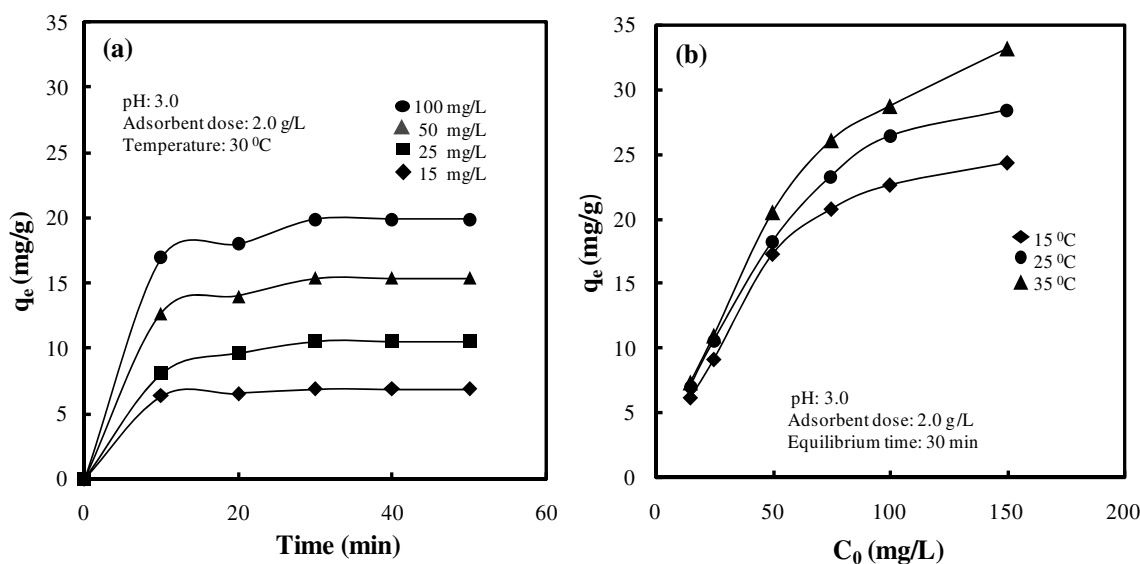


Fig. 1 Effect of **a** contact time and **b** temperature on phosphate adsorption onto ZPBC

experimental data obtained from contact time for various initial concentrations 15, 25, 50 and 100 mg/L were used for the calculation of using two prominent models: pseudo-first-order and pseudo-second-order [38, 39], and the equation is as follows:

Lagergren pseudo-first-order equation:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{6}$$

Mckay and Ho pseudo-second-order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

where k_1 (1/min) and k_2 (g/mg/min) are the pseudo-first-order and pseudo-second-order rate constants for an amount of phosphate adsorbed at equilibrium q_e and q_t in mg/g at time t (min), respectively. The values for k_1 and q_e were calculated from the slope and intercept by plotting $\log (q_e - q_t)$ against t (Fig. 2a), whereas k_2 and q_e were calculated from the slope and intercept of the plot t/q_t against t (Fig. 2b). Table 3 clearly shows the pseudo-second-order with higher R^2 value (0.998, 0.985, 0.984, 0.992) indicating chemisorption as the rate-limiting step in the

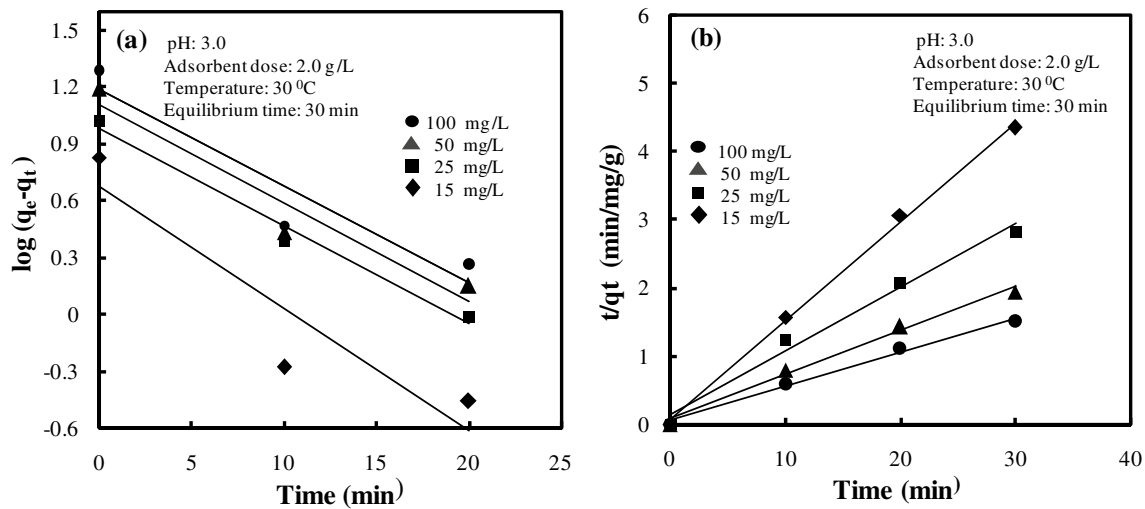


Fig. 2 a Pseudo-first-order, b pseudo-second-order kinetic plots for the adsorption of phosphate onto ZPBC

Table 3 Kinetic and isotherm parameters for the adsorption of phosphate onto ZPBC

Kinetic models	Parameters	Initial concentration (mg/L)			
		15	25	50	100
Pseudo-first-order	k_1 (1/min)	0.147	0.117	0.119	0.117
	q_e (mg/g)	4.73	9.57	12.88	15.35
	R^2	0.852	0.983	0.933	0.890
Pseudo-second-order	k_2 (g/mg/min)	0.329	0.063	0.062	0.055
	q_e (mg/g)	6.89	10.75	15.87	20.00
	R^2	0.998	0.985	0.984	0.992
Isotherm models	Parameters	Temperatures			
		15 °C	25 °C	35 °C	
Langmuir	Q^0 (mg/g)	27.03	30.30	35.71	
	b (L/mg)	0.09	0.15	0.17	
	R^2	0.997	0.996	0.992	
Freundlich	K_F (mg/g)	4.56	7.16	11.25	
	n (L/mg)	2.49	3.04	3.92	
	R^2	0.929	0.980	0.984	

phosphate adsorption process [40]. The rate constant k_2 , for the adsorption of phosphate, was found to decrease for various initial phosphate concentrations (15 mg/L to 100 mg/L). By obtaining pseudo-second-order kinetics, it is confirmed that sorption onto ZPBC proceeds by electrostatic interaction between adsorbent and adsorbate. Similar results are obtained for phosphate removal using other adsorbents [41, 42].

The adsorption capacity of the adsorbent is mathematically calculated by using two common models, Langmuir [43] and Freundlich [44], with the help of isotherm data for various temperatures 15, 25 and 35 °C. Langmuir isotherm occurs on the homogenous adsorbent surface indicating monolayer adsorption, but for Freundlich isotherm adsorption occurs on heterogeneous surfaces and more possibly adsorption is a multilayered one [45, 46]. The equations of these two models are given in Eqs. 8 and 9:

Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{bQ^0} + \frac{C_e}{Q^0} \tag{8}$$

Freundlich equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{9}$$

where q_e (mg/g) represents the amount of phosphate adsorbed on the solid zirconium-pillared adsorbent and C_e (mg/L) is the concentration of phosphate solution at equilibrium. Q^0 (mg/g) is the monolayer adsorption capacity, and b (L/mg) is the energy of adsorption. K_F is the Freundlich constant, and n represents the intensity of adsorption. The value of b and Q^0 is obtained from the plot C_e/q_e

versus C_e (Fig. 3a). The value for K_F and n is obtained from the $\log q_e$ versus $\log C_e$ (Fig. 3b). The favorability of the adsorption is represented by the equilibrium parameter R_L [47]:

$$R_L = \frac{1}{1 + bC_0} \tag{10}$$

where b is the Langmuir constant and C_0 is the initial concentration of phosphate solution. The favorability of the adsorption process is represented in the order $0 < R_L < 1$.

Table 3 shows the higher regression coefficient ($R^2 > 0.97$) for Langmuir isotherm indicating the suitability of the model in explaining the adsorption of phosphate onto pillared clay. As temperature rises (15 to 35 °C), Q^0 value (27.03 to 35.71 mg/g) also increases confirming the endothermic nature. The increase in b value (0.09 to 0.17) with the rise in temperature conveys the strength and affinity of the clay surface towards phosphate species as reported elsewhere [48]. The values of R_L were found to be between 0 and 1 for the various initial concentrations of phosphate (15–100 mg/L) confirming the favorability of the adsorption of phosphate species onto adsorbent [49]. A comparative study on phosphate adsorption using ZPBC and other modified bentonite clay minerals is presented in Table 4 and found that ZPBC prepared by the novel method is a better adsorbent than reported.

The spontaneity and feasibility of the adsorption process were studied using thermodynamic parameters (free energy ΔG^0 ; enthalpy ΔH^0 ; entropy ΔS^0) at optimized conditions pH 3.0, temperatures 15, 25 and 35 °C, adsorbent dose 2.0 g/L and various initial phosphate

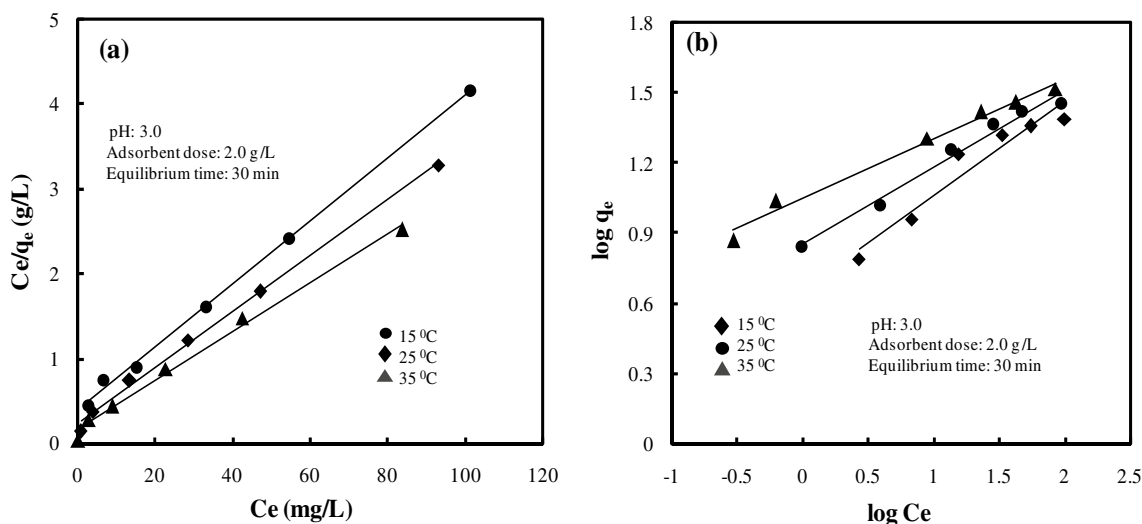


Fig. 3 a Langmuir, b Freundlich isotherm plots for the adsorption of phosphate onto ZPBC

Table 4 Comparison of adsorption capacity using various modified bentonite adsorbents for the removal of phosphate studies

Adsorbent	Q^0 (mg/g)	pH	Temp (°C)	Adsorbent dose (g/L)	Time (min)	Conc: (mg/L)	References
Zenith/Fe	11.15	7.0	25	0.4	120	0.05–5	[55]
Al-Bent	12.70	3.0	–	4.0	360	25–60	[56]
Fe-Bent	11.20	3.0	–	4.0	360	25–60	[56]
Al-ABn	12.87	5.0	25	2.0	360	2–60	[48]
Al-ABn-AB	11.11	5.0	25	2.0	720	2–60	[48]
NT-25La	14.00	6.0	25	0.75	60	0.5–80	[57]
Bephos™	26.5	7.0	25	0.4	30	0.05–20	[58]
ZrNaBT	7.25	7.0	25	1.0	1440	2–35	[59]
ZPBC	30.30	3.0	25	2.0	30	15–100	Present work
ZPBC	35.71	3.0	35	2.0	30	15–100	Present work

concentrations 15, 25, 50 and 100 mg/L. The relationship between these parameters is represented by the following equations:

$$\Delta G^0 = -RT \ln K_0 \quad (11)$$

$$\ln K_0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (12)$$

ΔG^0 is the Gibbs' free energy in kJ/mol, R is the universal gas constant ($R=8.314$ J/mol/K) and T is the absolute temperature in Kelvin. The equilibrium constant k_0 is calculated from the plot of $\ln q_e/C_e$ versus q_e and extrapolating to zero at three different temperatures. The value of ΔH^0 (kJ/mol) and ΔS^0 (J/mol/K) was calculated from the slope and intercept of the plot ($\ln k_0$ vs. $1/T$) (Fig. 4a). The results obtained are shown in Table S2. The value obtained for ΔG^0 ($-0.909, -2.428, -3.328$ kJ/mol) is negative indicating

the spontaneity of the adsorption process [18]. The value obtained for ΔG^0 (< -20 kJ/mol) indicates the importance of electrostatic interaction followed by surface complexation on phosphate adsorption onto pillared clay [50]. The positive value for ΔH^0 (38.24 kJ/mol) gives an idea that adsorption occurs by the endothermic process, and also the positive value for ΔS^0 (133.52 J/mol/K) indicates that there is an increase in randomness and also the affinity of phosphate ions towards the adsorbent surface. A similar observation was obtained for modified bentonite for the removal of the anionic pollutant from the aqueous phase [51, 52].

3.3 Application of the adsorbent into the riverine system

The efficiency of the adsorbent (ZPBC) for the removal of phosphate was confirmed by the real sample analysis of

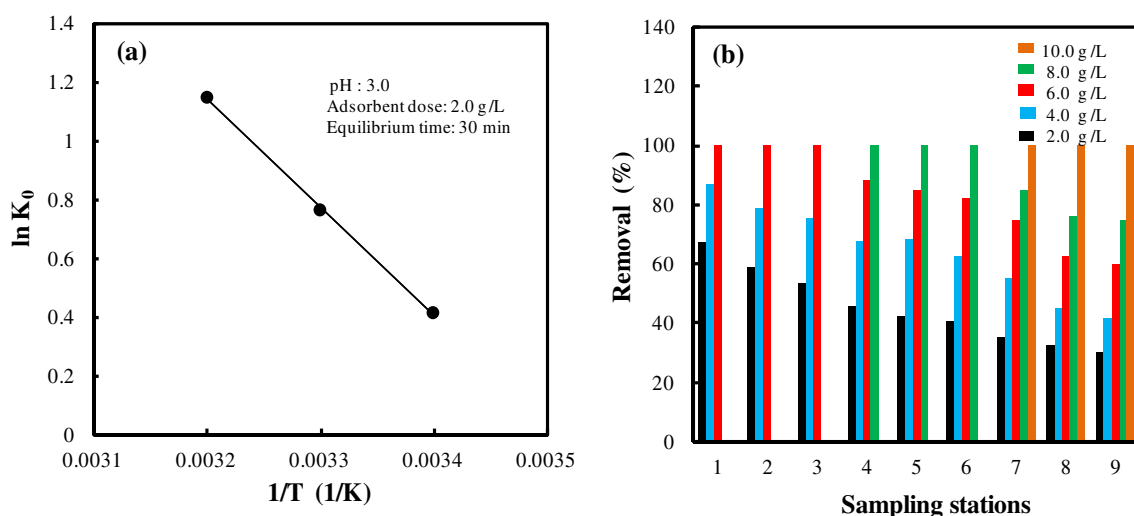


Fig. 4 **a** Plot of $\ln K_0$ versus $1/T$ for the adsorption of phosphate onto ZPBC, **b** effect of adsorbent dosage for the removal of phosphate species from Trivandrum urban area water samples by ZPBC [experimental conditions: contact time 30 min, temperature 30 °C]

riverine samples collected from nine stations. The composition of water samples is depicted in Table 1. The optimized conditions such as contact time (30 min), temperature (30 °C) and initial concentration (15 mg/L) were confirmed from the batch adsorption experiments. The pH of the solution was not adjusted (the same pH reported during fieldwork). The phosphate solution was spiked 13.02, 12.44, 12.73, 11.32, 11.16 and 9.08 mg/L, respectively, for the water samples from stations 1 to 6, and the collected water samples as such were used for the remaining stations. The effects of adsorbent dose (2.0, 4.0, 6.0, 8.0 and 10.0 g/L) were studied and are shown in Fig. 4b. It is evident from the figure that as the dosage amount increases the percentage removal of phosphate increases and almost complete removal of phosphate was obtained by using different dosages for different samples. Almost 99.9% phosphate removal was obtained for stations 1 to 3, 4 to 6 and 7 to 9 using 6.0, 8.0 and 10.0 g/L of the adsorbent.

3.4 WQI calculation after ZPBC treatment

The adsorbent-treated surface water samples were taken for the analysis of various physico-chemical parameters mentioned in WQI calculation, and the result obtained is shown in Table S3. The values obtained by WQI calculation for the ZPBC-treated surface water samples are as follows: 42.79 (station 1), 50.51 (station 2), 52.16 (station 3), 72.14 (station 4), 75.58 (station 5), 98.74 (station 6), 200.65 (station 7), 204.3 (station 8) and 256.65 (station 9). The values obtained are very lower when compared to WQI calculated for adsorbent untreated riverine sample (Table 2). This indicates that after treating with the adsorbent, a tremendous change in the quality of water has occurred. It was also found from Table S3, the anionic species that has been removed almost 99.9% from the adsorbent-treated surface water sample was phosphate. Before adsorbent treatment, the concentration of phosphate ions present in stations 1 to 9 was 1.98, 2.56, 2.27, 3.68, 3.84, 5.92, 15.02, 17.34 and 20.54 mg/L. But after treating with ZPBC, for stations 1 to 3; 0.005 mg/L, stations 4 to 6; 0.006, 0.007, 0.007 mg/L, and for stations 7 to 9; 0.007 mg/L of phosphate ions are only remaining in the water sample. This highlights the efficiency of ZPBC in removing phosphate ions from the surface water. This resulted in the tremendous decrease in WQI values. Another factor that promoted the decrease in WQI to a small extent is as follows: It is clear from Table S3 that the concentration of SO_4^{2-} , NO_3^- -N and NH_4^+ -N also varied. The slight decrease in the concentration of these anions follows the order: $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$ -N. The selectivity of an adsorbent towards a particular ions in the presence

of other ions depends on the type of interaction formed by the competing ions on the surface of the adsorbent. Phosphate ions are tetrahedral and form both inner and outer complexes with the adsorbent, and also zirconium-pillared clays have a high affinity towards phosphate species. Sulphate ions form inner sphere complex only to a small extent with the adsorbent, and as a result a slight decrease in concentration of SO_4^{2-} ions from the adsorbent-treated water sample occurred. Also, the availability of different forms of phosphate species (H_2PO_4^- and HPO_4^{2-}) in the adsorbent-treated water also makes the adsorbent more selective towards phosphate than sulphate ions. There are also other cationic species in the water, such as Ca^{2+} and Mg^{2+} , which can also influence phosphate adsorption. The binding of these ions can enhance phosphate adsorption by making the surface of the adsorbent more electropositive or by forming intermediate ternary complexes [20]. Other ions like Cl^- and NO_3^- -N form outersphere complexes (weaker interactions) with the adsorbent, and as a result the concentration of Cl^- and NO_3^- -N present in surface water slightly decreases, water quality increases and WQI decreases. The decrease in concentration of ammonium ions in adsorbent-treated riverine samples may be due to the conversion of ammonium to nitrate or by exchange with the interlayer cations of the adsorbent. A very small change in the concentration of DO occurred during the experiment, but it is not responsible for bringing down the WQI values. The values of pH also slightly decreased during adsorbent treatment onto surface water samples. The pH values after ZPBC treatment were within the surface standard limit of 6.5–9.2. The values for TDS were slightly decreased due to the adsorption of the anions and cations onto the adsorbent. Even though the values of EC and TDS for the adsorbent-treated water decreased, they are not within the surface water standard limit. This proves that ZPBC is a very good selective adsorbent for the removal of phosphate species from wastewaters. By using the adsorbent, the concentration of phosphate anions can be brought below 0.1 g/L (surface water standard); thereby, the eutrophic condition of the riverine system can be minimized to an extent. But some of the cations and anions present in the adsorbent-treated surface water samples are still above surface water standard limit. The decrease in WQI value after treatment with the pillared clay was mainly due to phosphate removal. For the domestic use of the riverine water, the concentration of these anions and cations has to be reduced. Thus, it is proved that our low-cost and eco-friendly adsorbent ZPBC is very efficient for the selective adsorption of phosphate, and in future, the investigated materials can be applied in the field in

order to construct permeable reactive barriers (PRBs) for phosphate removal in real conditions.

3.5 Design of single-stage batch reactor

The mathematically modelled equations from kinetic and isotherm studies can be used for optimizing the stages in the single-stage batch reactor [38, 53]. In this study, the single-stage batch reactor is designed by using Langmuir isotherm data of phosphate ions. The main purpose of the design is to reduce the phosphate solution from an initial concentration C_0 to C_t (mg/L) in a phosphate solution containing V (L) of water. At the same time when W (g) of ZPBC is added, there is a change in phosphate ion solution from q_0 to q_t . The mass balance equation for the removal of the phosphate ions from the aqueous phase to that loaded on the surface of the adsorbent is given by

$$(C_0 - C_t)V = (q_t - q_0)W. \tag{13}$$

At equilibrium conditions, $q_0=0$, $C_t=C_e$, $q_t=q_e$, $C_t=C_e$, Eq. (13) becomes

$$\frac{W}{V} = \frac{C_0 - C_e}{q_e}. \tag{14}$$

From (8), $q_e = \frac{Q^0 b C_e}{1 + b C_e}$. Substituting it in Eq. 14, we obtain

$$\frac{W}{V} = \frac{(C_0 - C_e)(1 + b C_e)}{Q^0 b C_e}. \tag{15}$$

Substituting Langmuir constants $Q^0=30.30$ and $b=0.15$ (298 K) from Table 4, then Eq. (15) becomes

$$\frac{W}{V} = \frac{(C_0 - C_e)(1 + 0.15C_e)}{4.545C_e}. \tag{16}$$

From Eq. (16), the mass of ZPBC required to achieve 93.46, 84.32, 72.96 and 62.16% removal by treating the definite volume of phosphate ion-containing effluent having an initial concentration C_0 (15, 25, 50, 75, 100 mL) can be calculated. The theoretical and experimental mass of ZPBC versus different volumes of effluent for different percentages of removal of phosphate is depicted in Fig. 5a. Also, the experimental and theoretical mass of adsorbent versus different initial concentrations and different volumes for the adsorption of phosphate ions from aqueous solutions is shown in Fig. 5b. Similar works for the development of a single-stage reactor are reported by other researchers [54].

3.6 Desorption studies and cost estimation of the adsorbent

The desorption capacity of the adsorbent determines its economic value for the mitigation of phosphate species from real water samples. The concentrations of Na_2CO_3 were varied from 0.005 to 0.1 M and found that by using 0.025 M Na_2CO_3 maximum phosphate was desorbed from ZPBC within 3 h. The adsorption–desorption experiment was carried out for five cycles using 0.025 M Na_2CO_3 , and the results are shown in Fig. S2. After five cycles, the adsorption capacity of pillared clay declined from 92.6 to 77.5% and recovery of phosphate decreased from 90.6 to 75.3%. The loss of the adsorbent during the five sorption cycles is found to be minimum, showing the capability of the pillared clay in batch reactor systems.

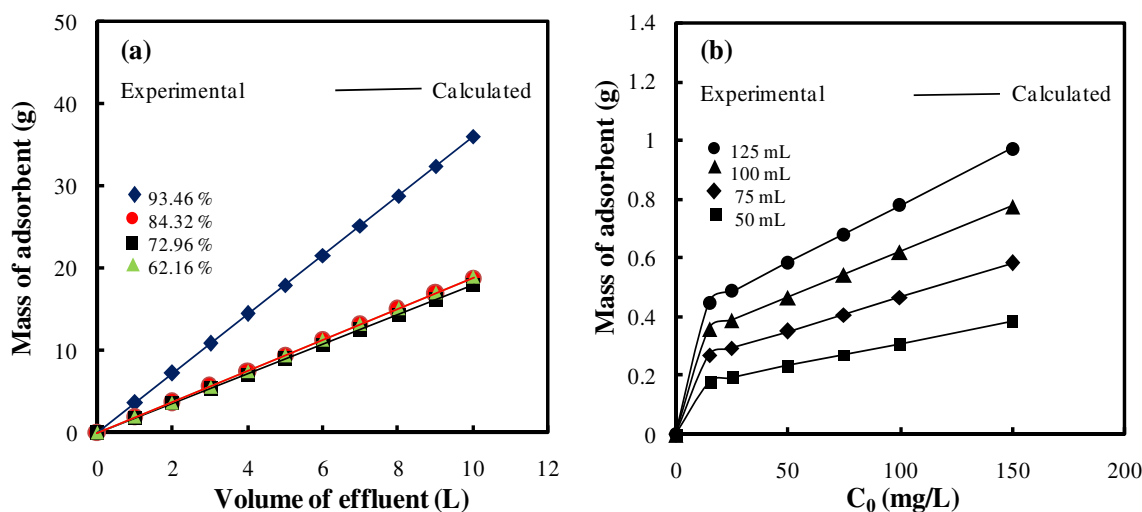


Fig. 5 **a** Mass of adsorbent ZPBC against different volumes for different percentage removal of phosphate ions and **b** mass of adsorbent ZPBC against different initial concentrations and different volumes for removal of phosphate ions from aqueous solutions

The economic utility of the ZPBC-based adsorption system for the removal of phosphate from the riverine samples faces major challenges such as the availability of material from the local market, low cost, desorption capacity and performance of the adsorbent towards adsorbate. Therefore, its cost estimation is a significant part of the work. The precursor material, bentonite clay, was obtained from Gujarat Clay mines at a reduced price. The final cost of the material was in the range of \$105–115 per ton after calculating the expenses for the transport of the material, chemicals and electrical energy.

4 Conclusions

The various physico-chemical parameters such as pH, EC, TDS, DO, Cl^- , HCO_3^- , SO_4^{2-} , NO_3^- -N, PO_4^{3-} -P and NH_4^+ -N of the riverine water of the Trivandrum urban area were analysed. WQI calculation using the surface water standards explores the eutrophic condition of the river basin. The concentration of phosphate anion (>0.1 mg/L) in the surface water is found to be very high. The novel adsorbent ZPBC was successfully tested on a simulated phosphate solution with various initial concentrations such as 15, 25, 50 and 100 mg/L. The kinetics of the adsorption was well fitted onto the pseudo-second-order model having a high regression coefficient (0.992). Langmuir isotherm model explained the monolayer adsorption of phosphate species onto ZPBC. Moreover, using this model single-stage batch reactor was designed from which the amount of ZPBC required to achieve 93.46, 84.32, 72.96 and 62.16% removal of phosphate species was calculated. The effect of ZPBC dosage on river water samples also conducted experimentally under optimized conditions such as contact time 30 min and temperature 30 °C. It was observed that as the dosage amount increases from 6.0 to 8.0 almost 99.9% phosphate removal was achieved. The WQI values obtained after adsorbent treatment also emphasized the selectivity of the pillared clay for the removal of phosphate and also the enhancement of quality of surface water. Thus, ZPBC is a promising adsorbent for the successful removal of phosphate species from the aqueous environment.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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