Preparation of pectin based adsorbent for the uptake of phosphate anion from water

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Abstract

The natural anion exchanger was prepared from pectin enriched biomass of Mango fruit (Magnifera indica) by saponification followed by loading with trivalent iron i.e Fe(III) to eliminate phosphate from water. Characterization of adsorbent was done by elemental analysis and functional groups identification techniques. The result denoted that the phosphate adsorption using Fe(III)-SMW was easily controlled by switching pH value. The hydroxyl ions were released during uptake of phosphate using Fe(III)-SMW. The maximum uptake of Fe(III)-SMW for phosphate was determined as 4.08 mgg^{-1}using Langmuir isotherm model. Phosphate concentration after adsorption sharply decreased with increasing solid-liquid ratio and reached 100% uptake by using Fe(III)-SMW. Adsorbed phosphate anion was effectively desorbed (99.56%) by using 1M NaOH solution. Therefore, Fe(III)-SMW adsorbent seems as a promising, low-priced and potential materialto treat trace amounts of phosphate anion present in polluted water.

Keywords: Phosphate anion, mango waste, Fe(III) loading, adsorption, anion exchanger.

Introduction

The phosphate is one of the very important components of metabolism in both plants and animals[1]. The major role of phosphate in the biological system is to transfer energy in the form of ATP, Nucleic acids are made up of polyester chains of phosphates and sugars with organic nitrogen bases. Nowadays, the phosphates and its compounds are extensively used for the production of chemical fertilizer, water softening, paints, soaps, detergents, pharmaceuticals, corrosion inhibitors, beverages andtoothpaste[2,3]. The wastewater produced from such processing contains a high concentration of phosphate that after discharging into water bodies such as lake, pond and river invites the pollution of phosphate that results in the excessive growth of algae, which in turn causes the deficiency of dissolved oxygen concentration (DOC) and finally eutrophication[4,5]. So that it is necessary to treat such phosphate-rich effluents before discharging.

Phosphate exists in the form of its oxo-anionic species such as $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} in water[3]. Several technologies like chemical precipitation, crystallization; ion-exchange, biological treatment and sorption have been proposed for the treatment of phosphate from water[1,4-6]. The precipitation of phosphate by using salts of trivalent metal such as Fe(III) salts is one of the widely used technology but the separation of chemically-bonded phosphate is difficult[7]. The crystallization using calcium or magnesium salt in the form of HAP (hydroxyapatite,

$Ca_{10}(OH)_2(PO_4)_6)$ and MAP (Magnesiumammoniumphosphate, $MgNH_4PO_4.6H_2O$) is most extensively used commercialized technique. Although these crystallization techniques are convenient for the treatment of excess amount of phosphate anion however, they are unsuitable for the remediation of water with trace concentration of phosphate[8]. The ultrafiltration and ion exchange are effective. Application of ultra-filtration for wastewater treatment is a little bit expensive and available anion exchange resins are less selective to phosphate anions[9]. Therefore, there is a desperate need of developing new, low-priced, more efficient and environmentally benign technology to remove trace amount of phosphate from water.

The application of biomass-based adsorbents for the sequester of phosphate, fluoride and arsenic other toxic substances has gained attention because of their functional diversity and are easy for incineration[8]. Adsorbents derived from agricultural by-products are most attractive because of their low cost, availability and easy for regeneration and post-treatment[10, 11]. Different agricultural by-products has so far been studied to prepare efficient and cost-effective adsorbents for phosphate anion[12-14]. The waste biomass of Mango fruit (*Magnifera indica*) is an agro based by-product generated from the juice factories and consist of about12-18% of pectic substance which can be easily modified into useful ion exchange material by simple chemical modification.

From our previous experience, the pectin-based adsorbent prepared by loading high valent metal ion effectively adsorbed fluoride ion from water[15-17]. Literature shows that the ion exchange resin containing Fe(III) is effective for phosphate ion removal[13]. Therefore, in the present investigation, the pectin enriched biomass of _M. indica_ waste was selected to prepare adsorbent for phosphate anion removal. The main objectives of the present work is to prepare the adsorbent by using locally available, low -priced and environmental friendly biomass of Mango waste into valuable anion exchanger for phosphate anion removal by loading Fe(III) onto polymeric matrix of _M. indica_ waste and systematically employed to sequester phosphate anion from aqueous solution.

Materials and methods

Chemicals and analysis: Every chemicals employed in this experiment were of pure RG/LR grades which were directly prepared without further purification. 1.8735g $NaH_2PO_{4*}2H_2O$ dissolved in 1000mL water was taken as the phosphate stock solution (1000mgL^{-1}). The other required phosphate concentration was freshly made diluting appropriate quantity of the stock solution successively. The Fe(III) solution was made from ferric chloride salt. The pH value was managed after using 0.01M hydrochloric acid or 0.01M sodium hydroxide and pH was measured using pH meter (CHEMI LINE CL-180). The concentration of phosphate ion before and after adsorption in the test solution was analyzed spectrophotometrically from CHEMI LINE CL-350 UV-visible spectrophotometer.

Development of Fe(III) loaded SMW: The preparation of adsorbent for phosphate ion uptake was studied according to the procedure explained in Paudyal _et al_[18]. The waste biomass of Mango fruit (_M. indica_) was collected from the local juice vendor in Kathmandu, Nepal. For the adsorbent preparation, 100g of _M. indica_ waste was treated with 500mL of the saturated lime water solution and add 1-2 pellet of NaOH than stirred for 12h at room temperature. The methyl ester part of _M. indica_ pectin was chemically modified into carboxyl groups by saponification reaction with Ca(OH)$_2$ as shown in Scheme-1. The product obtained after saponification is known as saponified Mango waste and abbreviated as SMW. The loading of Fe(III) onto SMW was carried as follows. Five gram of SMW (dry basis) was mixed with 500 mL of 0.1M FeCl$_3$ solution and was stirred for 24h to load the Fe(III) onto SMW by cation exchange mechanism as depicted in Scheme-1. After continuous stirring for 24h, it was filtered and the residue was washed with deionized water repeated times and then dried at 60 -70°C for 12h. Thus, the final product is known as Fe(III) loaded Saponified Mango waste and abbreviated as Fe(III)-SMW. The flow sheet for the details of the preparation and its application for the sequestration of phosphate ion is depicted in Figure-1.
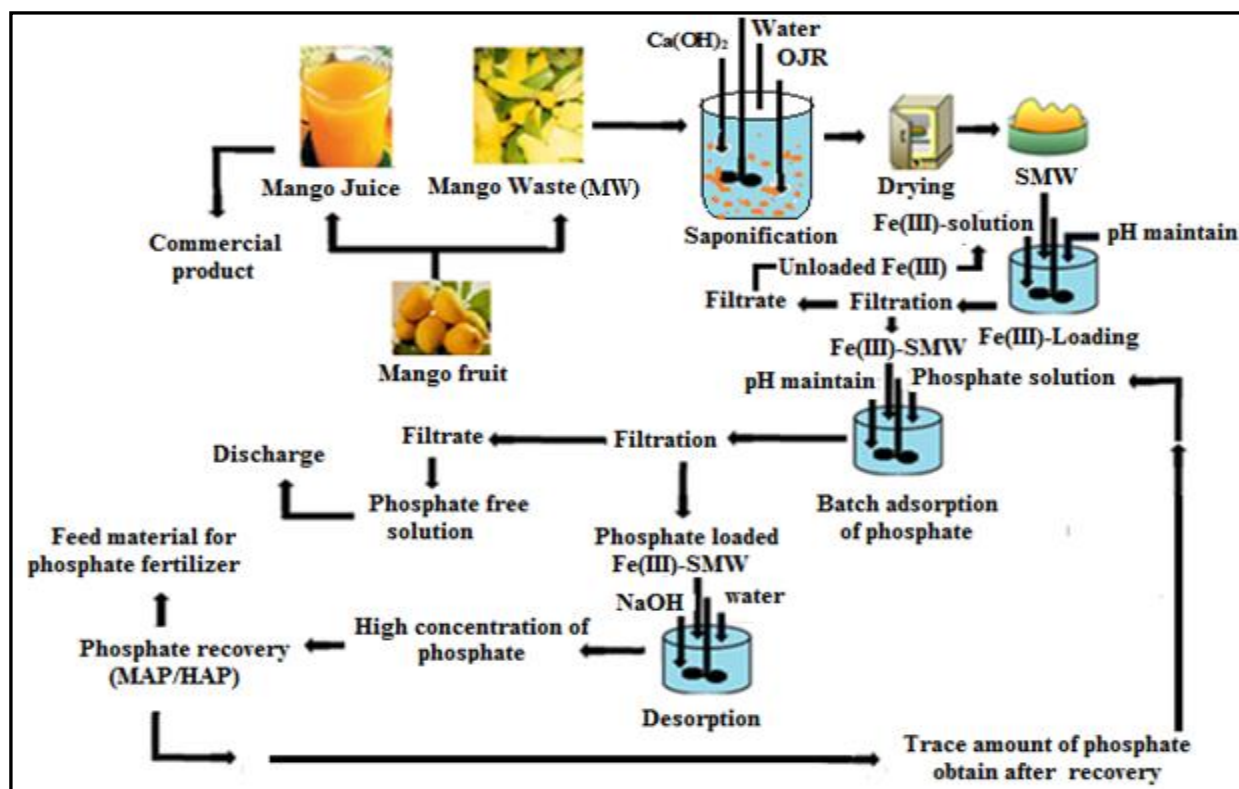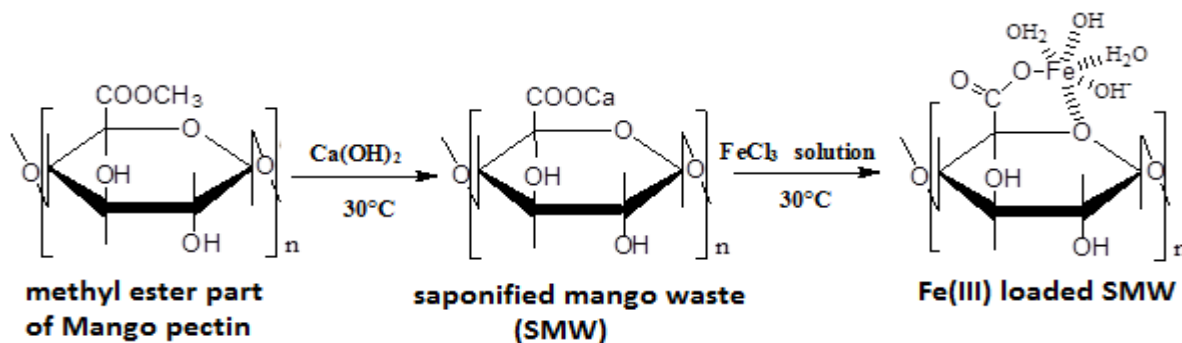

Figure-1: Flow sheet exhibiting the details of adsorbent preparation from waste biomass of Mango (_M. indica)_ fruit for the uptake of phosphate anion from water.

Scheme -1: Synthetic route of Fe(III) loaded Saponified Mango waste _i.e_ Fe(III)-SMW adsorbent.

Spectroscopic characterization by FTIR and EDX: The functional group changes during saponification and Fe(III) loading reaction were analyzed by recording the spectra using FT-IR spectrophotometer (SHIMADZU IR Affinity 1s model) between 4000 and 400cm^{-1}. The elemental content in the adsorbent of SMW before and afterwards loading Fe(III) were determined by energy dispersive X-ray (EDX) spectrometer microscopy(JEOL model JSM EDX).

Batch adsorption experiments: The typical batch adsorption experiments were performed in a 100mL reagent bottle to analyse the influence of pH, contact time, adsorbent dosage and initial phosphate concentration on the sorption of phosphate ion by using Fe(III)-SMW. For this 50mg of the Fe(III)-SMW was mixed with 25mL of 10mgL^{-1} of phosphate solution ranging pH from 2 to 12 was stirred for scheduled time periods to establish equilibrium. The equilibrated solution was separated by filtration and filtrate was appropriately diluted with deionized water for the measurement of residual phosphate concentration. The kinetic experiment was conducted in the same manner except that the samples were measured at varying contact times. The adsorption isotherm experiment was conducted at various range of concentration of phosphate anion at a solid-liquid ratio (S/L) of 2gL^{-1}. The quantity of phosphate was evaluated by spectrophotometer by developing blue colour phosphor molybdenum complex with ammoniummolybdate solution in acidic medium using hydrazine hydrate as a reducing agent[19]. The % of phosphate adsorption (A) and phosphate adsorption potential of Fe(III)-SMW were estimated from the given equations,

$$\% A = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

$$q = \frac{C_i - C_e}{W} \times V \tag{2}$$

Where: C_i and C_e (mg L^{-1}) are the concentration of phosphate before and after adsorption, respectively. Similarly, V (L) represents the volume of phosphate solution and W (g) is the weight of Fe(III)-SMW.

Desorption studies: Since it is clear from the adsorption experiment that the adsorption of phosphate was effective around neutral pH and it was analysed that adsorption is negligible in acidic and basic pH so that acidic or basic solution can be an effective solution for desorption. From the literature, it was found that the uses of acidic solution destroyed the active sites by desorbing loaded iron from metal loaded adsorbents. Therefore in the present investigative effective desorbing solution for phosphate from phosphate adsorbed Fe(III)-SMW was carried out using NaOH solution. For the desorption experiment, phosphate adsorbed loaded Fe(III)-SMW was prepared first by treating 500mg of Fe(III)-SMW with 200mL of phosphate solution (100mgL^{-1}) at neutral pH. After equilibration, it was filtered, washed till neutral pH and finally dried, which is known as phosphate adsorbed Fe(III)-SMW. The desorption of phosphate ion was continued by shaking 50 mg of phosphate ion adsorbed in Fe(III)-SMW with varying concentration of NaOH ranging from 0.01-2molL^{-1} at the S/L ratio of 0.5Lg^{-1} and shaked for 24h then filtered and filtrates were studied for the desorbed quantity of phosphate. The % of desorbed phosphate was calculated as,

$$\%D = \frac{D_{amount}}{A_{amount}} \times 100 \tag{3}$$

where, A_{amount} and D_{amount} are the amounts (mg) of phosphate anions adsorbed and desorbed.

Results and discussion

Characterizations of adsorbents: Modification of functional group by saponification and Fe(III) loading: The methyl ester groups present in mango waste biomass is expected to be changes after saponification and Fe(III) loading. To characterized these changes, the FTIR spectra of raw mango waste (RMW), SMW and Fe(III)-SMW were recorded as shown in Figure-2. The FTIR spectra of RMW showed broadband at around 3210-3460cm^{-1} because of the stretching vibration of hydroxyl groups of pectin, cellulose, hemicellulose and lignin compounds. The peaks at 2823 and 2939cm^{-1} are due to C-H stretching and the peaks at 1720 and 1651cm^{-1}are because of C=O stretching vibration of carboxylic acid and OH bending vibrations, respectively. After saponification reaction with

$Ca(OH)_2$, the peak at $1720cm^{-1}$ disappeared, and two peaks appeared at 1480 and $1641cm^{-1}$ which were characteristics of metal carboxylate bond i.e. calcium carboxylate in this case. The Fe(III) loading was done by replacing Ca(II) from Fe(III), which could be proved by the appearance of metal carboxylate adsorption band at a lower frequency (1423 and $1624cm^{-1}$) in Fe(III)-SMW than SMW which is because of the greater molecular weight of Fe(III) than Ca(II) ion.

Analysis of elemental contents by an EDX: To investigate elemental composition of the sample, EDX was carried out SMW before and after Fe(III) loading, the elemental examination of SMW and Fe(III)-SMW were done and the result are presented in Figure-3. As can be observed from the result of EDX spectra of SMW before Fe(III) loading that various metals such as K, Ti, Mn, Fe, Cu and Zn were observed at binding energy values of 3.34, 4.48, 5.88, 6.42, 8.06 and 8.64 keV respectively in addition to the intense peak of Ca at 3.70 and 4.02keV. The presence of the comparatively higher amount of calcium in the sample of SMW was evidenced by the observation of highly intensified peak value for Ca metal. Other metals such as Fe, Mn, Cu, K, Zn were observed with small intensity value suggesting that these metals ions are in trace concentration in the tested adsorbent of SMW.

After Fe(III) loading, the intensity of Fe was drastically increased from 1.16 cps/μA to 2255.56 cps/μA at energy values of 6.42keV. In addition to this, Fe was also detected at 8.02 keV and 12.80keV in Fe(III)-SMW which were not detected in the non-loaded sample. These results provide direct evidence that Fe(III) was loaded in an effective way onto the sample of SMW. Additionally, the intensity of Ca observed at 4.02keV was completely disappeared and intensity of Ca observed at 3.7 keV was reduced from 165.25cps/μA to 84.22cps/μA after Fe(III) loading. All of these fact strongly suggest that Fe(III) was successfully loaded onto SMW *via* a cation exchange reaction between Ca(II) or K(I) from SMW and Fe(III) from an aqueous solution of $FeCl_3$ employed for the loading reaction as depicted in Scheme-1.
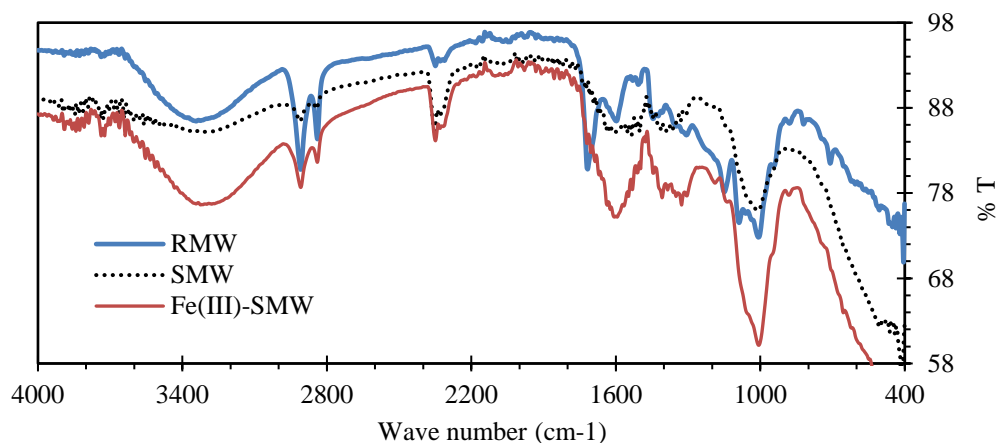

Figure-2: Functional group modification in mango waste biomass by saponification and Fe(III) loading.
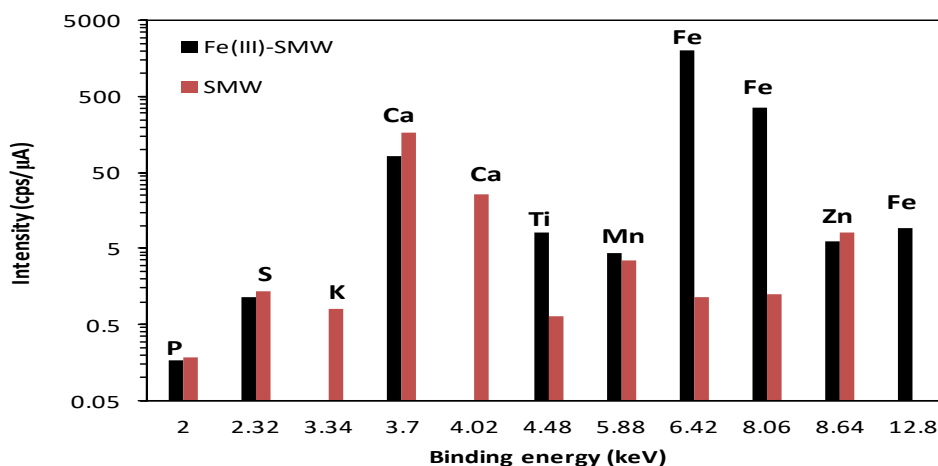

Figure-3: Qualitative analysis of different elements in the sample of (a) saponified Mango waste (SMW) and (b) Fe(III) loaded SMW *via* EDX spectroscopy.

Application of Fe(III) loaded SMW for phosphate ion adsorption: Influence of pH and adsorption mechanism: The pH of solution determines the speciation of phosphorus anions at different forms thus the adsorption process vary with the pH of solution together with the functional groups remain on the adsorbent surface. The distribution of various phosphorus species at different pH is depicted in Figure-4[20]. This figure suggested that tri-protonated species is dominant at pH below 2.12 whereas di-protonated and mono-protonated species were dominant at pH around 2.12 to 7.20 and 7.20 to 12.36, respectively. The non- protonated phosphate is dominant at pH higher than 12.36.
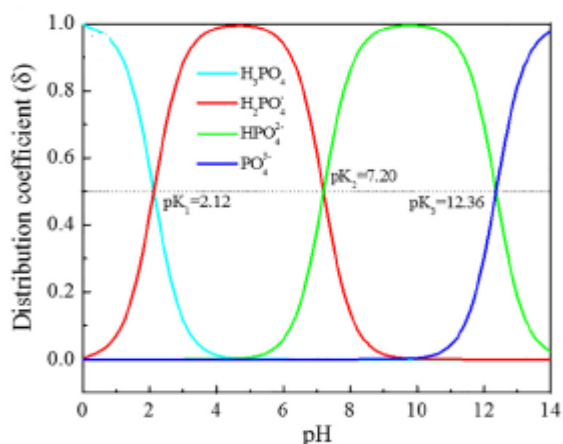

Figure-4: Speciation diagram of various phosphorus species at different pH[20].

Figure-5 highlights the relationship between the percentage adsorption of phosphate anions onto SMW before and after Fe(III) loading by varying pH range of 2-12. According to the result shown in this figure that adsorption of phosphate using non-loaded SMW was insignificant because percentage adsorption of phosphate was not higher than 7% even at optimum pH. However, in using Fe(III)-SMW, the percentage adsorption of phosphate drastically improved. The phosphate adsorption percentage increases with raising equilibrium pH and pH lower than 6 and attain maximum value around pH 7.5. After this, it was decreased with the further increase in equilibrium pH as shown in Figure-3.
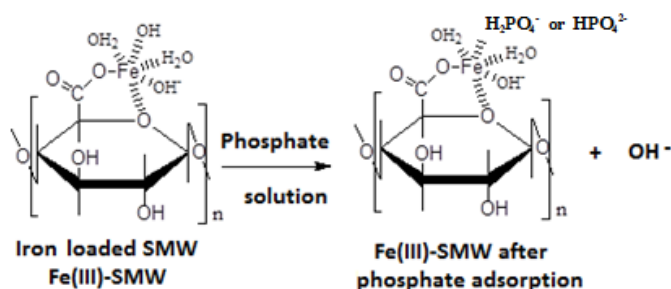
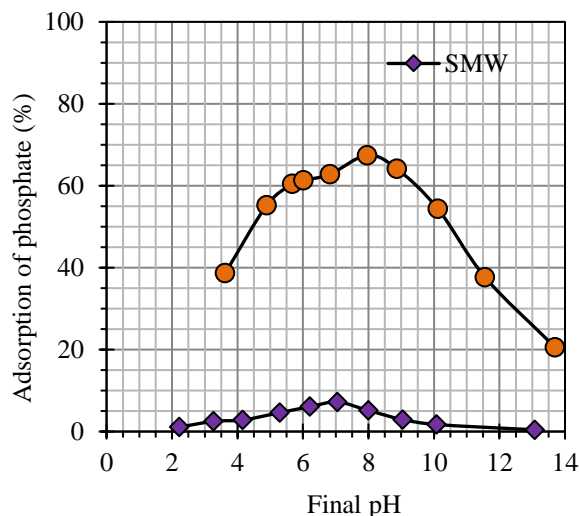**Scheme-2:** Plausible mechanism of adsorption of phosphate by Fe(III)-SMW.

Figure-5: Influence of pH on phosphate ion adsorption by Fe(III)-SMW (conditions: V = 25mL, adsorbent amount = 50 mg, phosphate concentration = 10mgL^{-1}, shaking speed = 200 rpm, shaking time = 24h and temperature = 25°C).

At acidic pH (below 3), the concentration of tri-protonated species (H_3PO_4) of phosphorus increases in the solution that difficulty adsorbed onto Fe(III)-SMW so that % adsorption of phosphate ion decreased at lower pH. The % A of phosphate was observed to be highest at pH around 6 to 9 therefore mono-protonated phosphate (HPO_4^{2-}) and di-protonated phosphate ($H_2PO_4^-$) species were effectively adsorbed onto Fe(III)-SMW by substituting hydroxyldue to ligand substitution mechanism as depicted in Scheme-2. With increase in pH, the quantity of hydroxyl ion also accelerates that may compete with phosphate anion for the adsorption site which ultimately decreases the percentage adsorption[22].Moreover, the pH was raised after adsorbed phosphate which is attributed by the displacement of hydroxyl ions which is the prime support of giving hydroxyl ion during phosphate adsorption as demonstrated in scheme 2. A similar observation was reported by Biswas *et al*[21] and Paudyal *et al*[3] for the sorption of phosphate using Zr(IV) loaded spent cation exchange resin and Zr(IV) loaded orange waste, respectively.

Adsorption isotherm of phosphate: Adsorption isotherm of phosphate is a plot that shows the relationship between the phosphate uptake capacities of adsorbent versus equilibrium phosphate anion concentration. For the investigation of sorption potential of adsorbent, the effect of phosphate concentration during adsorption on to Fe(III)-SMW was carried out at pH 7 and the data is depicted in Figure-6. From the result of this Figure illustrated that the uptake of phosphate enhanced with gradual increase of phosphate concentration at low concentration region, whereas it signifies a plateau value at high concentration indicating the monolayer formation of phosphate on the surface of Fe(III)-SMW. To investigate the appropriate model for adsorption of phosphate, the adsorption equilibrium data were fitted to Langmuir and Freundlich equation. The

linear form of the Langmuir monolayer adsorption model can be shown mathematically (Equation-4) in linear form as[23]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}b} + \frac{C_e}{Q_{max}}$$ (4)

where, C_e (mgL^{-1})is the equilibrium concentration and Q_e (mg g^{-1}) is quantity of adsorbed phosphate at equilibrium. Similarly, Q_{max} is the maximum loading capability and b is the Langmuir adsorption equilibrium constant related to the energy of adsorption. The maximum adsorption capability (Q_{max}) and adsorption equilibrium constant (b) were determined from the slope and intercept of the linear plot of C_e/Q_e *versus* C_e (Figure-7a). These values are depicted in Table-1. The Freundlich isotherm model can be specified in the form of the following equation (Equation 5) as[24].

$$\log Q_e = \log K_F + (1/n) \log C_e$$ (5)

Freundlich constants K_F and n are related to the adsorption capacity and intensity, respectively. The value of K_F and n were evaluated from the intercept and slope of the log Q_e *versus log C_e plot* as shown in Figure-7b. The evaluated values are also shown in Table-1. From the result presented in this table shows that higher value of the correlation coefficient was observed in case of Langmuir model ($R^2 = 0.99$) whereas in the Freundlich isotherm model, the value of R^2 was only 0.96. It strongly suggests that Langmuir isotherm model is good fit to equilibrium data more than Freundlich isotherm model.

Moreover, for the inspection of the suitability of an adsorption process, a dimensionless parameter (R_L) was applied which was determined by using the following equation[25].

$$R_L = \frac{1}{1+bC_i}$$ (6)

Table-1: Isotherm model for phosphate adsorption by Fe(III)-SMW.

Langmuir isotherm	$Q_{max..}$ (mgg^{-1})	4.08
	b (Lmg^{-1})	0.27
	R^2	0.99
Freundlich isotherm	K_F (mgg^{-1})	1.27
	n	4.38
	R^2	0.96

where b (Lmg^{-1}) is Langmuir equilibrium constant, C_i(mgL^{-1}) is the initial concentration of phosphate anion. The value of R_L may be zero, one, or greater than one showing irreversible, linear, and unfavourable nature of adsorption reaction, respectively. From the experimental result of all the concentration examined it was found that the value of R_L for initial phosphate concentration of 4.86, 9.43, 18.86, 29.14, 38.71, 49.29, 58.00, 68.43 and 79.29 mgL^{-1} were found to be 0.43, 0.21, 0.16, 0.11, 0.08, 0.06, 0.05 and 0.05, respectively. All of these values are less than unity *i.e.* $0 < R_L < 1$, which implies that the adsorption of phosphate onto Fe(III)-SMW is favourable.
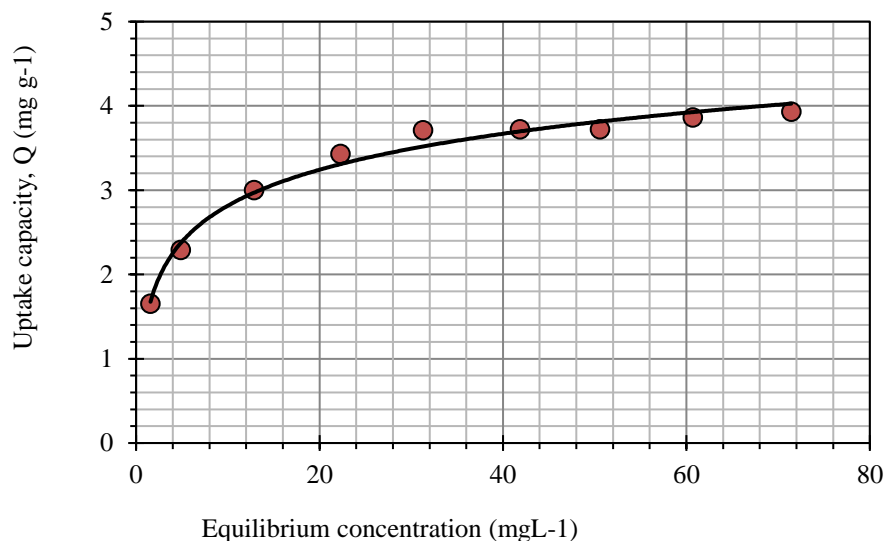

Figure-6: Adsorption isotherm of phosphate using Fe(III)-SMW from aqueous solution. Water (conditions: phosphate solution = 25 ml, adsorbent = 50 mg, pH = 7, shaking speed = 200 rpm, shaking = 24h and temperature = 25°C).
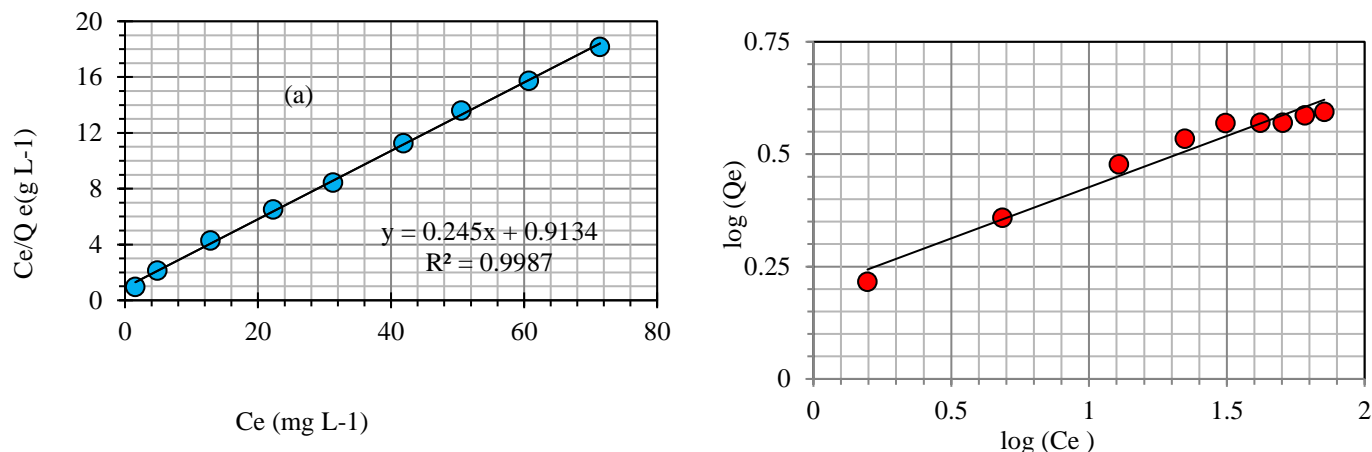
Figure-7: Modelling of experimental data using (a) Langmuir isotherm and (b) Freundlich isotherm.

Effect of S/L ratio: To investigate the potentiality of Fe(III)-SMW for the uptake of trace concentration of phosphate, the adsorption test of phosphate was carried out at various S/L ratio varying from 0.2 to 8gL^{-1} and the data is depicted in Figure-8. It is illustrated that the residual concentration of phosphate sharply decreased with raising solid-liquid ratio. The phosphate concentration after adsorption was reached from 9.71mgL^{-1} to 2.29mg L^{-1} by taking 2g L^{-1} of Fe(III)-SMW whereas only 6gL^{-1} is sufficient to lower the phosphate concentration down to 0.05 mg L^{-1}. Moreover, more than 7g L^{-1} of Fe(III)-SMW fortunately uptake 100% of phosphate from water. Therefore, Fe(III)-SMW analysed in this experiment can be a leading material to treat the trace concentration of phosphate anion carrying effluents in water.
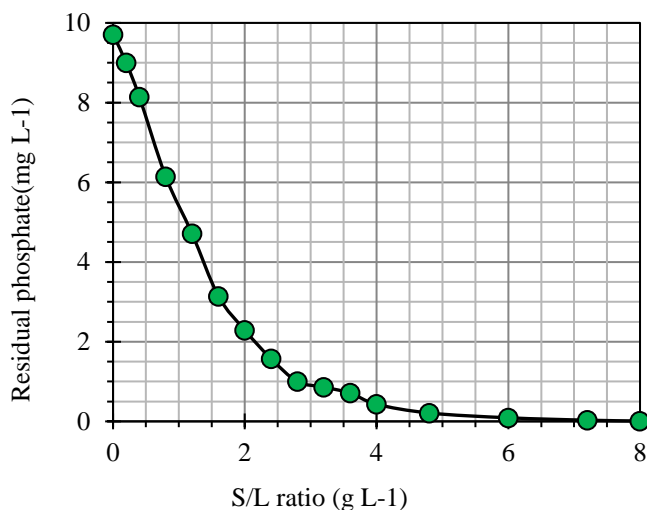

Figure-8: Effect of S/L ratio for the adsorptive uptake of phosphate from water (conditions: phosphate solution = 10mL, phosphate concentration =9.71mgL^{-1}, pH = 7, shaking time = 24h and temperature = 25°C).

Desorption study: From the previous literature, the desorption using acidic solution destroyed the active sites by leaching loaded metal ions from metal loaded adsorbents[13,21], so that basic solution was employed for the optimization of adesorbent in the present investigation. The relationship between the percentage desorption of phosphate from phosphate loaded Fe(III)-SMW as a function of NaOH concentration is represented in Figure-9. It can be understood from the outcome of this figure that % A of phosphate anion sharply increased from 1.86% to 97.59% by gradual increase of NaOH concentration from 0.01 to 1M then it was slow and reached 99.56% by using 1.5M NaOH. Nearly complete desorption of (99.86%) of adsorbed phosphorus can be achieved by using 2M NaOH solution. The inferred mechanism for the desorption of phosphate ion from phosphate loaded Fe(III)-SMW is shown in Scheme-3. As can be observed from this scheme that desorption of phosphate anions occurred by the ligand substitution reaction between adsorbed phosphate from phosphate loaded Fe(III)-SMW and hydroxyl ions from NaOH solution so that % desorption of phosphate anion increased reasonably with increasing concentration of NaOH solution.
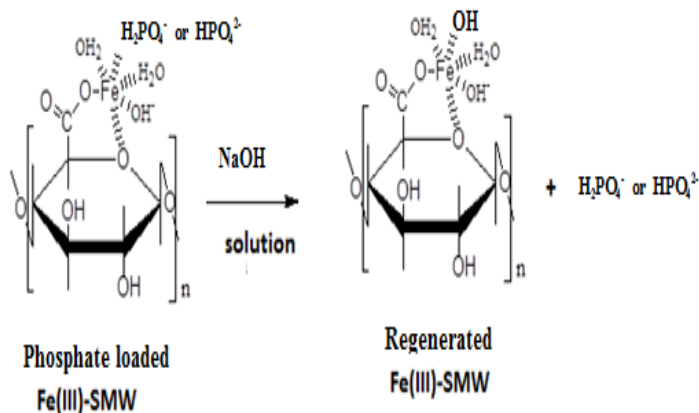
Scheme-3: Desorption of adsorbed phosphate ion from phosphate loaded Fe(III)-SMW.
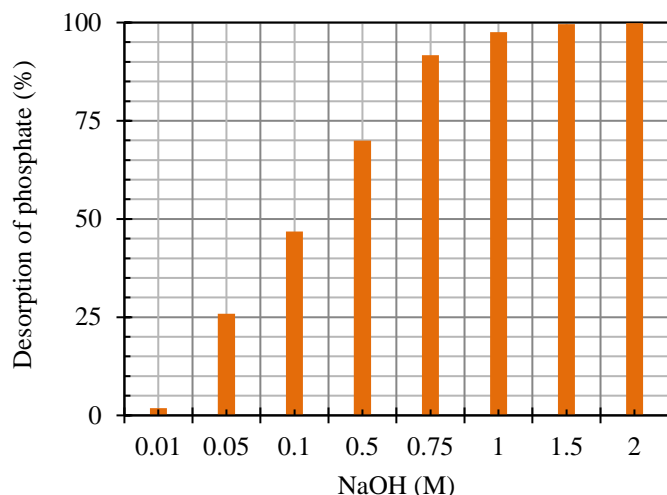
Figure-9: Desorption of phosphate using NaOH solution (conditions: volume of NaOH = 10mL, phosphate amount = 1.8 mgg^{-1}, pH = 7, shaking speed = 200rpm, shaking time = 24h and temperature = 25°C).

Conclusion

Natural anion exchanger for phosphate ion removal was developed from waste biomass of Mangofruit (*M. indica*) by saponification followed by Fe(III) loading in this work. The Ca(II) from SMW was substituted by Fe(III) during loading reaction which was evidenced from EDX analysis. The percentage adsorption of phosphate by Fe(III)-SMW was found to be maximum at pH around 7.5. The capability of this adsorbent for phosphate adsorption accelerate sharply with gradual rise in concentration at low concentration region and attains constant or plateau value at a higher concentration from which the nature of adsorption is concluded to be Langmuir type adsorption. Phosphate concentration after adsorption was decreased sharply with the increase of Fe(III)-SMW dosage, is concluded because of the increase of active adsorption sites for phosphate anion. Phosphate anion adsorbed onto the Fe(III)-SMW is proficiently desorbed by adding caustic soda solution for the recovery and regeneration of adsorbent. Therefore the Fe(III)-SMW adsorbent studied here can be an innovative adsorbent to treatphosphate from water.

Acknowledgements

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