EVALUATING SLOW RELEASE FERTILIZER PREPARED BY LOADING PHOSPHORUS ON SURFACE MODIFIED NANO SYRIAN ZEOLITIC TUFF

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ABSTRACT

This study was aimed to assessment of using nano Syrian zeolitic tuff (NSZT) as carrier to produce slow release phosphate fertilizer was executed. phosphate salt was loaded to modified nano-zeolite by HDTMA-Br (*hexadecyl trimethyl ammonium bromide*) surfactant application. Two main treatments (SMZ1, SMZ2), making approximately monolayer (83%) and bilayer (190%) real coverage of external cationic exchange capacity respectively. Phosphate was loaded on SMZ to prepare slow release fertilizer (SRF_1, SRF_2) respectively. Surface characteristics were conducted by using XRD and SEM techniques. Adsorption/ release experiments and incubation column were studied. Results showed that Langmuir isotherm was better to give good estimation of phosphorus sorption about nature of homogeneity. Phosphate release time into water solution from SRFs increased as surface modification ratio increased. Elovich model was good tool to predict the phosphate release ratio coefficient which was independent of HDTMA-Br modification coverage ratio. After 40 days of incubation experiment in columns, soil effect dropped up the leached phosphate in the flux less than 10% of the initial P loading concentration. Incubation column experiment confirms expectations about the anion exchange mechanism between phosphate and bilayer on NSZT.

Key words: Nano Syrian Zeolitic Tuff NSZT, Suface modification, Column study.

تقييم سماد بطيء التحرير المُحضر عبر تحميل الفوسفور على الطف الزيوليتي السوري النانوي المعدل سطحياً

سلامة، بتول ليلى حبيب أريج عدرة زياد حاتم

المستخلص

أُعدت دراسة مساهمة من مواد نانوية أساسها الطف الزيوليتي السوري (NSZT) كمادة حاملة لإنتاج سماد فوسفاتي بطيء التحرير. تم تحميل ملح فوسفاتي على السطح الزيوليتي بعد تعديل سطحه بمادة محفزة وهي هيكسا ديسيل تراي متيل بروماید الأمونيوم (HDTMA-Br). استُخدم معدلا تغطية حقيقيان لسطح النانوزيوليت هما 83% و190% من السعة التبادلية الكاتيونية الخارجية، لتحقيق طبقة مفردة أو طبقة مضاعفة من HDTMA-Br أطلق عليهما SMZ_1 وSMZ2 على التوالي. وتم عليهما تحميل الفوسفات للحصول على معاملتي السماد الفوسفاتي البطيء التحرير (SRF_1 وSRF2). أجري توصيف المعاملات باستعمال تقنيتي الأشعة السينية XRD والمجهر الالكتروني SEM. ونفذت تجارب امتزاز وتحرر الفوسفور. بينت نتائج الادمصاص توافقها مع نموذج لانكماير من حيث إن الامتزاز يتم على سطوح متجانسة. ووجد ازدياد في تركيز الفوسفور المتحرر إلى الوسط المائي مع الزمن بازدياد معدل التغطية. وقدم موديل إيلوفيتش أداة جيدة في التنبؤ بمؤشر معدل تحرر الفوسفور مع الزمن، لكن هذا المؤشر مستقل عن معدل التغطية بالمحفز. وفي تجربة التحضين بالعمود خفض تأثير التربة الكمية المفقودة من الفوسفات إلى أقل من 10 % من التركيز الأولي للفوسفات عند معاملة SRF_2 بعد انقضاءأربعين يوماً من التجربة. ما يؤكد أن التبادل الأيوني كان العملية المنظمة لربط الفوسفات مع الطبقة المضاعفة على NSZT.

الكلمات المفتاحية: الطف الزيوليتي السوري النانوي، تعديل السطح، التحميل بالفوسفور، دراسة التحضين بالعمود

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INTRODUCTION

Zeolites are naturally hydrated aluminosilicate minerals. It belongs to tectosilicates, where Si^{4+} occupies framework tetrahedral, that can be substituted by Al^{3+}, leading to surface negative charge. Furthermore, its unique structure have got high content of alkali /alkali earth metals and H_2O molecules in extra positions of the framework, cavities and ordered channels. However, electrical characteristics i.e. thermal stability, porosity, polar molecules affinity and cationic adsorptive capacity provide such useful advantages that can be manipulated for synthetic purposes.(42). Nanofertilizers are promised solution and best alternative to traditional fertilizers regarding plant response (11), productivity (27), and tolerance to different types of plant stress [i.e salinity (55), soil pollution by heavy metals (32), considering impacts in environment (31). Nanotechnology tends to treat the disadvantages of traditional or commercial fertilizers, such as nutrients loss by volatilization and leaching (55), leading into excessive costs and precarious environmental consequences (48). Nano-sized particles of fertilizers is considered convenient selective transporting nutrient agents for target root plant cell via porous translocation and biotransformation pathways (49). Previous studies indicate that zeolites can be feasible material to formulate N,P, and K formulations of slow release fertilizers (SRF) with sustainable ability to release available nutrients to soil solution, considering its ability to desorb natural counterions [K^+, Ca^{2+}] into soil solution for plant growth and productivity (29,30,55). These components were usually fabricated in either granular or micro particles for direct application into the soil. In the other hand, fertilization process in soil depends on factors such as mass transport, diffusion in soil solution, and biological activity (4,49). Dubey & Mailapalli (13) investigated that granular matrix of urea – zeolite – Acrylic used to prepare a slow release fertilizer, it is shown that N- release decreased 54% compared to the other trail structures and commercial urea, and less as much 63% in leachate. Bhardawaj et al (5) assumed that clinoptilolite zeolite and montmorillonite clay minerals can be hydrothermally synthesized to formulate Nitrate SRF modified by HDTMA-Br (*hexadecyl decyl trimethyl ammonium bromide*) as an efficient surfactant. Loaded NO_3^- concentration approximately was 125 $mg.g^{-1}$, and under soil column percolating system, It is observed that 11- 20 days for NO_3^- released in leachate. A study by *del* Pino (40) basically performed *Phosphorus* slow release fertilizer (*P*-SRF) from KH_2PO_4 salt directly onto philipsite zeolite particles, it is observed that treatment provided controlled release of available phosphate and potassium in leachate through 50 days under continuous percolation reactor. In similar experimental conditions, Bansiwal et al (3) prepared modified zeolite-A to produce a P-SRF by using HDTMA-Br as surfactant, they illustrated low stable phosphate release rate as much of 1.4-1.8 $mmol.L^{-1}$ in leachate throughout 11- 40 days of percolating time. However, P loaded on modified SRF is multiplied by 4.9 times than P-loaded on unmodified zeolite treatment. Regarding to previous studies suggesting that modifying the porous material like zeolites into nanoparticle in order to prepare slow release fertilizers by loading phosphate salts on nano natural zeolite. Syrian zeolitic tuff (SZT) mineralogy is well ascribed (14,41,44,45) and studies had major interest in environmental aspects, upon that SZT is efficient adsorbent to inorganic pollutants (8,20), and organic molecules. Currently, noteworthy studies lightened on its agricultural potential use as N nutrition resource. Habib and Younes (17) illustrated that SZT could be a good slow release fertilizer for ammonium, through which is loaded by 8.45 mg $NH_4^+{}_{(eq)}$ per g^{-1} zeolite. Therefore, an elementary pot experiment carried on by rye grass plant *Lolium perenne*. It's observed that the treatment (3.27% of NH_4-N on SZT soil) gave the best N concentrations in plant during experimental time after three cuts with 28 days intervals. Kinetic study in close system medium illustrated that natural SZT has good affinity to absorb ammonia gas into surface and internal porous enhanced by initial moistening as much of 25% w:w (18). P availability by SZT is still pending study since preliminary assessment was observed by (20) that SZT has ability to bonding P from 100%

to 70% as initial P concentration increases 5 - 50 mg.L^{-1} in water solution. The objective of this study was to investigate phosphorus (P) release from nano powder slow release fertilizer which is prepared by loading phosphorus salt on from natural nanozeolitic tuff (NSZT) modified by using HDTMA- Br as a surfactant, in addition to, evaluate P release in presence of soil particles effects.

MATERIAIS AND METHODS

Nano zeolite preparation

SZT was obtained from 170 Km south eastern Damascus -Syria, this area belongs to Tell Al-Sis formation 37°15'-37°30' North 33°15'-33°30' east (24). Raw material had the following chemical composition (by weight): 38.26 % SiO_2, 10.2% Al_2O_3, 10.86% Fe_2O_3, 0.14% MnO, 9.90% MgO, 11.94% CaO, 1.78% TiO_2, 0.56% P_2O_5, 2.44% Na_2O, 1.03% K_2O and 12.8% LOI (loss on ignition as CO_2 and H_2O content) (46). Sample was washed with distilled water and oven dried at 40°C. In order to obtain nano-scale powders of natural zeolite with particles diameter less than 100 nm, a planetary ball mill (Retsch PM 100 CM) is obtained to high energy pulverization.

Surface modification

HDTMA- Br ($C_{19}H_{42}NBr$) was used as a surfactant to modify the external surface feature of NSZT. Thus, An aliquots of ($1_{HDTMA\text{-}Br}$:5_{H2O}) solutions was performed and applied to sample according to ECEC value 26.5 cmol.Kg^{-1} (table1). Therefore, when 100 ml of HDTMA-Br solution 2.65 cmol.L^{-1} is applied to 1 g nano-sized NSZT, for preparing modified surfactant sample with 100% of ECEC. Two treatments of HDTMA-Br solutions to perform surface modified NSZT at 100 and 300% of ECEC called SMZ1 and SMZ2 respectively. (1: 100 w:v) Suspensions was undertaken and shaked for 24 h, centrifuged at 2500 g for 15 min, and filtered by using MN *640d* filter papers. Afterward, Sample dried up at 40°C, stored in desiccator for the following analysis. The real loading of HDTMA-Br was 83% and 190% of ECEC% for SMZ1 and SMZ2 respectively (Table 2).

Physiochemical characterization

1.XRD Analysis: by STOE transmission diffractometer system STADI-P; XRD patterns have been analyzed by (Match!, 3.15 Crystal Impact, Bonn Germany) to define the main minerals.

Scanning electron microscope– Energy dispersive X-ray spectroscopy (SEM-EDX) microscopy: In order to cover an accurate surface morphology before and after modification procedure. Current study implemented SEM- EDX apparatus Model (TESCAN VEGA II -XMU, Czech Republic) to produce Images captured using [2.5 – 5 Kev] accelerating voltage with SE detector, scanning speed 5-10 ms per pixel. Samples are prepared by dispersing samples layer onto Aluminum plate coated with carbon adhesive material.

Table1. Main characteristics of NSZ, proceeded by (40).

CEC(*cmol*.Kg^{-1})		EG-SS!!	PZC†
TCEC[#]	ECEC[$]	$m^2.g^{-1}$	
80	26.5	9.76	8.8

[#] Total cationic exchange capacity by (26,46).
[$] External cationic exchange capacity = determined after saturating the predicted external positions in the surface with HDTMA-Br.
[!!] Specific surface by Ethylene glycol mono ether method (51).
[†] Point zero charge by Acid- base titration curve method according to (12).

Tabl e2. HDTMA- Br loading ratio to the external positions of nano scaled modified zeolite SMZ_1 and SMZ_2

surface modification treatments	HDTMA-Br (g)	HDTMA- Br meq. g^{-1}	OC $Cg.g^{-1}$ zeolite	Cal-ECEC † (%)
SMZ_1	0.08	0.080	0.050	83
SMZ_2	0.184	0.504	0.115	190

The theoretical loading ratio of HDTMA-Br as much 100%, and 300% of the ECEC onto NSZT sample respectively).
†: Calculated loading ratio of HDTMA- Br according to determination of organic carbon that is titrametrically proceeded by method (53), where no organic carbon composite is detected in the sample.

Fourier transform infrared spectroscopy (FTIR): By using IR- spectrometer model (ST/IR 460 plus, Jasco); Infrared spectra were collected in the mid-IR region between 4000 and 400 cm^{-1} at 4 cm^{-1} resolution (2 cm-1 steps) with 16 scans.

P adsorption study: Batch experiment is aimed to test the affinity of P on modified surfactant NSZT surface in two treatments SMZ_1 and SMZ_2. Therefore, 0.20 g aliquots and 20 mL of phosphorus solutions (5, 10, 20, 30, 40, 50, 60 $mg.L^{-1}$) were mixed into 50-mL centrifuge tubes. Experiment carried out in triplicates, shaken at 180 rpm, and centrifuged at 1500 g for 30 min. Supernatants were filtered by *45 µm* Millipore filters.

P loading on surface modified zeolite: in order to prepare slow release fertilizer (SRF) 1: 100 (w: v) suspension has been shaken on trial by using 1 *M* of KH_2PO_4 solution with modified surface samples. SMZ_1 and, SMZ_2 The products was called SRF_1 and SRF_2 respectively.

Phosphate release Experiments (P– release):

Desorption experiment: Similar to adsorption batch experiment conditions, the desorption study is performed using 0.2 g of SRF_1 or SRF_2, diluted in 20 mL of distilled water (t = 25 ^{O}C) for time series (20 min to 100 h) in 16 hrs intervals. Same procedures repeated in triplicates, shaken period, centrifugation, and filtration sequences.

Incubation column study: Although mass transfer experiments provides an assessment of the kinetic dynamics of phosphate in the liquid phase, but is not feasible for fertilizer applications, Hypothesize were undertaken in the column incubation experiment. This is because the release of any nutrient into the solution must take into account the moisture state of the soil and its changes, so it was necessary to develop this experiment that highlights this effect. A column experiment was performed. Columns are a 60 mL plastic tubes, 32 mm inner diameter × 137 mm height. Mini reactor in the column consists of (1:1) soil and sand. It is assumed that mixing with silicate sand enhances the permeability and eliminate the expected compression. Soil was collected from olive orchard in Latakia countryside located in 35 51^{o} north and 35 92^{o} east, and it was selected according to its lack content of bioavailable P determined by Olsen method where (Olsen –P = traces, Total– P = 585.53 $mg.Kg^{-1}$). Soil was calssified as calcic Entisol, total carbonate = 47%, total physical clay = 46%, organic matter= 0.31%, CEC=26 $cmol.Kg^{-1}$ Langmuir maximum adsorbed P = 435 $mg.Kg^{-1}{}_{soil}$ (46). A pretreatment was done for sandy part of each core by acidification with 0.01M HCl for two days, washing several times with distilled water to wash out all chlorides, afterward dried, and sieved by 35 mesh sieve. The core of (10 g soil: 10 g sand) was laid on a sandy bed 0.5 mm thickness mixed thoroughly, in addition to that, another layer of sand mixed with studied fertilizers sources (mineral source or SRFs). Overall height for bed columns were 11.8 cm, bed volume is 35% of total porosity. Columns designed in duplicates. Incubation column study is aimed to test the effectiveness of P-release between SRF_1 and SRF_2 comparing with equalized amount as much as 31 mg P of KH_2PO_4 powder treated as a blank. Incubation study started with pre-saturating using distilled water from bottom to top to make sure that no restricted air in the macro pores could hinder transfer of water in the column, then left to flow out all gravity water. Wetting stage consists of 10 rinses during ten hours, fluidity was stopped into every column, and the tip was covered by parafilm tapes from up and down the column to prevent any infiltrate water, while incubation stage takes 5 days intervals up the next wetting time. Overall time lasted 40 days. Infiltration rate was adjusted at 1 bed volume per hour.

Phosphate determination: Phosphate concentration is determined by spectro-photometer using the P- molybdate ascorbic acid complex method at λ=882 nm (39).

RESUITS AND DISCUSSION

Diagnostic properties of NSZT and SRFs:

XRD chart: Also (Fig 1.A) represents remarkable peaks for calcite phase, in the other hand, the same 2θ positions peaks are not distinguished in the (Fig 1.B), what can be attributed to dispersion of diffracted rays as a result of surface modification procedure with HDTMA organic material with phosphate formations. In fact, XRD chart Fig (1.B) represented defined peaks of phosphate conformable to Brushite phase, It means that

calcium diphosphate ($CaHPO_4$. $2H_2O$) is the abundant phosphate type, this can be explained by suitable conditions of nucleation , which is assumed that is formed isothermally with Ca^{2+} on to the interface of the HDTMA-Br layer as the following equation at initial pH conditions (> 10) as the following (28,50):

$$Ca^{2+} + HPO_4^{2-} \leftrightarrow CaHPO^0_{4\,(eq)} pK = 7.0 \quad (1)$$

It is revealed that HDTMA- Br surface modification is beneficial practice provided homogeneity for the surface complex nanoparticles of NSZT. Clay mineral (mont-morillonite phase) may rule a deterrent for possible surface complexes with phosphate. While, carbonate component plays an isomorphic substituent agent between carbonate ions and phosphates on the calcites particles. It is likely related to co-precipitation phenomena as it is suggested by (25).

Scanning electron microscopy (SEM):

Fig (2-A) visualized the morphology of natural milled samples. Calcite structures seemed with sharp edges rhombohedral crystal symmetry. Besides, Analcime structures (ANA) displayed round edges with sharp corners Edges. Clay coatings of Montmorillonite (Mm) showed a fine powder appearance and micro crusts depositions, while HDTMA-Br coating featured more grainy particles in the a+ and b+ area in (Fig 2-B), besides chains of surfactant layer seemed as white duvets hided the distinguishable dissimilar structures in the natural sample, which can provide an advantage in purpose of surface homogeneity (9). Phosphate salt effect changed the micro assemblages as presented in Fig 2-C : potassium diphosphate - loading gave a "French fries" structures due to Calcium diphosphate formations, besides plates micro depositions were discernible in agreement with Brushite at 20 µm scale charts. as well as described by (37). Majdan et al (36) supposed that negative surface heterogeneous assemblages bind with the polar organic layer of HDTMA-Br. In addition to that, alkali cations in solution (i.e Ca^{2+}) contribute to form micro bridges with the Br part of HDTMA-Br chains. Another assumption, phosphate ions located in outer-sphere complex between HDTMA-Br and cationic bridge of calcium. Studied modified sample is compatible with mineralogical results revealed by (7). They found that HDTMA-Br has got good tendency to format bilayer coverage on the natural zeolitic frameworks. This affords an opportunity for PO_4 oxianions to develop outer surface complexes with bilayer HDTMA.

Fourier transform infrared spectroscopy (FTIR spectra): Fig (3.A) clearly represents sharp peak approximately between 720 – 780 cm^{-1}, it indicates the symmetric stretching vibration of internal tetrahedral unit. Also common peak in the range 1020 - 1040 cm^{-1} and the band in the 1650 cm^{-1} is recognized, by which internal antisymmetric T-O_4 stretching similar to observations by (2), distinguishing the common features of the PHI and ANA fingerprints bands where both meant minerals belongs to S_4R group of zeolite minerals (6). In Addition, peaks observed in the range 3500 – 4000 cm^{-1} indicates the vibrations of zeolitic coordination water, accompanied with either of Fe and Mg linkage with external OH- groups (23). Chart (b) indicates conformity with the natural sample. Besides, position of CH_2- CH_2 groups stretching in spectra range of 2700- 3000 cm^{-1} related to HDTMA- Br is observed (16). An enhanced bands in the range 900 -1100 cm^{-1} may correspond to C-C antisymmetric stretch of one layer of HDTMA- Br. (52). It is concluded to successive procedure of the surface modification on the nano sized particles by HDTM-Br. Peaks in the range 1400 – 1500 cm^{-1} indicates the asymmetric C-O bonds of the carbonate components in the natural zeolite (43).

P Adsorption study on NSZT: The most important approach used to understand either the qualitative or quantitative aspects of adsorption phenomena is adsorption isotherm, it represents the function between the adsorbed amount onto solid phase surfaces (Q_{ads}) and the equilibrium concentration of adsorbate (P) in the liquid phase C_e. Current study used Langmuir and Dubinin Radushkevich linear isotherms

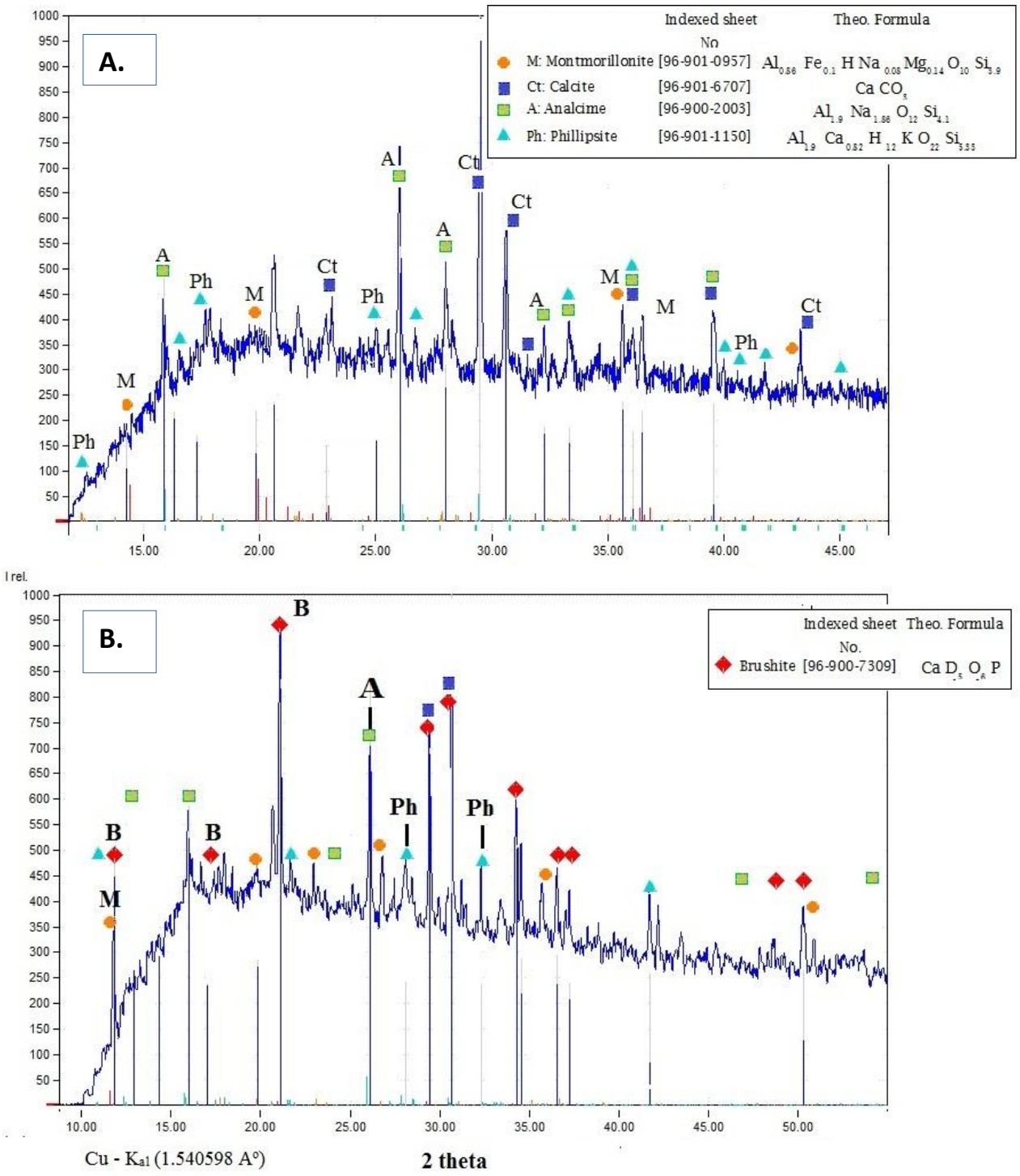

Fig 1. Qualitative analysis results of samples X-ray diffraction patterns, chart (A.) for surfactant modified Zeolite (HDTMA loading 190%) (SMZ2) sample, chart (B.) for slow release fertilizer prepare from SMZ2 (SRF_2) sample. Ph: Phillipsite, Ct: Calcite, A: Analcime, M: Montmorillonite and B: Brushite.

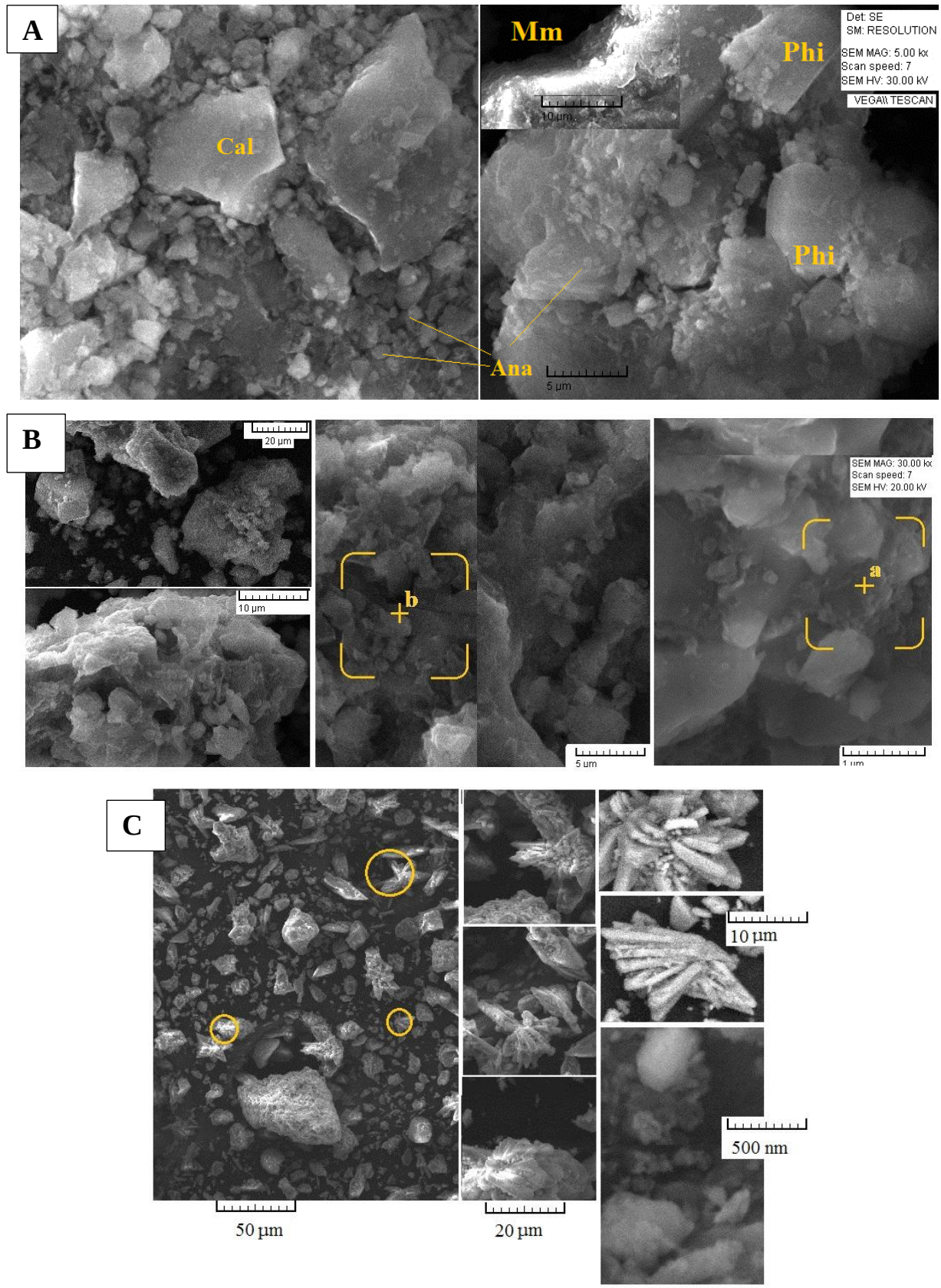

Fig 2. Scanning electron micrographs captured in gradient micro scales 20 – 500 nm for : A) Natural nano Zeolite. fine milled unmodified samples. B) HDTMA-Br surface double layer of 180% coverage level. C) P-loaded modified natural zeolites

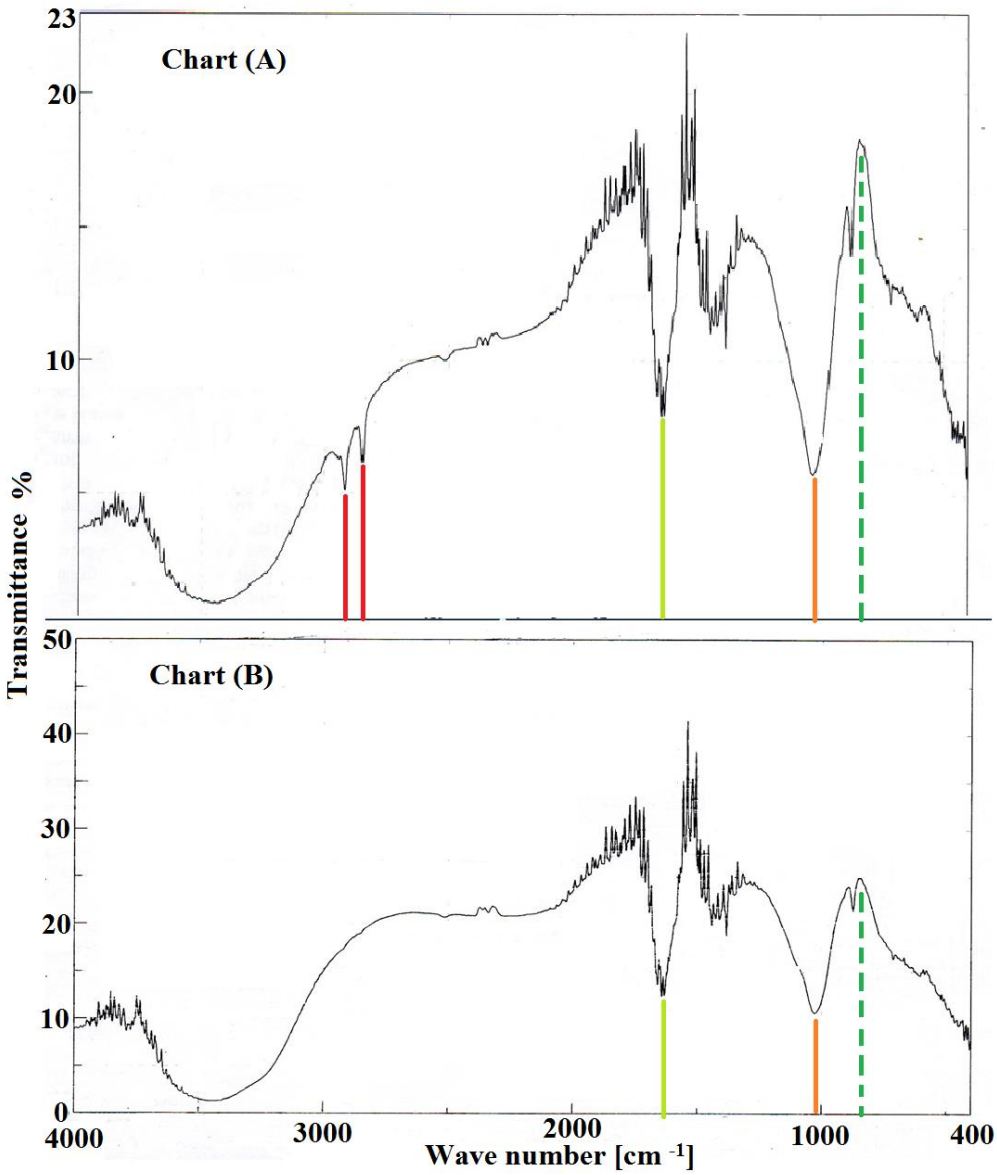

Fig 3. FTIR spectra for NSZT samples (chart B.) compared with SMZ sample (chart A.).

Langmuir adsorption isotherm used to describe P adsorption from aqueous solutions, assuming that process is occurred as a result of P occupation the external positions of the micelle layer of HDTMA-Br loaded on NSZT. The expression of the Langmuir model given by following Linear formula Eq2.:

$$\frac{C_e}{Q} = \frac{1}{K_L.Q_{max,L}} + \frac{1}{Q_{max,L}} . C_e \quad (2)$$

Where, C_e: The equilibrium concentration of P($mg.L^{-1}$), Q: The amount of adsorbed P ($mg.g^{-1}$), $Q_{max,L}$: Maximum monolayer coverage capacity for P ($mg.g^{-1}$). $\boldsymbol{K_L}$ Langmuir isotherm constant ($L.mg^{-1}$).

Dubinin Radushkevich isotherm: commonly used to describe the adsorption characteristics on surfaces that have porous structures (1,8). It is given in the following linear equation Eq 3. :

$$Ln\ Q_e = \ln Q_{max,DR} - K_{DR} . \varepsilon^2$$

$$: \quad \varepsilon = RT \ln(1 + 1/C_e) \quad (3)$$

Where : Q ($mg.g^{-1}$): The adsorbed amount of P per unit mass, Q. ($mg.g^{-1}$): sorption capacity of zeolite sample per unit mass, ε ($J.mol^{-1}$): is Polanyi adsorption potential, K_{DR} ($mol^2.J^{-2}$). Dubinin- Radushkevich adsorption constant at T (300 ^{0}K). C_e ($mg.L^{-1}$): equilibrium solution concentration of the phosphate. R is gas constant (8.3147×10^{-3} J. mol^{-1}. K^{-1}):. DR and Langmuir isotherms are both contradicted modules, they utilized to describe the surface sorption affinity to adsorbate (Phosphate) (20). (Table 3) represented DR model Correlation factor R^2 > 0.8 for SMZ_1 SMZ_2, whereas Langmuir isotherm demonstrated R^2 > 0.95 for SMZ_1, SMZ_2.

Table 3. Parameters of adsorption linear models of surface modified SMZs.

Treatment	R^2	$Q_{max, L}$ mg.g^{-1}	K_L L.mg^{-1}	Linear equation
		Langmuir (L)		
SMZ_1	**0.972**	**2.24**	**0.146**	**Ce/Q = 0.00076 Ce + 0.0225**
SMZ_2	**0.999**	**4.29**	**0.117**	**Ce/Q = 0.00035 Ce + 0.0012**
		Dubinin-Radushkevich (DR)		
	R^2	**$Q_{max, DR}$ mg.g^{-1}**	**K_{DR} L.mg^{-1}**	**Linear equation**
SMZ_1	**0.82**	**0.52**	**0.017**	**Ln Q = 0.024 ε^2 + 6.508**
SMZ_2	**0.85**	**0.67**	**0.024**	**Ln Q = 0.017 ε^2 + 6.261**

Although, accompanying phases of natural Syrian zeolites such as calcite and iron oxides play a significant rule in P binding from aqueous solution (18) in macro particles material. This study observed that the higher loading amount of HDTMA-Br, the higher adsorption capacity of Phosphate on SMZ samples. SMZ_1 sample were 83% of ECEC coverage by HDTMA-Br represents about one layer, it showed that $Q_{max,L}$ = 2.24 mg.g^{-1}, Whereas SMZ_2 represents approximate bilayer of HDTMA- Br coverage level to (190% of ECEC%) showed $Q_{max,L}$ =4.29 mg.g^{-1} . Surface HDTMA-Br modification tend to change the P sorption characteristics for natural sample into better estimations as well as similar research on Chromate (36)**.** Cappelliti et al (7) showed similar results on counterions, they found that HDTMA-Br coverage level didn't affect the adsorption capacity, also studied surfactant was independent factor corresponding to the type of counterion and type of zeolitic structure. This is endorsing that surface modified NSZT with double layer HDTMA (SMZ2) was better to bind phosphate. Similar to Langmuir model, it is indicated that DR isotherm is moderately fitted to describe the P- Sorption on surface modified zeolite, it mathematically confirms that adsorption is undertaken on non-porous surfaces. DR model can provide an initial judgment whereas adsorption nature is attributed to physical free energy (20). The benefit of using adsorption isotherms is to define adsorption capacity of zeolite, where $Q_{max, L}$ from Langmuir isotherm were better to be dedicated.

Phosphate desorption experiments:

Desorption models: Second order kinetic module: Eq.4 represents the linear relation between desorption time t and released phosphate concentration q_{des} (19,21):

$$\frac{1}{q_{des}} = \frac{1}{q_{0,cal}} + k_{2th,des}.t \qquad (4)$$

Where $k_{2th\text{-}des}$ is the rate constant of second-order equation (g.mg^{-1}min^{-1}). $q_{0,\ cal}$ represent computed value of desorbed amount of phosphate at equilibrium according to the reciprocal of intercept of Eq. (4). half- reaction time $t_{1/2}$ extrapolated from this model as it follows the initial desorption rate (21) as following equation: $t_{1/2}$= 1/ $k_{2th,\ des}$. $q_{\ 0,cal}$. Model assumed that half-reaction time is correlated to the initial concentration of P desorbed.

Elovich model: Model is primarily developed to describe the phosphate desorption in solution from soils (54), hypothesizing that sorption (adsorption/desorption) is decreased exponentially with time, passing through Sposito 1984 who preferred to use Elovich model for describing PO_4^{3-} sorption kinetics on soils as in soil minerals solutions. Therefore, Elovich linear equation can be written by the following Eq (5):

$$Q_{des,t} = \frac{1}{b}\ln(\alpha\,.\,b) + \frac{1}{b} ln\, t \qquad (5)$$

Where $Q_{des,t}$ (µg.L^{-1}) desorbed $PO_4^{3-} - P$ into solution by the time t (min), α (µg.L^{-1}.day $^{-1}$) is an initial desorption rate, b (L.µg^{-1}) is a constant indicates the desorption rate.

Phosphate desorption in solution:

Executed experiment of phosphate releasing in water solution aimed to find out the exhausted time, and to find the good surfactant coverage ratio useful for P desorption. Experimental study showed that SRF_1 discard the loaded quantity of phosphate after 1460 minutes,

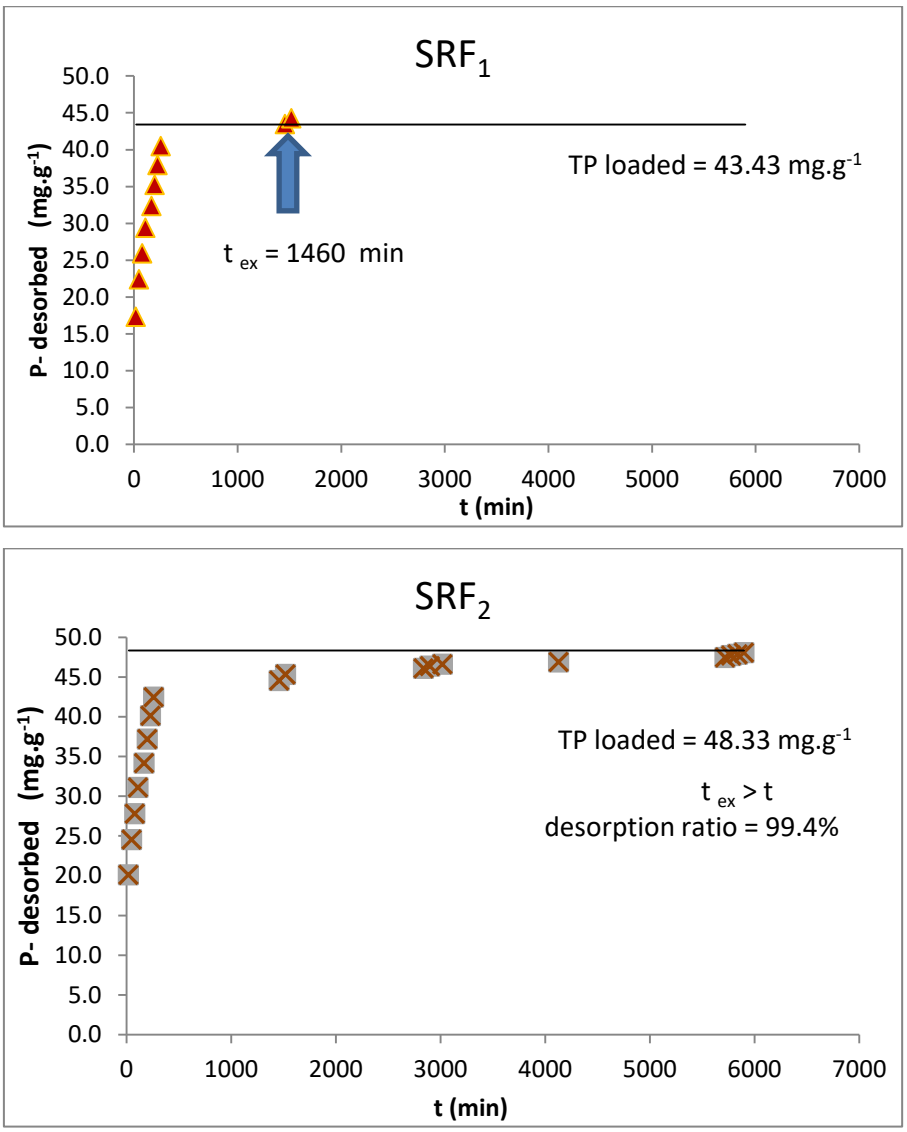

Fig 4. P desorption into liquid phase (distilled water) for two samples of P loaded SMZs

while **SRF_2** reached 99.4 % of phosphate loaded quantity at the end of study (5900 minutes). Fig. (4) illustrates phosphate release rate from SRF samples could be divided into two phases; high release rate due to fast desorption, which is related to weekly bounded – phosphate on to surfactant layer after 1460 minutes similar to (3). The other phase is low desorption rate, where it is explained by anion exchange reaction between phosphate on the surfactant layer and OH^- and/or carbonate equilibrium types in liquid phase, where it can be explained that outer sphere complexes developed after physical-nature-bounds were established between adsorbed phosphate and micelle layer on SMZ. This mechanisms is familiar for oxyanions linkage with HDTM-Br surfactant on clay minerals or zeolites (10,33). However, **SRF_2** with bilayer surfactant on natural samples has the advantage of increasing exhausted time of modified sample, besides , there is approximately 11% of total P loaded was released during the second period of desorption. This indicates that bilayer has a noteworthy rule on P release in solution. This result can be used as a primal significant indicator for assess SRF samples in the field experiments application.

Incubation column study:

- Incubation study equalized the initial concentration of phosphate comparing with potassium phosphate salt (as a blank). Soil used in the column experiment was calcic (Total CO_3 – C > 40%), therefore. calcium carbonate the basic component rule to the phosphate transport through column porosity .
- There is differentiation between P-loading as fast water-soluble (blank), and the expected multi layers of phosphate clusters

onto surface modified samples in relation to the initial desorpion transport in the flux. That's what is found in the early stages of 5-10 days (fig 5 .a). Griffin and Jurinack (15) showed primer explanation, that critical clusters of phosphate passed into solution at the first stage, hindered by the interaction process between phosphate and colloidal carbonate particles. Shahabifar et al (47) confirmed this concept since CEC and calcium carbonate lead to stabilize the P- desorption into porous solution. Current study indicated that less of 10% P- loaded transported through flux during 40 days, with no forgetting the fact that studied soil has maximum P adsorption capacity 0.5 $g.Kg^{-1}$ soil (4).

- Second order model can provide good estimation of P desorption rate linear decrease with time. While, elovich Eq. is well fitted to predict desorption rate decrease exponentially with time (R^2> 0.9). P desorbing rate constant into soil solution assigned by (k_{2th}) in Table (4) gave the series (blank<SRF_2< SRF_1) where the parameter k_{2th} = 0.0011, 0.002 , 0.0025 $L.\mu g^{-1}.dy^{-1}$ respectively. SRF_2 showed less virtual tendency to control desorption comparing with blank, with insignificant differences between SRF_1 and SRF_2.
- Interactions between blank and soil particles is indefinitely dissimilar with SRF samples. Blank (orthophosphate salt) represents the maximum aliquot. Empirically, model can be used to calculate half time reaction time since. SRF_2 ($t_{1/2}$) = 3.8 days, while SRF_1 ($t_{1/2}$) = 2 days less than blank $t_{(1/2)}$ = 4.56 days. Micro and nano particles assemblages of SMZ (500 nm – 35 µm) is classified - in other cases - as reactive phosphorus, and theoretically bioavailable-P. Micro and nano phosphate particles permeated through the micro porous of columns. Interaction between ortho-phosphate (blank) and surface soil particles is directly undertaken, and adsorption process is common phenomena. Blank, herein, represents the maximum loading. While, phosphate clusters on the surface modified zeolite have got more complicated types process of interactions with soil in the incubation column. Therefore, P - Fixation process with calcic component of soils is faster with phosphate anions (blank P - loadings), thus the calculated desorption half time is higher than SRF samples.
- Current study illustrated that correlation constant R^2 which is computed from Elovich power function is better to describe the release mechanism (R^2> 0.9), that diagnose the electrical characteristics of PO_4 sorption on modified surfactant (SRF) as much as well predicting model to distinguishing the chemisorption mechanism for PO_4^{3-}on to heterogeneous surfaces in the aqueous phases (19,54,).
- Similar to second order data, desorption rate (β) recorded is found that SRF_2 is higher to release P, as it has got the lowest quantitative desorbed measured (less than 10% of loaded quantity). Surface modification of Surfactant unified the surface characteristics, in other hand, is no rule on desorption release coefficient. The surface coverage ratio specified the phosphate physical adsorption nature. Interactions between micro particles SMZ and soil surface is still unclear. But, It concluded that bilayer formation of HDTMA-Br on zeolite particles is better to develop anion exchange linkage between phosphate and SMZ in SRF samples, this concept came in accordance with (33).
- Incubation column study is still primer study comparing with field experiments in presence of biological factor (plant and microorganisms), where desorption process takes simultaneously 400-500 days (34 ,35). Besides, this procedure can be useful for approximate statement about what is occurred between P in soil solution and the surfaces of granular aggregates on microscale standings. Considering the effectiveness of P loaded on nSZT, It is evaluated the rate of P release in water solution with time, by using kinetic modules.

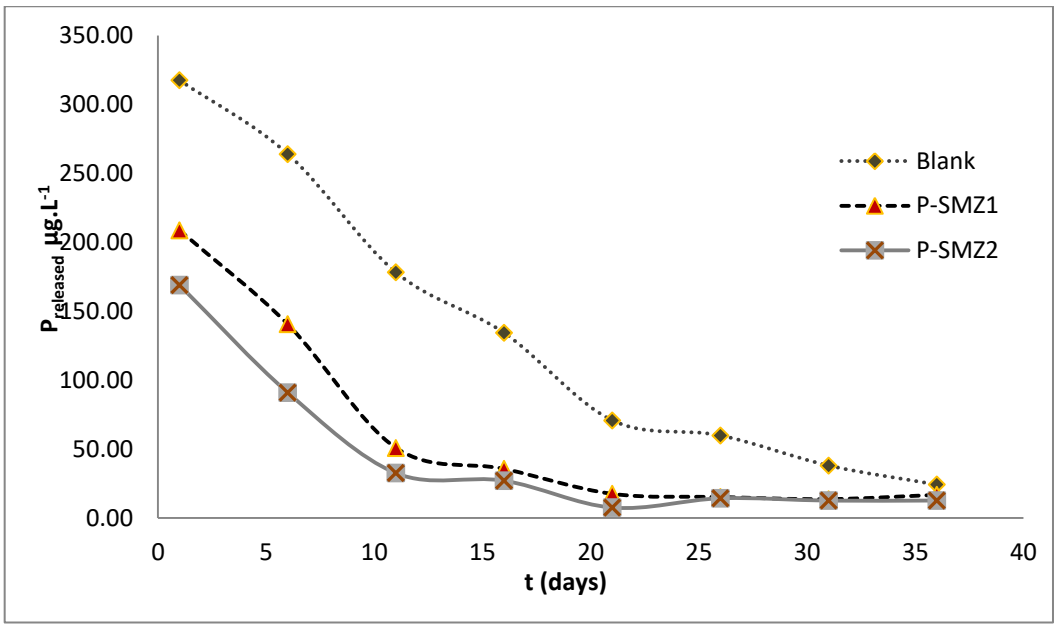

Fig. 5.a. Incubation column study, Desorption of phosphate (µg.L^{-1}) vs time (days)

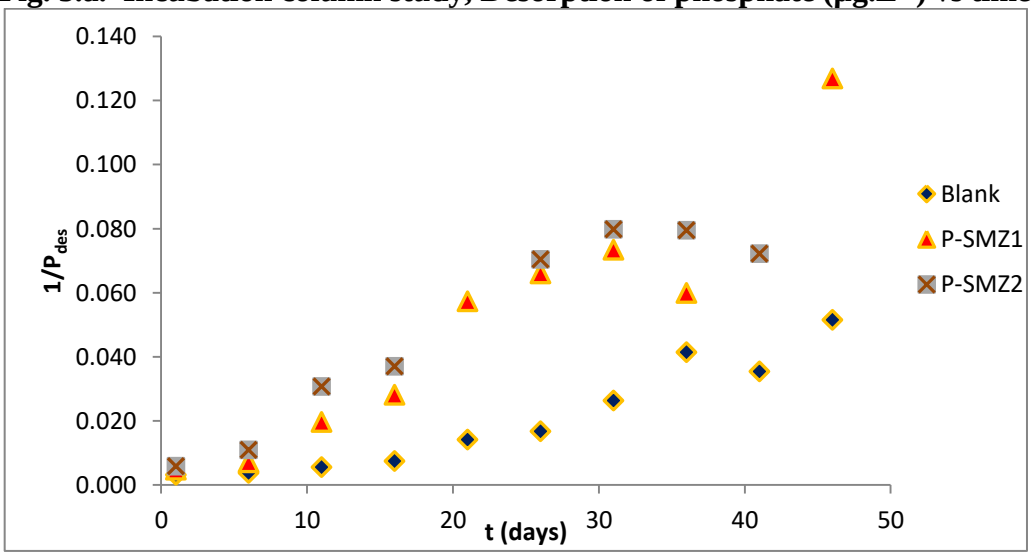

Fig 5.b. Second order model for P desorption onto incubation columns.

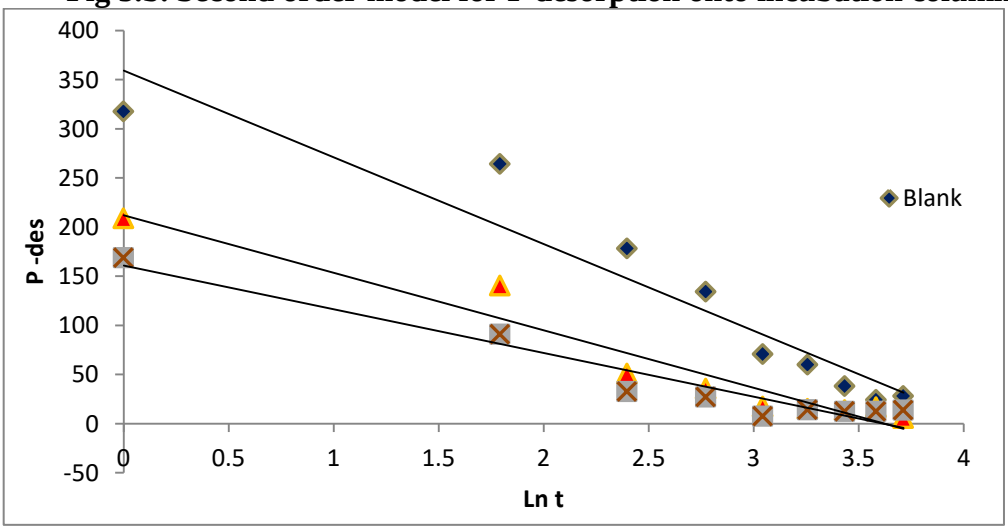

Fig. 5.c. Elovich linear charts – Incubation column samples comparing with potassium diphosphate (blank sample).

Table 4. Incubation column linear models and experimental statistics.

---- Test linear models ----				
2th order module Equation		R^2	k_{2th} L. µmol^{-1}.dy^{-1}	$t_{1/2}$ (days)
Blank	$1/P_{des} = 0.0011\ t - 0.005$	0.904	0.0011	4.56
P-SMZ$_1$	$1/P_{des} = 0.0025\ t - 0.0052$	0.905	0.0025	2.01
P-SMZ$_2$	$1/P_{des} = 0.002\ t + 0.0062$	0.909	0.002	3.08
Elovich module Equation		R^2	β mL. µmol $^{-1}$	h day^{-1}
Blank	$P_{el} = -88.21\ ln\ t + 359.1$	0.912	0.011	0.017
P-SMZ$_1$	$P_{el} = -58.48\ ln\ t + 211.9$	0.940	0.017	0.027
P-SMZ$_2$	$P_{el} = -44.52\ ln\ t + 160.9$	0.934	0.022	0.027
---- Overall statistics -----				
	P- loaded (mg)	Added Weight (mg)	Pdes.Tot # (mg. L^{-1})	B.V. (mL)	Ā %
Blank		4.4	6.35		20.5
P-SMZ$_1$	31	0.714	3.88	465	12.5
P-SMZ$_2$		0.64	3.05		9.8

B. V. Total bed volumes collected from experiment.
h (day^{-1}) = α . β . Desorption rapidity coefficient.
Ā% = 100* Average/ P- loading . Mean of desorbed P through in column.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

DECLARATION OF FUND

The authors declare that they have not received a fund.

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