



PHOSPHATE REMOVAL FROM NATURAL WATERS BY NATURAL SYRIAN ZEOLITIC ORE: SORPTION STUDY

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ABSTRACT

Background: Eutrophication occurs in lakes and fresh water when total Phosphate (P) concentrations content exceeds 0.1 mg.L⁻¹. Therefore, P- removal is an important procedure for water purification. In the last decades, adsorption is low-cost technology and one of best solutions for water and wastewater purification. Natural Syrian zeolitic ore (NSZO) gets more attention in Syria. Many researchers suggest NSZO as well-surfactant raw material to be used as promising fertilizer, and for removal of heavy metals and ammonium from drink and waste waters. **Objectives:** This Research aims to characterize NSZO and to study its efficiency in P- removal from water solutions. **Methods:** In order to identify the main characteristics of NSZO, XRD pattern analysis is carried out to point out main minerals in the natural ore. Batch experiment used to study P adsorption (removal) and factors that affect P- removal by NSZO. **Results:** XRD data identified Calcite, Quartz, and zeolite as the main components of NSZO, where Analcime and Phillipsite was the main zeolitic minerals. Otherwise, Phosphate sorption may attribute to Fe–OH sites in oxides components of NSZO, considering Fe (III) oxides content (181.4 g.Kg⁻¹). P-removal increases between 100% and 70% as initial P concentration varies from 5 to 60 mg.L⁻¹. Besides, All used adsorption models (Langmuir, Freundlich and Dubinin - Radushkevich) describe well adsorption as favorable mechanism (R²>0.9), other mechanisms like precipitation or even chemisorption may take place quietly slow. **Conclusions.** NSZO seemed to be a promising material for P- removal from water solutions. It is suggested that NSZO efficiency in P- removal is caused by zeolites, iron oxides and calcite.

Keywords: Phosphate, Removal efficiency, Analcime, Phillipsite .

1. INTRODUCTION

Anthropogenic and industrial activities are major causes of water pollution. Eutrophication occurs when total Phosphate (P) concentrations content exceeds 0.1 mg.L⁻¹ [17]. Many countries are seriously concerned in effective technologies for water purification process [1,30]. In the last decades, adsorption is studied as low-cost technology and one of best reactions for water and wastewater purification. Many kinds of adsorbents were used such as industrial byproducts [34,56], carbonate, oxides, and clay minerals [10,16,42,43,51,57], while other researchers used zeolites [31,41]. Zeolites are used effectively to remove cationic and organic contaminants from water and wastewater [24,36,54,55]. Despite of high cation capacity, and high specific surface area, zeolites have less affinity to anionic adsorption (i.e phosphorus as orthophosphate (P)). Therefore, in order to enhance the anionic adsorption efficiency, many researches focused on modifying natural zeolite surfaces with elements have good affinity to bind phosphate such as iron [22,58], acidification treatments [4,23], saturating the negative sites with organic materials [7,24], or inorganic salt treatment [9]. Furthermore, Uzonova and Mikosch (2016) studied directly phosphate sorption by natural Clinoptilolite, assuming that the presence of Brønsted acid sites together with Lewis basic sites would increase zeolite adsorption capacities [52]. Sorption efficiency are related to (Si/Al) ratio in framework structure and the number of metal atoms combining rings and pores [3, 15].

In the last decades, Natural Syrian zeolitic ore (NSZO) became more interesting, where many researchers evaluated its effect on soil as an amendment [50], and removal efficiency for heavy metals and ammonium as a well surfactant material for drink and waste waters treatment [44, 45].

NSZO has a significant content of calcite by which it is classified [46, 47], and up to 30% of iron oxides content in raw material in some zones [45]. Therefore, this research assumes that the presence of calcite and iron oxides with zeolite minerals leads to phosphate adsorption from aqueous solutions. Thus, the objectives of this study is to identify NSZO, and evaluate P- removal from aqueous solutions by proceeding adsorption experiment.

2. MATERIALS AND METHODS

2.1 Material sampling: NSZO is obtained from 170 Km southeastern Damascus – Syria. This area belongs to Tell Al-Sis formation 37° 15' 37° 30' North 33° 15' 33° 3' east [26], which petrographically consists of pyroclastic components, olivins (Forsterite), volcanic glass, as well as zeolites. It was observed that Zeolites are secondary phases in presence with calcite and smectites [26, 47]. Raw material had the following chemical composition (by weight): 38.26 % SiO₂, 10.2% Al₂O₃, 10.86% Fe₂O₃, 0.14% MnO, 9.90% MgO, 11.94% CaO, 1.78% TiO₂, 0.56% P₂O₅, 2.44% Na₂O, 1.03% K₂O and 12.8% LOI

(loss on ignition as CO_2 and H_2O content) [46]. Sample was fine-crushed, grinded and washed by deionized water in order to remove soluble salts, dried at $80^\circ C$, and sieved ($<1\text{ mm}$). Material, then, is stored to be used for adsorption/ desorption experiments. NSZO samples were pre-treated according to [32] for XRD Analysis by STOE transmission diffractometer system STADI-P; XRD patterns have been analysed by X-Powder12 in order to identify the main minerals.

2.2 NSZO Properties: Total Organic Carbon (TOC) by [53], Total Carbonate by Loss on ignition method at $550^\circ C$ for 3 hours, Cation exchange capacity (CEC) by [11], pH (1:10, w:v suspension ratio). Total Iron is determined as ferric iron Fe (III) by direct titration with EDTA (0.02 M) at (pH = 2.2 ± 0.1), using salicylic acid as indicator in presence of sodium persulfate powder [8,13]. Surface Area (SA) is determined by Sears method as following: triplicate of 0.5 g NSZO is added to 40 mL distilled water and 10 g NaCl powder, stirred together for two hours, then 0.1N of HCl is added to drop pH to 3.5, the volume is completed to 50 mL by distilled water. Then the sample is titrated by 0.1N NaOH. (V) is the NaOH volume needed to raise pH from 4 to 9. Surface area (SA) ($m^2.g^{-1}$) is calculated by the following experimental formula [48]:

$$SA = 32 \times V - 25. \quad (1)$$

2.3 Adsorption-desorption experiments: P solutions are prepared in 0.01M $CaCl_2$ solution, conditioned at $293 \pm 1\text{ K}$, and adjusted to pH 8.5 ± 0.2 . Batch experiment is carried out in 50 mL centrifuge tubes where 1.00 g of NSZO and 20 mL of phosphorus solution (5, 10, 20, 30, 40, 50, 60 $mg.L^{-1}$) were added. Batches carried out in duplicates, shaken at 180 rpm, centrifuged at 1500 g for 10 min, supernatants filtered by 45 μm Millipore filters. Adsorbed P on NSZO Qads ($mg.g^{-1}$), is calculated by the following equation Eq.(2):

$$Q_{ads} = (C_i - C_e) \cdot V_e / w \quad (2)$$

Where C_i and C_e ($mg.L^{-1}$) are liquid-phase concentrations of phosphorus at initial (i) and equilibrium (e), respectively. While (V_e) is solution volume (L) and w is dry mass of NSZO (g).

Removal efficiency RE%: is calculated in the following Eq.(3):

$$RE\% = [C_i - C_e] / C_i \times 100 \quad (3)$$

Desorption experiment is followed by adding 20 mL of 0.01 M $CaCl_2$ electrolyte to centrifuge tubes after removing equilibrated phosphate solutions, then it is shaken as previous. At equilibrium, the desorbed P in supernatant (Q_{des}) ($mg.g^{-1}$) is calculated in Eq. (4):

$$Q_{des} = (C_{des}) \cdot V_{des} / w \quad (4)$$

Where C_{des} is liquid-phase concentrations of desorbed phosphate, V_{des} is Volume of desorbing solution (L). Desorbability ratio DR (%) was calculated as viewed in Eq. (5):

$$DR(\%) = Q_{des} / Q_{ads} \times 100 \quad (5)$$

The residual sorbed -P on NSZO surface is expressed as reliable adsorbed-P, which means the subtraction between the RE% and DR% curves.

2.4 Phosphate determination: Phosphate concentration is determined by spectrophotometer using the P- Molybdate-Ascorbic acid complex method at $\lambda=880\text{ nm}$ [40].

2.5 pH effect: 20 mL of P solution 50 $mg.L^{-1}$ is added to 50 mL centrifuge tubes containing 0.2 g of NSZO. pH value ($pH_{initial}$) of suspensions is adjusted to (4, 6.2, 7.4, 8.2, 9, 11), and shaken for 4 hours at room temperature. pH-value re-measured before centrifugation (pH_{final}) to calculate ΔpH as mentioned in Eq. (6):

$$\Delta pH = pH_{final} - pH_{initial} \quad (6)$$

2.6 Electrolyte effect: Initial P solutions of 5 $mg.L^{-1}$ are prepared in variety of $CaCl_2$ concentrations (0 to 0.5 M), where adsorption is proceeded as mentioned before.

2.7 Adsorption theories: Langmuir, Freundlich and Dubinin-Radushkevich (D-R model) isotherms are commonly used models. **Langmuir** adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between sorbed molecules [35]. Langmuir adsorption isotherm is successfully used to explain phosphate adsorption from aqueous solutions. The expression of the Langmuir model is given by following Eq. (7):

$$Q = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \quad (7)$$

It can be linearized form as following:

$$\frac{C_e}{Q} = \frac{1}{K_L Q_{max}} + \frac{1}{Q_{max}} \cdot C_e \quad (8)$$

Where C_e (mg.L⁻¹) is The equilibrium concentration of phosphate. Q (mg.g⁻¹) is amount of phosphate adsorbed at equilibrium. Q_{max} (mg.g⁻¹) is Maximum monolayer coverage capacity for phosphate. K_L (L.mg⁻¹) is Langmuir isotherm constant appropriate to calculate dimensionless constant of R_L as separation factor from Eq. (9):

$$R_L = 1 / (1 + K_L \times C_i) \quad (9)$$

Where C_i is the initial solution P concentration; Hence, R_L evaluates the adsorption as: **a)** favorable: ($0 < R_L < 1$), **b)** unfavorable: ($R_L > 1$) and **c)** reversible: ($R_L \rightarrow 0$).

Freundlich isotherm is commonly used to describe adsorption characteristics on heterogeneous surface. It is given in the following Eq. (10) :

$$Q = K_f C_e^{1/n} \quad (10)$$

Where K_f (L.g⁻¹) is Freundlich isotherm constant. $1/n$ indicates the adsorption intensity; C_e (mg.L⁻¹) is equilibrium concentration of phosphate. Q (mg.g⁻¹) is amount of phosphate adsorbed at equilibrium. Linearizing Eq. (10) :

$$\log Q = \log K_f + \frac{1}{n} \log C_e \quad (11)$$

Plotting $\log C_e$ as x-axis versus $\log Q$ as y-axis provides a line of slope ($1/n$) and intercepts the y-axis at $\log K_f$. The constant K_f is an approximate indicator of adsorption capacity and evaluates the status, while $1/n$ is a function of the strength of adsorption through adsorption process. When $1/n$ value equals to:

- a) $1/n \rightarrow 1$: Partition between the two phases are independent of the concentration.
- b) $1/n < 1$: Normal adsorption fitted with L- type.
- c) $1/n > 1$: Cooperative adsorption curve is plotted as S-Curve, and adsorption – in this case – will be developed into clusters on mineral surface [21,33,43].

D-R isotherm is an appropriate model since no high concentration of adsorbate and unsaturated surface of adsorbent, where the linear logarithmic equation is:

$$\ln Q = \ln Q_{max} + K_{DR} \cdot \varepsilon^2 \quad ; \quad \varepsilon = RT \ln(1 + 1/C_e) \quad (12)$$

Where: Q (mg.g⁻¹) is the adsorbed amount of P, Q_{max} (mg.g⁻¹) is sorption capacity of zeolite sample, ε (J.mol⁻¹) is Polanyi adsorption potential, K_{DR} (mol².J⁻²) represents Dubinin- Radushkevich adsorption constant at T (300 °K). C_e (mg.L⁻¹) is the equilibrium solution concentration of the phosphate. R (8.3147 × 10⁻³ J. mol⁻¹. K⁻¹) is gas constant.

3. RESULTS

3.1 NSZO characteristics: Results indicate that the NSZO sample classified as a material rich in carbonate where the dominant component is calcite as illustrated in (Table 1). This result is compatible with results of [47]. Besides, Ca²⁺ and Mg²⁺ are the dominant extractable cations. It is suggested that effect of Fe–OH sites in the oxides components of NSZO can be tributary on phosphate sorption process, considering iron oxides content (181.4 g.Kg⁻¹).

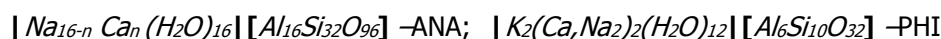
Table 1: The chemical characteristics of natural Syrian Zeolite Ore (NSZO).

pH *	TOC	CO ₃ Total	Fe _{Total}	ex-Ca	ex-Mg	CEC	SA
	-----	g.Kg ⁻¹ -----	-----	mg.Kg ⁻¹ -----	-----	cmol.Kg ⁻¹	m ² .g ⁻¹
9.7 (8.7)	0.0	197.8	181.4	24.02	9.99	113	183

TOC: Total organic carbon; *: between brackets indicates the pH value of salts- washed- NSZO samples.

XRD analysis characteristics for NSZO sample shown in (Figure 1) where calcite is the main mineral of NSZO material, followed by Quartz. Zeolites are investigated as corresponding phases. Therefore, Analcime (ANA) and Phillipsite (PHI) are the dominant types of zeolite minerals. It obviously show the appearance of calcite peaks, and more intense distinguished peaks for zeolite phases.

Baerlocher et al. (2007) illustrated framework structures for Analcime (ANA) and Phillipsite (PHI) (Fig 2) [6]. They have the common formula, respectively as following:



Furthermore, ANA and PHI are both classified as low Si/Al ratios where Si/Al equals [2-3] for ANA and [2-4] for PHI [28]. It means that both minerals show less stability to thermal and acid treatment, less crystallinity, and more affinity to ion exchange [2]. The dimensions of rings along [001] is (4.2×1.6 °Å) for ANA and (3.8×3.8 °Å) for PHI, volume of pores is another limit factor affects to ion exchange [6].

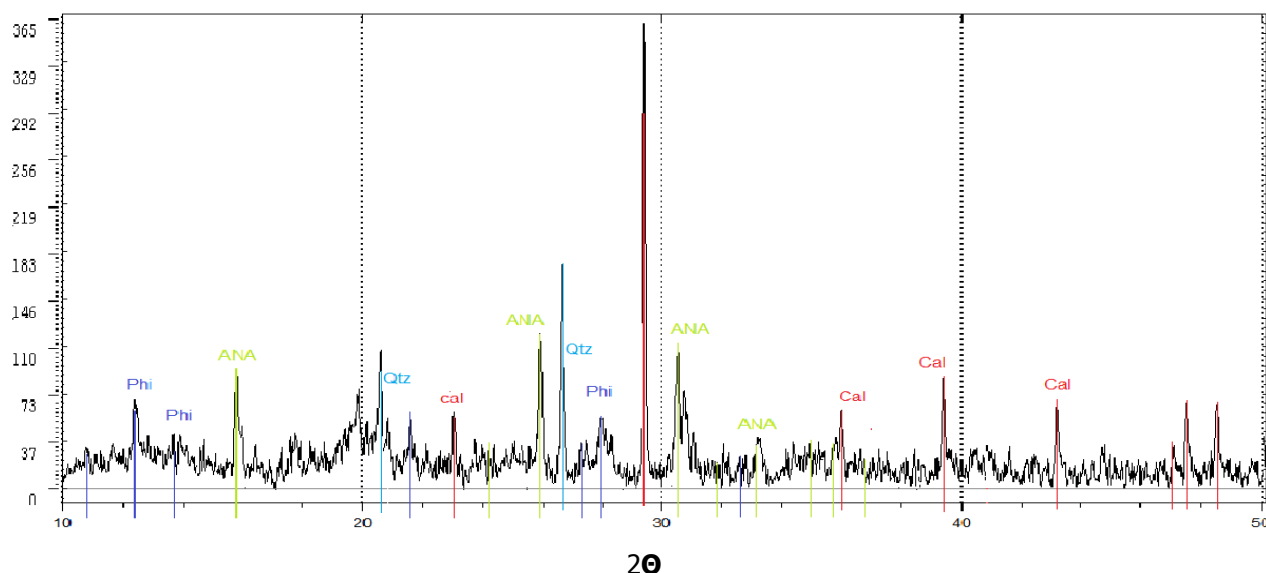


Figure 1: XRD analysis patterns of (NSZO) through which: Green line marks for ANA, Blue line for PHI, red lines for calcite and violet lines marks for quartz as the main non-zeolitic components of NSZO.

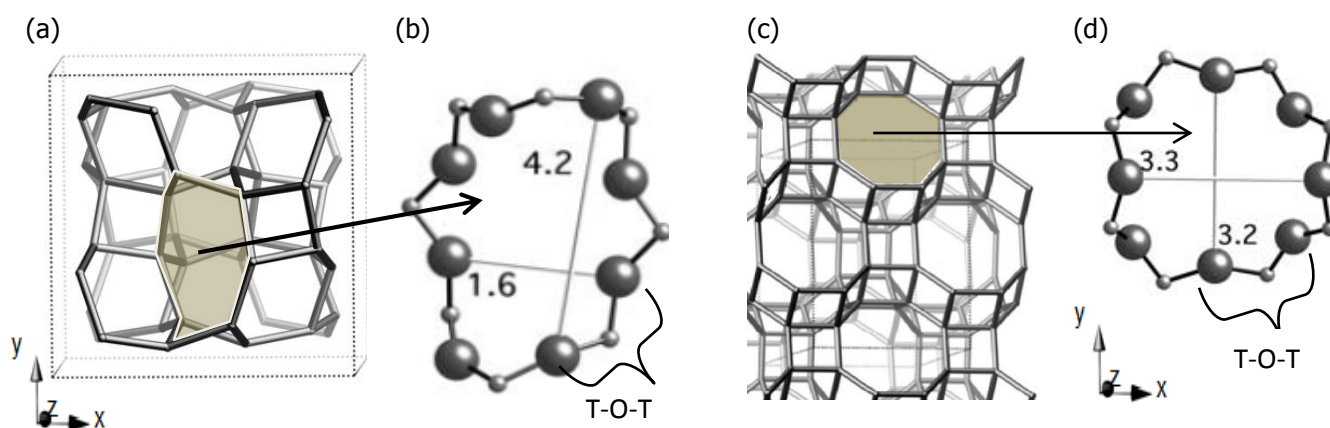


Figure (2): Framework type data for Analcime (ANA) and Phillipsite (PHI). **T-O-T:** Sequence of Oxygen atoms and T atoms (Si or Al) inside framework. **(a)** Framework of ANA along $[001]$. **(b)** Irregular channels formed by highly distorted 8-rings along $[110]$. Space is $4.2\text{Å} \times 1.6\text{Å}$. **(c)** Framework of PHI along $[001]$. **(d)** Shape of six channels shapes formed by 8-rings along $[001]$. Space is $3.3\text{Å} \times 3.2\text{Å}$ (adopted from [6]).

3.1 Adsorption – desorption study: The relationship between (C_{eq}) and (Q_{ads}) belongs to L-curve type as it is described in (Figure 3.a). It shows high affinity at first initial concentrations, between P in solution and adsorbent, then affinity decreases slowly towards equilibrium [18].

Moreover, P-desorption is limited compared to P- sorption (Figure 3.a), while (Figure 3.b) presents DR percentage. REpercentage decreases from 100% to 77.4 % as initial concentration increases from 10 to 50 mg.L^{-1} , while DR percentage increases from 0% to 2.8% at 10 and 50 mg.L^{-1} initial concentrations respectively.

Besides, We can label zone located between removal efficiency curve and desorbability ratio curve as “*Reliable P- removal zone*” (Figure 3.b); It indicates that the reliable P- removal amount equals 74.6 % - 100% respectively assuming that high initial concentrations lead to slight decrease of removal efficiency. Similar to Montalvo et al, (2011) who indicated that phosphate in wastewater removed by highly performance by lime sequenced with natural zeolite, the removal decreased from 67% to 58% as the initial concentration in solution increased from 40 mg.L^{-1} to 80 mg.L^{-1} [39].

On the contrary, Moharami and Jalali (2013) investigated P- removal by Iranian zeolite and other minerals under different operation conditions; They found that only 20% of the total phosphorus in solution is removed by natural Iranian zeolite comparing with calcite which was more efficient [38].

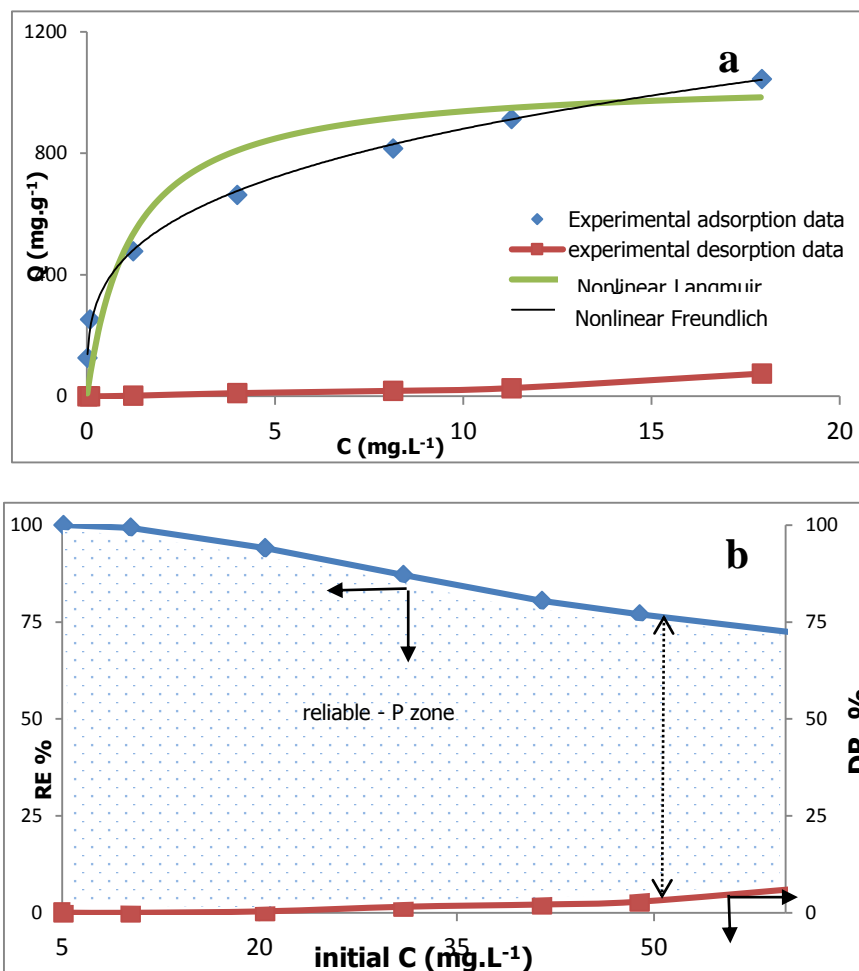


Figure (3): (a) Adsorption – desorption isotherms of phosphate on NSZO. **(b):** Removal efficiency (RE %) and Desorb-ability ratio (DR %) by NSZO in relation to initial concentrations of phosphorus in solution.

3.2 pH effect: pH has slight effect on P- removal since RE percentage has increased from 71% to 85% as pH has increased from 4 to 11, with a good correlation ($R^2=0.82$) (Figure 4). In contrast, High pH variation (ΔpH) is observed at $pH < 6$ then it decreases as initial pH increases, and similar slight pH decreasing is observed from 6 to 11 initial pH.

3.3 Electrolyte effect: (Figure 5) illustrates that RE percentage increases from 70 % to 98.4% when (CaCl₂) concentration raises from 0 up to 0.025M; then RE percentage drops and stabilizes around $\sim 50 \pm 5$ % when (CaCl₂) concentration is $>0.05M$. It seems that Ca²⁺ promotes P- removal from solution at low concentrations of CaCl₂. In contrary, the more increasing of concentration may enhance calcium phosphate precipitation.

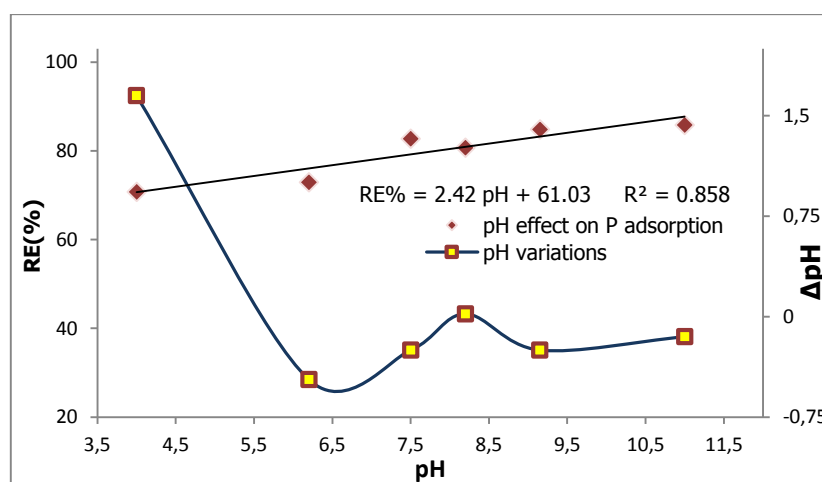


Figure 4: pH effect on P- Removal Efficiency (RE %) of Phosphate by NSZO and equilibrium pH variation (ΔpH).

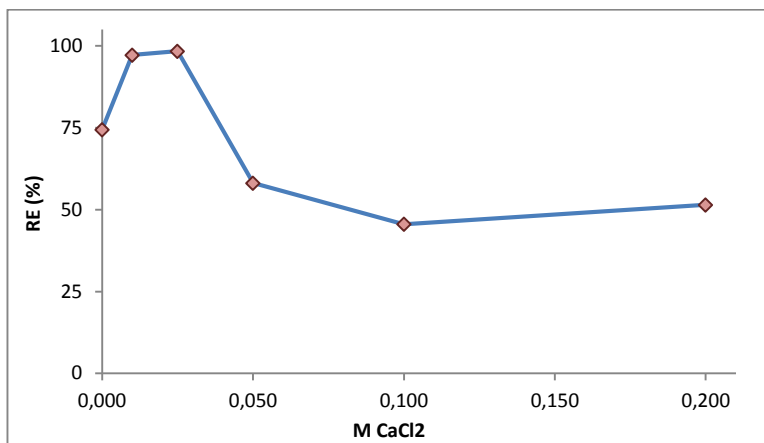


Figure 5: Electrolyte effect EI (M) on removal efficiency (RE %) of Phosphate by NSZO.

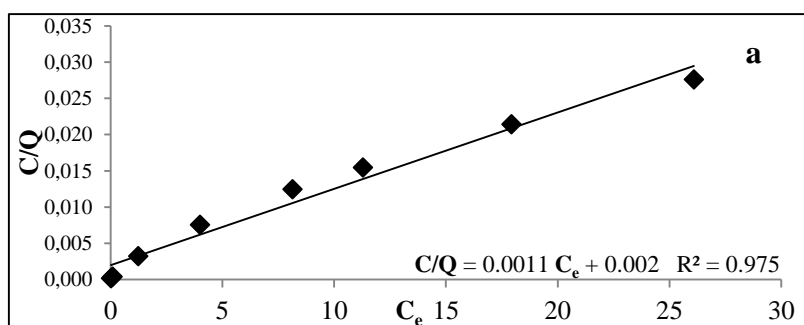
3.4 Sorption models: (Figure 6) and (Table 2) represent adsorption theories curves and data where Freundlich isotherm model gives a better estimation for describing the affinity between phosphate and NSZO ($R^2 > 0.99$), than Langmuir and (D-R) model ($R^2 = 0.978$) do, concluding that adsorption is probably occurred on heterogeneous surfaces.

Table 2: Parameters of Langmuir, Freundlich and D-R models to describe P adsorption on NSZO.

Langmuir model			
R^2	K_{Lang}	Q_{max}	R_L
0.978	0.844	1049.3	0.001
Freundlich model			
R^2	K_f	$1/n$	
0.993	453.3	0.3	
D-R model			
R^2	K_{DR}	Q_{max}	E (KJ.mol ⁻¹)
0.978	4.45×10^{-3}	975.9	3.31

Besides, $K_f = 453.3$ (Table 2) is high enough to understand the distribution between phosphate in solute and phosphate on the surface of NSZO, $1/n = 0.3$ describes the favorability of adsorption ($1/n$ in the range of [0-1]). The maximum monolayer capacity of adsorption calculated with respect to Langmuir isotherm is 1049 mg.g^{-1} .

Based on Langmuir constant value K_L (0.844), value of R_L equals 0.001 in terms of C_i varies from 5 mg.L^{-1} into 60 mg.L^{-1} , indicating that the adsorption is typically favorable.



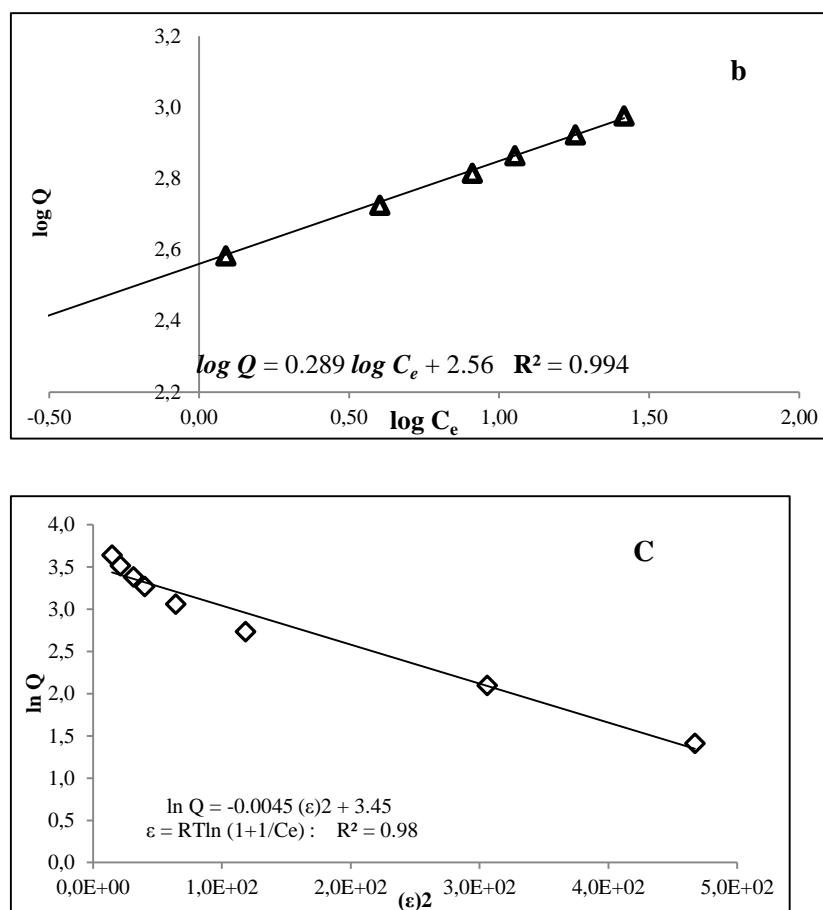


Figure 6: Linear curves derived from equations (7,10,11) where: **a.)** Langmuir, **b.)** Freundlich, and **c.)** Dubinin- Radushkevich (D-R).

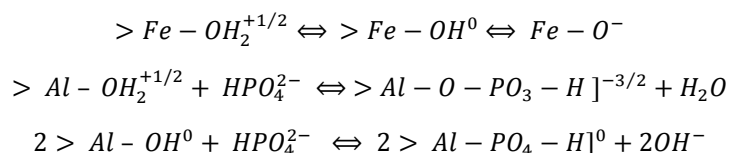
Since the Freundlich and Langmuir are independent of temperature, D-R model was usually applied to distinguish the physical adsorption on heterogeneous surfaces [14, 37]. D-R model fits for describing adsorption, considering the bases of: **i)** porous nature of zeolites, **b)** physical forces would be dominant mechanism in adsorption, and **c)** adsorption occurs due to pore-filling mechanism rather than layer-by-layer surface coverage [21, 25]. Adsorption heat E (KJ.mol^{-1}) is computed by the following equation $E = 1/\sqrt{2 K_{DR}}$ so that $E=3.31 \text{ KJ.mol}^{-1}$ which enhances the assumption of physical nature for P- adsorption on NSZO surface.

4. DISCUSSION

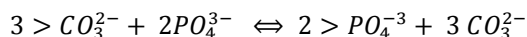
Adsorption study investigates that NSZO is a good surfactant for P- removal from water solution. It assumed that P- removal is up to 70% at 50 mg.L^{-1} initial concentration, and efficiency is increased close to 100% when initial concentration reach to 5 mg.L^{-1} .

All adsorption models indicate the preferability of adsorption, but are not adequate for describing the sorption mechanism. Inside channels, two H_2O molecules and one counter ion of either of (Na^+ , Ca^{2+} , K^+ ..) are settled to neutralize the negative charge for ANA [19]. Similar to ANA, PHI mineral is more complicated with Ca^{2+} , Mg^{2+} , K^+ ions located inside framework and more coordinated water inside the channels [20]. Overall, the more bonded- H_2O , the more acidity for zeolite, related to Si/Al ratio [5]. Fe oxides, zeolite minerals with unique framework and calcite are basically responsible for P- removal from solution by NSZO.

An electrostatic attraction could be the main mechanism that explains the sorption relationship between phosphate and NSZO. This physical nature of reaction could be developed into inner sphere complexes (mono and bidental ligands) at low pH value of solution ($\text{pH} < 6$), via protonated sites of oxides and Zeolites surfaces [49]. Besides, these reactions lead to OH^- release leading to pH increase (Fig. 4) [35,56].



Where $> \text{Al-OH}^0$ and $> \text{Fe-OH}^0$ mean hydroxyl groups in the Zeolite and Fe oxides interface respectively. On the other hand, at pH value ($\text{pH} > 7.4$) adsorption is probably promoted by calcite in NSZO, Since Ca^{2+} cations on calcite surface play as bridges between phosphate and surface, or carbonate in calcite lattice could be substituted by equivalent quantity of phosphate from solution as following [27]:



Where $> \text{CO}_3^{2-}$ means the carbonate in calcite lattice. Considering the physical adsorption, which is distinguished by electrolyte effect on adsorption as well as pH variation does, It assumed that chemisorption and precipitation are other corresponding mechanisms that occurred with adsorption but quietly slow.

5. CONCLUSION

This research illustrated that calcite, oxides and zeolites are the main components contribute in P- removal from water solutions, cooperating through adsorption and precipitation mechanisms. Besides, adsorption is dependent on pH variation, affecting the mechanism of surface – P linking.

All adsorption models fit well for describing phosphate sorption from water solution, predicting another mechanism during adsorption reaction like precipitation, or developing into chemical bound between phosphate and the surfactant. This explains the high affinity of NSZO to P- removal. Thus, NSZO could be presented as promising material in removing phosphate from water solutions.

6. REFERENCES

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