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Zirconium-Modified Sweet Orange (Junar) Peel for Efficient Removal of Phosphate from Water

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Abstract

Phosphate pollution poses a major threat to aquatic ecosystems, causing eutrophication and degrades aquatic system. Despite numerous reported adsorbents, the lack of viable low-cost, and efficient bioadsorbents remains a critical research gap. This study investigates zirconium (IV)-modified saponified sweet orange (Junar) peel powder (Zr(IV)-SJP) as an eco-friendly biosorbent for removing phosphate from water. Batch experiments were conducted with zirconium (IV)-modified saponified sweet orange (Junar) peel powder (Zr(IV)-SJP). Maximum phosphate removal was achieved at pH 4, with equilibrium reached within 150 minutes. Adsorption followed pseudo-second-order (PSO) kinetics and the Langmuir isotherm, with adsorption capacity of 114.03 mg/g. Characterization using FTIR and XRD confirmed the successful modification and strong affinity of Zr(IV)-SJP toward phosphate ions. These results highlight Zr(IV)-SJP as a cost-effective, eco-friendly bioadsorbent capable of efficiently mitigating phosphate contamination in water.

Keywords: Adsorption capacity, Bioadsorbent, Junar peel, Phosphate, Zr(IV) loading

Introduction

Phosphorus (P) is commonly occurring in natural systems such as phosphate and forming key components of DNA, RNA, ATP, and cellular structures (Corbridge, 2013; Pokhrel *et al.*, 2019). Its widespread application in fertilizers, detergents, corrosion inhibitors, food and chemical industries results in significant phosphate inputs into water bodies through agricultural runoff, domestic wastewater, and industrial discharges (Song *et al.*, 2011; Mustaffa *et al.*, 2019). When circulated more than the regulatory limits of 5 ppm, phosphate produces eutrophication, harmful algal blooms, and oxygen depletion, initiating severe ecological risks (HMG/MoPE, 2012; Wurtsbaugh *et al.*, 2019; Rahman *et al.*, 2020). Various techniques have been developed to control phosphate pollution, including precipitation, crystallization, membrane filtration, ion exchange, and adsorption techniques (Huang *et al.*,

2014; Lee *et al.*, 2019). However, many conventional techniques are constrained by high operating cost, sludge generation limitation, or reduced efficiency at low phosphate concentrations (Desmidt *et al.*, 2015; Ajmal *et al.*, 2018). Biosorption has emerged as an effective and economical alternative due to its ease of operation technique, low sludge production, and adaptability for treating dilute phosphate solutions (Awual *et al.*, 2011; Pokhrel *et al.*, 2019).

Agricultural wastes are particularly promising biosorbents because of their natural polymers, such as cellulose, lignin, and pectin, which carry functional groups in the biological molecules capable of interacting with anionic contaminants (Nguyen *et al.*, 2014; Yadav *et al.*, 2015). The adsorption performance of such biomass materials can be significantly improved through loading multivalent metal ions, especially zirconium, iron, aluminum, and cerium, which possess strong affinity for phosphate (Biswas *et al.*, 2008; Zeng *et al.*, 2018; Aryal *et al.*, 2022; Pant *et al.*, 2024). Numerous metal-loaded biosorbents, including Zr-modified orange peel, Zr-treated okara, Fe-loaded skin waste, and Zr-functionalized watermelon rind, have shown high phosphate removal efficiency (Biswas *et al.*, 2008; Nguyen *et al.*, 2014; Aryal *et al.*, 2022). Sweet orange (*Citrus sinensis*), known locally in Nepal as "Junar", generates considerable peel waste that is rich in pectin and other polysaccharides capable of binding metal ions (Poudel *et al.*, 2022; Yadav *et al.*, 2015).

Although citrus peels have been studied for other adsorption applications, the use of Junar peel for phosphate-specific biosorption remains limited. Modified Junar peel with Zr(IV) offers a viable pathway to produce a high affinity bio-adsorbent suited for phosphate removal (Awual *et al.*, 2011; Biswas *et al.*, 2008). The aim of this work was to prepare and characterize a Zr(IV)-SJP and to evaluate its execution for removing phosphate by batch adsorption experiments.

Materials and Methods

Reagents

$ZrOCl_2 \cdot 8H_2O$, ≥99% purity and NaH_2PO_4, ≥99% purity were used as chemical reagents. All solutions were prepared using deionized water with a pH of 6.8–7.0.

Preparation of Adsorbents

Junar peels were collected from different fruit shops of Kalimati. They were washed with water and subjected to sunlight for drying. The dried peels were chopped into small pieces and were grinded. Then the powder was sieved through a 180-micron sieve to obtain a definite particle size and washed and dried for 24 h for preparation of raw Junar peel powder (RJP). 10 g of RJP was treated with 50mL of saturated $Ca(OH)_2$ solution in a beaker and stirred for 24 hours under an intense magnetic stirrer. The mixture was maintained at a pH around 12. The washing process with deionized

water was repeated until the mixture got to a neutral pH. The oven dried mixture over 12 hours at 60 °C was grinded to obtain fine particles designated as saponified Junar peel powder (SJP). 5 g of SJP was treated with 50 mL of 0.1 M $ZrOCl_2.8H_2O$ maintaining at pH 2.2. The mixture was stirred for 24 hours then filtered, washed with distilled water, and dried. The dried mixture was grinded to obtain fine powder of Zr(IV)-SJP.

Characterization

A PerkinElmer Spectrum IR (version 10.6.2) FTIR spectrometer was utilized to identify the functionality present in bioadsorbents. A Rigaku diffractometer was used for XRD examination to assess the crystallinity of the bioadsorbent.

Batch pH experiment

25 mL of pH-adjusted 20 mg/L of PO_4^{3-} solution with 25 mg of an biosorbent were stirred for 24 hours to attain equilibrium over a wide range of values of pH from 1 to 12 by using solutions of 0.1M HCl as well as 0.1M and 1M NaOH. After equilibration, the solutions were filtered. The filtrate was analyzed to determine the final phosphate concentrations using molybdenum blue method (Subedi *et al.*, 2022).

Percentage adsorption (%) and adsorption capacity (mg/g) at equilibrium are computed using the subsequent formula:

$$\%A = \frac{C_i - C_e}{C_i} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$q = \frac{C_i - C_e}{W} \times V \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where C_i represents the adsorbate solution's starting concentration and C_e represents its equilibrium concentration. W stands for the weight of the adsorbent and V for the volume of adsorbate solution in the adsorption tests.

Effect of Initial Concentrations

Biosorption isotherms studies were performed by the changing initial concentration of PO_4^{3-}. 25 mL of corresponding optimum pH adjusted solution of different concentration. The solutions were agitated for 24 hours with an adsorbent dose of 25 mg. The final PO_4^{3-} concentration in the filtrate was measured spectrophotometrically.

Effect of Contact Time

25 mL of corresponding optimum pH-adjusted Phosphate solution of 20 mg/L concentration was taken in a 100 mL conical flask, and 25 mg of corresponding adsorbents were added and the mixture was shaken. It was filtered, and the PO_4^{3-} concentration in the filtrate was inspected spectrophotometrically.

Results and Discussion

Characterization

The FTIR spectra of bioadsorbent were measured in the range of 4000 - 400 cm^1. **Figure 1** displays the FTIR spectra of RJP and Zr(IV)-SJP. Functional groups like hydroxyl, carboxyl, ketonic, aromatic, and aliphatic stretching were seen in the bioadsorbent surface. The FTIR spectra of Zr(IV) loaded sample shows that some changes have been taken place as the band at 1031 cm^{-1}, 1265 $cm^{-1}$and 1654 cm^{-1}.

The XRD pattern of SJP and Zr(IV)-SJP, as shown in **Figure 2** of both samples shows a slight broadening in between the 2θ values of 15-19 and 21-24, which indicates the formation of Calcium pectate during the saponification process and crystallization of zirconium hydroxide in the Zr(IV) loading process (Poudel *et al.*, 2021).

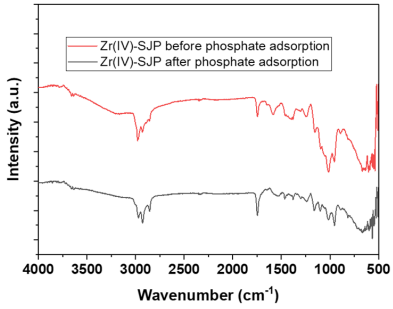

Figure 1: *FTIR Spectrum of adsorbent before and after adsorption.*

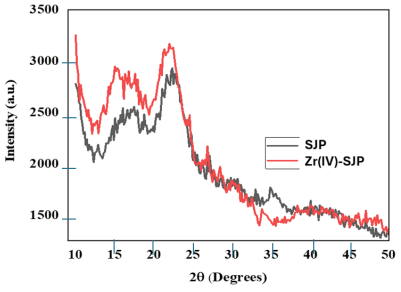

Figure 2: *XRD pattern of SJP and Zr(IV)-SJP measured at 2θ values ranging from 10 to 50 degrees.*

Effect of pH

The q_{max} is strongly influenced by the solution pH and the surface chemistry of the solid material (Biswas et al., 2007). **Figure 3** shows that for both RJP and Zr(IV)-SJC, the slightly acidic condition was favourable for phosphate adsorption. Both these adsorbents showed maximum adsorption at pH 4.0, which aligns well with the study carried out by Bashyal *et al.* (2023).

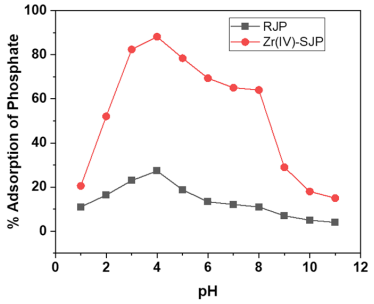

Figure 3: *Effect of pH on removal of* PO_4^{3-}.

Depending upon the pH of the solutions, phosphate exists in three different ionic species mono, di and trivalent ions i.e. $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} ions, respectively. At pH values below 2, H_3PO_4 is the predominant species in the solution however between pH 2 to 9. $H_2PO_4^-$ and HPO_4^{2-} ions become the dominant species. These ions are likely adsorbed onto the adsorbent through a substitution reaction involving OH^- ions or H_2O molecules coordinated with Zr(IV) ions in their hydrated state. At pH < 2, the dominant species $H_2PO_4^-$ becomes protonated to H_3PO_4. These neutral molecules have a low likeness towards the adsorption site, which leads to low adsorption at low pH. At pH > 9, HPO_4^{2-} and PO_4^{3-} are predominant. The weak affinity of these species for the adsorption site is associated with effective competition between OH^- ions and PO_4^{3-} ions (Biswas *et al.*, 2008). The optimum pH for removing phosphate on RJP and Zr(IV)-SJP was found to be 4.0.

Effect of Contact Time and Kinetic Modeling

The result of the effect of contact time on adsorption of PO_4^{3-} onto Zr(IV)-SJP is shown in **Figure 4.** The study illustrates that the equilibrium contact time for removing phosphate on Zr(IV)-SJP accomplished within 150 min at pH 4.0. The result implies that phosphate uptake took place rapidly during the initial stage of contact, which can be ascribed to the abundance of accessible active sites on the biosorbent surface, permitting efficient adsorption. As the process progressed, the biosorption rate slowly diminished and eventually reached equilibrium for Zr(IV)-SJP at a defined contact time. Beyond this point, no noticeable improvement in adsorption was observed, which is associated with the increasing occupation of active sites and saturation of the adsorbent surface, leading to a constant adsorption capacity.

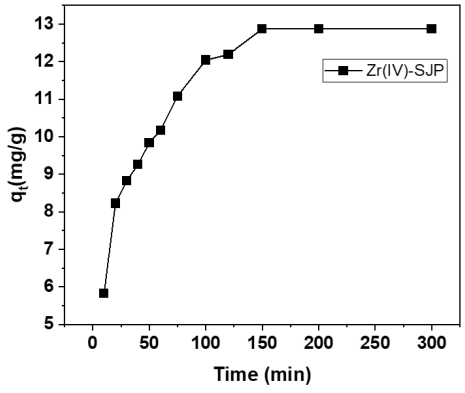

Figure 4: *Effect of contact time for the removal of PO_4^{3-} onto Zr(IV)-SJP.*

The parameters of kinetics of adsorption of phosphate on Zr(IV)-SJP are tabulated in **Table 1**. The study shows that R^2 for the PSO model is higher than that for the pseudo-First-order (PFO) model for Zr(IV)-SJP. **Figure 5** denotes a non-linear kinetic.

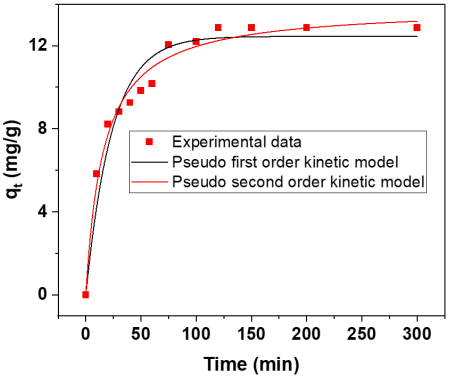

Figure 5: *Non-linear plot of PFO and PSO models.*

Table 1: *Kinetic parameters for removal of phosphate onto Zr(IV)-SJP*

Order	R^2	q_e (exp) (mg/g)	q_e (cal) (mg/g)	k_1 (min^{-1})	k_2 (mg/g/min)
PSO	0.982	13.73	13.88	-	0.004
PFO	0.950	13.73	11.35	0.05	-

Impact of Phosphate Concentration and Isotherm Modeling

The impact of adsorbate concentration was investigated at the optimum pH 4.0. The adsorption of phosphate increases with rise in the initial concentration and attains an equilibrium after which it happens to almost

constantly. This behavior is attributed to the limited availability of unoccupied adsorption sites. Higher phosphate concentrations enhance the driving force for mass transfer, thereby increasing the adsorption capacity at elevated concentrations. Nonlinear isotherm modelling along with experimental data has been displayed in **Figure 6**. The estimated values of isotherm parameters are listed in **Table 2**.

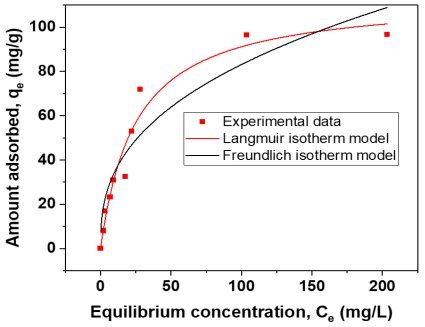

Figure 6: *Non-linear isotherms modelling for adsorption of phosphate onto Zr(IV)-SJP.*

Table 2: *Estimated values of isotherm parameters that determine for the removal of phosphate adsorbed onto Zr(IV)-SJP*

Adsorbate	Langmuir model			Freundlich model		
	q_{max} (mg/g)	K_L (L/mg)	R^2	K_F [(mg g^{-1}) (L $mg^{-1})^{1/n}$]	1/n	R^2
Phosphate	114.03	0.040	0.97	14.43	0.38	0.88

Table 3: *q_{max} of several adsorbents conveyed in the literature*

Biodsorbent	Optimum pH	q_{max} (mg/g)	Reference
Zn(II) activated coir pith	3-10	5.10	Namasivayam & Sngeetha, 2004
Acid mine drainage treated juniper fiber	6.4	7.08	Han *et al.*, 2005
Wood modified by carboxymethyl cellulose/ $FeCl_2$	-	17.38	Liao *et al.*, 2006
Fe(III) loaded Okara	7.6-7.8	16.39	Nguyen *et al.*, 2014
Zr(IV) loaded apple peels	2-6	20.35	Mallampati & Valiyavettil, 2013
Fe(III) loaded carboxylated polyacrylamide grafted saw dust	2.5	28.79	Unnithan, 2002
Bagasse fiber carboxylmethylated on surface and doped with $FeCl_2$	-	53.8	Carvalho *et al.*, 2011
Zr(IV) loaded orange waste gel	7.0	175	Biswas *et al.*, 2008
Zr(IV) loaded SJP	4.0	114.03	Present study

The Langmuir model displayed a R^2 matched to the values Freundlich model, implying a better match to the experimental data. This implies that biosorption process involves monolayers on a homogeneous surface with uniformly distributed active sites. From Langmuir isotherm model, the value of q_{max} for Zr(IV)-SJP obtained to be 114.03 mg/g.

An assessment of q_{max} of inspected adsorbents with the various adsorbents reported in the literature is demonstrated in **Table 3**. It shows adsorption capacity of adsorbents containing Zr(IV) is high for phosphate ions. In addition to this, the Zr(IV) loaded adsorbents investigated in this study possess high adsorption capacity among the adsorbent reported in the above table, indicating that the Zr(IV)-SJP investigated here could be the promising materials for removing phosphate ion.

Conclusion

Zirconium (IV)-modified saponified junar peel powder (Zr(IV)-SJP) proved to be an effective and sustainable biosorbent for removing phosphate from water. FTIR analysis endorsed the existence of surface functionality involved in phosphate binding, while XRD analysis revealed the predominantly amorphous nature of the adsorbent, which is favorable for adsorption. Optimal conditions-pH 4, yielded a high q_{max} of 114.03 mg/g. The process pursued the Langmuir isotherm and PSO kinetics, revealing monolayer chemisorption. Compared with many reported materials, Zr(IV)-SJP offers superior performance, highlighting its promise as affordable eco-sustainable solution for controlling phosphate pollution. A limitation of the present study is the absence of surface area (BET) and SEM–EDX analyses due to instrumental constraints.

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Author's Contribution

"Bhoj Raj Poudel: Writing - original draft, Investigation, Formal analysis, Conceptualization, Data curation. **Shanti Gajmer; Mamata Singh:** Writing - review and editing, Validation, Methodology, Formal analysis, Conceptualization. **Janaki Baral:** Writing - review and editing, Validation, Methodology, Supervision, Conceptualization."

Conflict of Interest

The authors declare no conflicts of interest.

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