# Adsorptive Removal of Phosphate from Water using Zr(IV)-Loaded Spent Cation Exchange Resin

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## Abstract

*In this study, the sulphonic acid type spent cation exchange resin (SCER) was pulverized and loaded with Zr(IV) in order to make as an adsorbent for anionic pollutants like phosphate from water. The adsorbents were characterized by FTIR and chemical analysis that provided evidences for effective loading of Zr(IV). The effects of temperature, pH and phosphate concentration on phosphate removal were investigated. SCER generated from the industries of silicon semiconductors and solar panels was loaded with Zr(IV) to develop adsorption sites for phosphate anion. The adsorption behavior of SCER before and after Zr(IV) loading towards phosphate was compared. Zr(IV) loaded SCER could adsorb almost complete phosphate from aqueous solution even from trace concentration. The influence of solution pH, contact time and concentration towards phosphate from modeled solution was studied in detail by batch adsorption method. The maximum removal capacity SCER before and after Zr(IV) loading were calculated as 0.31 and 2.03 mmol/g, respectively using best fit (Langmuir) isotherm model. In addition, the phosphate from aqueous medium was quantitative adsorption and adsorbed phosphate also desored quantitatively using 0.2M NaOH solution. Therefore, present results provide a new approach of effective usage of SCER for the removal and recovery of phosphate from the aqueous solution.*

***Key words:*** *Spent Cation exchange resin (SCER), Pulverization, Zr(IV) loading, Phosphate, Adsorption isotherm*

## Introduction

Phosphate is one of a major pollutant in water and large volume of wastewater containing high concentration of phosphate will deteriorate natural ecosystems. Phosphate exists in the form of its oxo-anionic species such as, $H_2PO_4^-$, $HPO_4^{2-}$ and $PO_4^{3-}$ in water. There has been a great increase and accumulation of phosphate in environment due to the rapid industrialization over the years especially from chemical fertilizer, phosphate mining and refining industries[1]. Discharge of high concentration of phosphate into the water bodies such as lake, pond, water reservoir or river results in excess algae growth, which in turn causes deficiency in dissolved oxygen concentration and eutrophication. Therefore, it is necessary to eliminate phosphate from the environment, and it is also essential that the effluents should be treated before discharging into aquatic environments. A number of physicochemical methods have been developed for the removal of phosphate including chemical precipitation[1, 2], biological treatment [3, 4] and adsorption by using appropriate adsorbents [5-7] among them adsorption technology is emerging as prominent candidate because of its easy operation, low operating cost and invulnerability to coexisting

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pollutants [8, 9]. The uses of inexpensive material like wasted resin powder can be a promising alternative to prepare adsorbent for phosphate anion from water.

In recent years, synthetic cation exchange resins have been extensively employed in a variety of fields such as water softening, wastewater treatment, precious metals recovery, food industries and catalytic processes. Although cation exchange resins can be regenerated a considerable number of times, they gradually deteriorate through the formation of many cracks which impede smooth column operation and become unusable after many cycles of adsorption followed by regeneration steps. Consequently, large quantities of spent cation exchange resins are discarded every year all over the world by land filling at special dumping sites or by incineration. Therefore, reutilization of such a cation exchange looks more promising from the view point of economic reason.

In this work, a simple method was developed to synthesize adsorbent for phosphate using spent cation exchange resin produced from the industries of silicon semiconductors and solar panels. The spent cation exchange resin (SCER) is effective for metal ions adsorption whereas they negligibly adsorb anionic species such as phosphate anion. In a previous study, metal loaded spent cation exchange resin was employed to remove fluoride from aqueous solution together with inorganic coagulant [10]. Here, Zr(IV) was loaded onto the polymer matrix of SCER in order to develop anion exchange sites and it was used as an adsorbent for the removal of phosphate from aqueous solution.

## Experimental Method

### *Preparation of adsorbent from spent cation exchange resin*

The sample of spent strongly acidic cation exchange resin, MUROMAC MBX8-WH, which had been employed for the production of ion exchange water, was kindly supplied by Muromachi Chemical Co. Ltd., Omuta, Japan. The polymer matrices of this resin are polystyrene cross-linked by divinylbenzene and contain functional groups of sulphonic acid. This sample was pulverized into fine powders, the average particle size of which was around 20 micrometers. The resultant resin powder is abbreviated as SCER (Spent Cation Exchange Resin), hereafter. To create adsorption sites for anionic pollutants like phosphate anion, Zr(IV) ion was loaded onto the SCER according to the procedure described in our previous paper [10]. For this, 3 g of SCER was mixed together with 500 mL of 0.1 M zirconium oxychloride octahydrate (ZrOCl$_2$ 8H$_2$O) solution at pH 2.2. After that it was stirred for one day at 30°C for the immobilization of Zr(IV) onto the polymer matrix of SCER.The product was filtered and residue was washed several times by distilled water to remove unadsorbed Zr(IV) from SCER. It was dried in a convection oven at 70° C and stored in plastic bottle which was used in the adsorption of phosphate at the time of experiment. During the loading reaction of Zr(IV), the proton from the sulfonic acid functional groups of SCER are substituted with Zr(IV) through cation exchange mechanism as shown in **Scheme 1**



Spent Cation Exchange Resin
**SCER**

Zr(IV)-loaded Spent Cation Exchange Resin
**Zr(IV)-SCER**
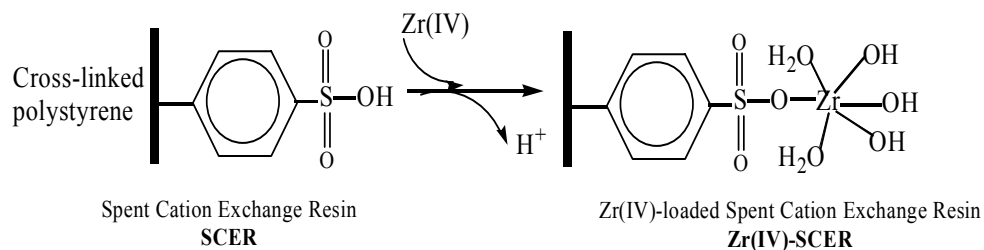
**Sceme1** *Synthetic route of Zr(IV) loaded SCER via cation exchange mechanism.*

### Batch wise studies for the adsorption of phosphate anions

The adsorption behavior of phosphate onto SCER before and after Zr(IV) loading was investigated at different pH ranging from 1.5 -12 using 23.50 mg/L (0.75 mmol/L) phosphate solution. For this 25 mg of adsorbent was mixed with 10 mL of phosphate solution. Kinetic measurements were performed by changing contact time between the adsorbents and phosphate solutions at a solid liquid ratio of 2.5 g/L. The adsorption isotherm test of phosphate for SCER before and after Zr(IV) loading were carried out by varying the phosphate concentration (0.15 - 8.9 mmol/L) at a pH of 6.7 and solid liquid ratio of 2.5 g/L. Except for the kinetics tests, the mixtures used for the adsorption tests were stirred agitated at 150 rpm for 24 h at 30° C. After 24 h of agitating the suspensions, the mixtures were filtered and filtrates were analyzed for residual phosphate concentration using ICP-AES. All these adsorption experiments were replicated at least two times. The percentage adsorption of metal ions (A%) and the amount of metal ions adsorbed (q) were calculated as follows

$$q = \frac{C_i - C_e}{W} \times V \tag{1}$$

$$\%A = \frac{C_i - C_e}{C_i} \times 100 \tag{2}$$

where, $C_i$ and $C_e$ are initial and equilibrium phosphate concentration(mmol/L), respectively, W is the dry weight of adsorbent (g) and V is the volume of feed solution in liter.

### Desorption and regeneration studies

For the actual industrial application of Zr(IV)-SCER effectively, it should be economically viable. So that reutilization of Zr(IV)-SCER for phosphate recovery for many times is necessary. This requires complete desorption of previously adsorbed phosphate and regeneration of the Zr(IV)-SCER to its original state. An experiment was conducted where phosphate (100 mL, 20 mg/L) was adsorbed first by Zr(IV)-SCER then it was desorbed using 0.1M HCl, 0.1M NaOH and 0.1M NaCl at solid liquid ratio of 5 g/L. After filtration, the residue was washed with deionized water several times and dried in a convection oven at 70° C overnight then adsorption was carried out as earlier using 20 mg/L phosphate solution.

### Dissolution test using aqua-regia solution

In order to find out the total amount of Zr (IV) loaded onto the SCER, dissolution test using aqua-regia solution was carried out at 5 g/L solid liquid ratio. For this 250 mg of Zr(IV)-SCER was mixed with 50 mL of aqua-rea solution and stirred at the stirring speed of 200 rpm for 24 h at 30° C. Then after, it was filtered and filtrate was analyzed for Zr(IV) using ICP-AES.

## Results and Discussion

### Analysis of functional group by FTIR spectroscopy

The analysis of various functional groups is necessary for the required chemical modification in order to generate new active sites for phosphate adsorption. **Figure. 1** shows the FTIR spectra of the SCER where broad band observed at 3200- 3400 cm$^{-1}$ is due to OH stretching vibration while the peak at 2933 cm$^{-1}$ is due to C-H stretching vibration of aliphatic group, and those at around 1623 and 1597 cm$^{-1}$ is indicated C=C stretching mode of aromatic ring. The S=O stretching mode is indicated due to the presence of intense peak at 1246 cm$^{-1}$. Similarly, the peak observed at 1419 cm$^{-1}$ is due to the SO$_2$ group.

In addition, the peaks observed at around 1246, 1125, 1049and 1006 cm^{-1} shows the strong indication of the presence of the sulphonic acid functional group in the tested sample of SCER, suggesting that the SCER employed in this work contains sulphonic acid groups as major functional groups.
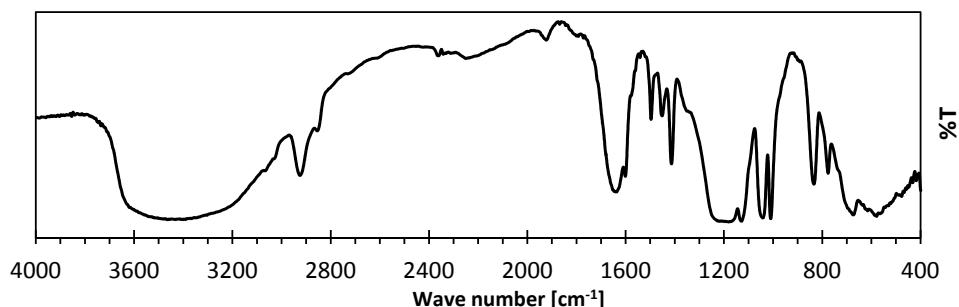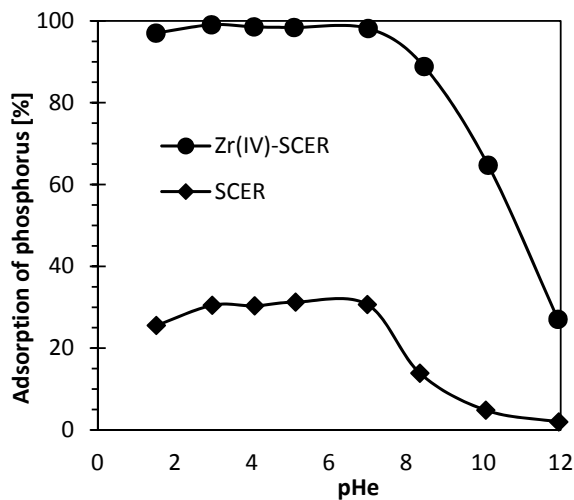


***Figure: 1*** *FTIR spectra of spent cation exchange resin showing different functional groups.*

### Measurement of total amount of Zr(IV) content in Zr(IV)-SCER

The aqua-regia solution is one of the strong leaching solutions for various metal ions. It is believed that complete dissolution can be achieved by using aqua-regia solution[10]. Total amount of Zr(IV) loaded onto Zr(IV)-SCER was determined by dissolving Zr(IV)-SCER using aqua-regia at 5 g/L and analysing the Zr(IV) concentration by ICP-AES , which gives 1.05 mmol/g .

### Effect of pH on the removal of phosphate ions

The adsorption of phosphate is affected by various physical and chemical factors and these factors determine the overall adsorption performance. Among various factors, solution pH has been known to be the most important regulator of the entire adsorption phenomena. The pH affects the solution chemistry of phosphate itself, the activity of functional groups on the adsorbent surface and the competition of coexisting ions in the aqueous solution. The influence of pH for phosphate adsorption using SCER before and after Zr(IV) loading is illustrated in **Figure. 2**. The result showed that the removal efficiency of phosphate was increased with increasing equilibrium pH from 1.5 to 2.95 in both the case. In the case of non-loaded SCER, the phosphate adsorption was observed to be



***Figure: 2*** *Effect of pH for the adsorption of phosphate using SCER before and after Zr(IV) loading.*

around 30% until pH 6.9 then decreased with further increase of pH. On the other hand, the % adsorption of phosphate was found to be higher than 98% from pH 2.9 to 7.2 in case of Zr(IV) loaded SCER then

start decreasing at higher pH. After Zr(IV) loading, the adsorption efficiency of SCER for phosphate reached 99.2% at pH = 2.9. The value was around 4 times higher than that of non-loaded SCER at similar experimental conditions. Such a drastic improvement of adsorption performance could be attributed to the development of new active anion exchange sites for phosphate anion during Zr(IV) loading. At extremely acidic pH (<1), some fraction of phosphate anion was converted into neutral phosphoric acid molecule ($H_3PO_4$) which was difficultly adsorbed onto the adsorbent whereas at pH around 1.5 to 10 it exist in its anionic species such as $H_2PO_4^-$, $HPO_4^{2-}$ and $PO_4^{3-}$ which were easily adsorbed onto the anion exchange site of Zr(IV) loaded SCER.

### *Adsorption isotherm of Zr(IV)-SCER for phosphate*

Adsorption isotherms are significant prerequisites to establish the most appropriate relationship between adsorbate and adsorbent and are critical in optimizing the design of an adsorption system for phosphate removal. The quantification of phosphate adsorption by SCER before and after Zr(IV) loading is fundamental for the evaluation of its potential. Phosphate adsorption ability of the adsorbent can be easily determined by mechanistic or empirical models; the former can explain and represent the experimental behavior, while the latter do not explain the mechanism, but can reflect the experimental plots. **Figure. 3A** shows the equilibrium adsorption isotherm of phosphate onto SCER before and after Zr(IV) loading at pH 6.7. The result shows that the adsorption of phosphate was observed to be increased with increasing equilibrium phosphate concentration at low concentration region where as it was observed to be level off or became constant or plateau value at higher concentration for both the adsorbents. In order to investigate the best fit model for phosphate adsorption, the experimental data were analysed using Freundlich, Langmuir and Flory-Huggins isotherm. The linear forms of Freundlich isotherm model is expressed by the equation as [11]

$$\log Q_e = \log K_F + (\ 1/n\ ) \log C_e \qquad (3)$$

where $K_F$ and n are the adsorption constants of Freundlich isotherm model generally related to the strength of interaction between adsorbate and sorbent. The values of $K_F$ and $1/n$ were determined from the intercept and slope, respectively, of the linear plot of experimental data of log ($q_e$) versus log ($C_e$) as shown in **Figure. 3B**. Similarly, a linear form of the Langmuir model is represented by the following equation [12].

$$\frac{C_e}{q_e} \quad = \quad \frac{1}{q_{max}b} \quad + \frac{C_e}{q_{max}} \qquad (4)$$

where $C_e$ (mmol/L) is the ultimate concentration of phosphate at equilibrium and $q_e$ (mmoL/g) is the corresponding adsorption capacity. $q_{max}$ (mmoL/g ) is the theoretical maximum monolayer phosphate adsorption capacity, and b (L/mmoL) is the Langmuir isotherm coefficients related to the binding energy and adsorption equilibrium constant. The value of equilibrium constant (b) and maximum loading capacity ($q_{max}$) were obtained respectively from the slope and intercept of straight line plot of $C_e/q_e$ *versus* $1/\ C_e$, (**Figure. 3C**). The evaluated values of isotherms constants were listed in the *Table 1.* The results showed that the maximum adsorption capacities of SCER and Zr(IV)-SCER for phosphate were found to be 0.31 and 2.03 mmol/g, respectively. The values of correlation regression coefficient for Langmuir model ($r^2 = 0.99$) was comparatively higher than Freundlich model which is only 0.96 for Zr(IV)-SCER and 0.93 for SCER, which indicates that the Langmuir model is the best fitted model for the adsorption of phosphate onto both SCER and Zr(IV)-SCER.

**Table 1** *Langmuir and Freundlich parameters for the adsorption of phosphate using SCER and Zr(IV)-SCER.*

| Adsorbents | pH | Langmuir Parameters | | | Freundlich Parameters | | |
|---|---|---|---|---|---|---|---|
| | | $q_{max}$ [mmol/g] | b [L/mmol] | $R^2$ | $K_F$ [mmol/ g] | n | $R^2$ |
| SCER | 6.7 | 0.31 | 7.7 | 0.99 | 0.54 | 5.7 | 0.93 |
| Zr(IV)-SCER | 6.7 | 2.03 | 2.4 | 0.99 | 1.02 | 2.0 | 0.96 |
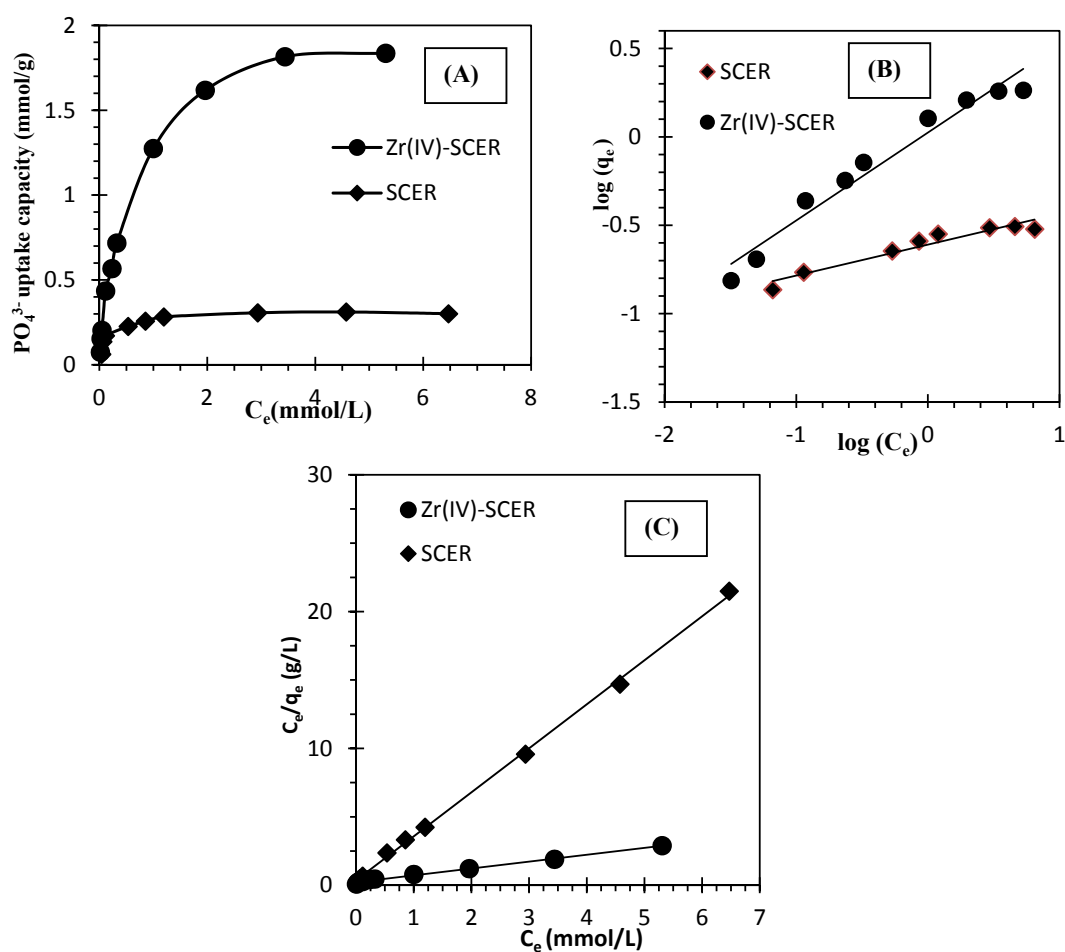


**Fig. 3** *Adsorption isotherm of SCER before and after Zr(IV) loading (A) Experimental plot, (B) Freundlich isotherm modeling and (c) Langmuir isotherm modeling.*

### Desorption and regeneration studies

Application of investigated adsorbent for real industrial application, maximum utilization of adsorption capacity of the adsorbent, regeneration and reuse for several cycles is preferred. Therefore, desorption behavior of phosphate from phosphate adsorbed Zr(IV)-SCER was evaluated. For this, desorption of phosphate from phosphate adsorbed Zr(IV)-SCER was carried out using deionized $H_2O$, 0.1M HCl, 0.1M NaCl and 0.1M NaOH solution. It was found that only 1.3 % of adsorbed phosphate was observed to be desorbed by using demonized water as desorbing solution where as it was 13.7, 68.2, and 94.7 % by using 0.1M NaCl, 0.1M HCl and 0.1M NaOH, respectively. Thus, desorption of phosphate using varying concentration of HCl and NaOH was carried out and the result is presented in **Figure. 4A**. It shows that desorption of phosphate from phosphate adsorbed Zr(IV)-SCER increase from 11% to 93% with increasing HCl concentration from 0.005 to 0.4 M and becomes nearly constant with further increase of HCl concentration. Similarly, the % desorption of phosphate also increased from 36 to 98.5% by increasing NaOH concentration from 0.005 to 0.2 M then become constant at higher concentration. Although HCl desorbs adsorbed phosphate effectively from phosphate adsorbed Zr(IV)-SCER, it potentially destroyed the active site by desorbing loaded Zr(IV) from the Zr(IV)-SCER.
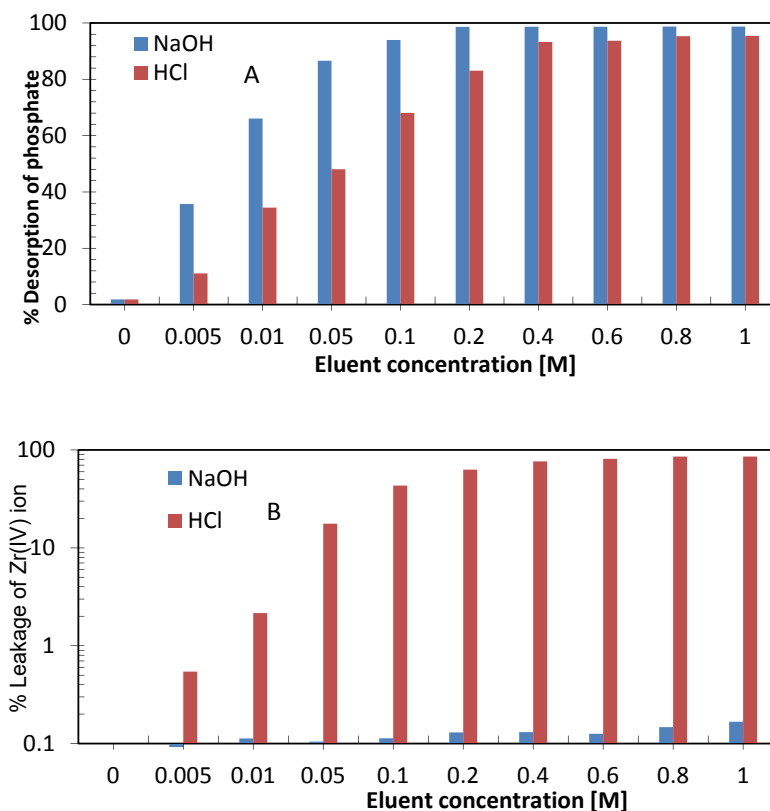


**Figure 4:** *Desorption of phosphate using varying concentration of HCl and NaOH (A) Desorption phosphate (B) Leakage of loaded Zr(IV) during desorption.*

**Figure 4B** shows the destruction of active sites of phosphate by desorbing loaded Zr(IV) using varying concentration of HCl and NaOH. The results shows that % leakage of Zr(IV) increased from 0.54 to 76.8 % by increasing HCl concentration from 0.005 to 0.4 M whereas it was less than 1% in similar concentration range by using NaOH solution. These result shows that 0.2M NaOH is more effective desorbing solution for the desorption of phosphate from phosphate adsorbed Zr(IV)-SCER.

*Mechanism of phosphate adsorption/desorption*

It is inferred that during the loading of high valent metal ions like Zr(IV), the neutralization of all four positive charges of Zr(IV) is difficult by large polymeric size of sulphonic acid rich SCER due to strong steric hindrance. Therefore, some positive charges of Zr(IV) ions are neutralized by sulfonic acid functional groups of SCER whereas rest were neutralized by hydroxyl ions from aqueous solution which are the main active sites for the removal of phosphate anion. These hydroxyl ions were likely to be substituted by anionic species of phosphate via ligand exchange mechanism as demonstrated in **Scheme 2** during adsorption process. Similarly, the adsorbed phosphate ions were inferred to be replaced by hydroxyl ions supplied from alkali solution during the desorption of adsorbed phosphate using NaOH solution as shown also in **Scheme 2**. Similar type of ligand exchange mechanism was described in our previous work for removal of fluoride using Zr(IV) loaded bio-sorbents [13-15]. Therefore, the plausible mechanism of phosphate adsorption/desorption is anion exchange reaction via ligand substitution mechanism.
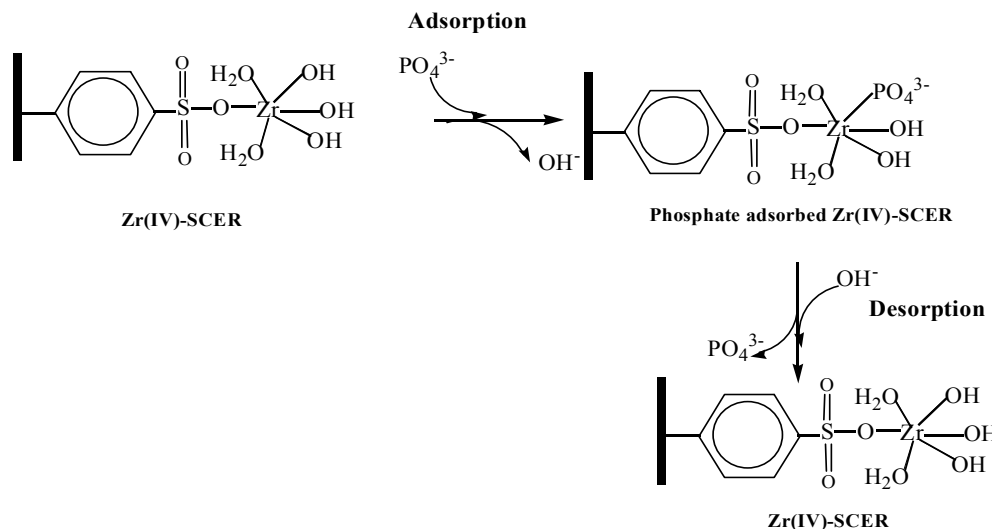


**Scheme 2** *Plausible mechanism of phosphate adsorption/desorption using Zr(IV)-SCER.*

## Conclusions

The anion exchange type adsorbent prepared by loading Zr(IV) onto SCER powder exhibited high adsorption capacity towards phosphate anion from water at slightly acidic to neutral pH condition. The adsorption isotherm studies showed that adsorption of phosphate by Zr(IV)-SCER follows typical Langmuir isotherm model indicating monolayer adsorption process. The trace amount of phosphate can be pre concentrated in continuous mode operation by using a column packed with Zr(IV)-SCER. Nearly

quantitative desorption of adsorbed phosphate has been achieved in short time by using dilute alkali solution. As the adsorption and desorption of phosphate onto the present adsorbents is pH dependent, the anion exchange mechanism is considered to be responsible for the preferential uptake of phosphate anion from aqueous medium. Therefore, the Zr(IV)-SCER adsorbent investigated in this study  has great potential for the removal and recovery of phosphate from water.

## Acknowledgement

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