



(RESEARCH ARTICLE)



Improving the quality of superphosphate fertilizer resulting from the use of low-quality phosphate rock

Mahmoud Mohammed Ahmed ^{1,*}, Emad E. El-Katori ¹, Atef Hemdan Ali ² and Wafaa Mahmoud Abd-Elhamied ³

¹ Chemistry Department, Faculty of science, New Valley University, Egypt.

² Company Drinking Water and Sanitation in Assuit and New Valley, Assuit, Egypt.

³ Production Sector at EFIC, Assuit, Egypt.

World Journal of Advanced Engineering Technology and Sciences, 2021, 03(02), 038–049

Publication history: Received on 08 September 2021; revised on 23 October 2021; accepted on 25 October 2021

Article DOI: <https://doi.org/10.30574/wjaets.2021.3.2.0069>

Abstract

The aim of this paper is to improve the quality of superphosphate fertilizer resulting from the use of low quality phosphate rock by the use of additives as Illite clay, The use of Glaucosite rock (green sand) and illite rock (green clay) in the abu tartur phosphate's region – new valley and mixing it with low quality phosphate rock (22%) for the production of fertilizers with higher quality and rich with the essential elements for plants (N, K) which aren't exist in low quality phosphate rock individually, an industrial sample test had been done and a mixed fertilizer had been produced (Elayte rock and low quality phosphate (22%) as 1:1).

Keywords: Improvement; low quality; Phosphate rock; New Valley; Illite Clay; Glaucosite ore; Abu Tartur mine.

1. Introduction

The Abu Tartur mine is located 650 km southwest of Cairo, Egypt, in the Western Desert (Figure 1) at 25°25' north and 30°05' east. The sediments in the mine are Upper Cretaceous (Campanian – Maastrichtian) phosphorites, black shales and glauconitic sandstones belonging to the widespread shallow-marine deposits of the Duwi Formation. This formation underlies the Lower Maastrichtian to Upper Paleocene Dakhla shale and overlies the Lower Campanian Quseir Formation. Lithologically, it consists of phosphate beds interbedded with black and gray claystone, sandstone, siltstone and glauconite beds, The contact between the Duwi and Dakhla formations marks the Campanian-Maastrichtian boundary and is dated at about 71 Ma [1,2,3,4,5,6,7,8,9].

The Abu Tartur Plateau has attracted the attention of several geologists since the discovery of significant phosphate deposits in the Duwi Formation in 1967. These Upper Cretaceous marine sediments have been of intense economic interest because of the phosphate-rich deposits of the Duwi Formation that form part of an extensive Middle Eastern - North African phosphate province. This province accounts for the greatest accumulation of marine phosphorites known, possibly in excess of 70 billion metric tons of phosphate rocks. The phosphate resources in Egypt alone have been estimated to exceed 3 billion metric tons [10,11,12].

1.1. Glaucosite ore

Glaucosite (Figure 2) exists in abu tatur (new vally governerate) at the top of the phosphate rock [12,13], and its on of the comon minerals in the Sedimentary rocks which is rich of potassium (K) especially in Green sand deposits ١١ج, It's a Green, shiny material resembling mica flakes or clay blocks, The semi-pure type is called green sand, which is uses as a water soft. The chemical formula of Gauconite is $(K,Na)(Fe_{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$ [6,7,12,13,14,15,16]. And

* Corresponding author: M Ahmed
Chemistry Department, Faculty of science, New Vally University.

hardness of the metal relative to glauconite is 2% , It has a complete dissociation in one direction, which is the vertical crystal axis, And the specific gravity ranges between 2.4% – 2.95% , its Refractive index is 01062 ,and The percentage of potassium ranges in glauconite according to XRF analysis between 6%-9 % [6,7,8,18,19,20,21,22,23,24].

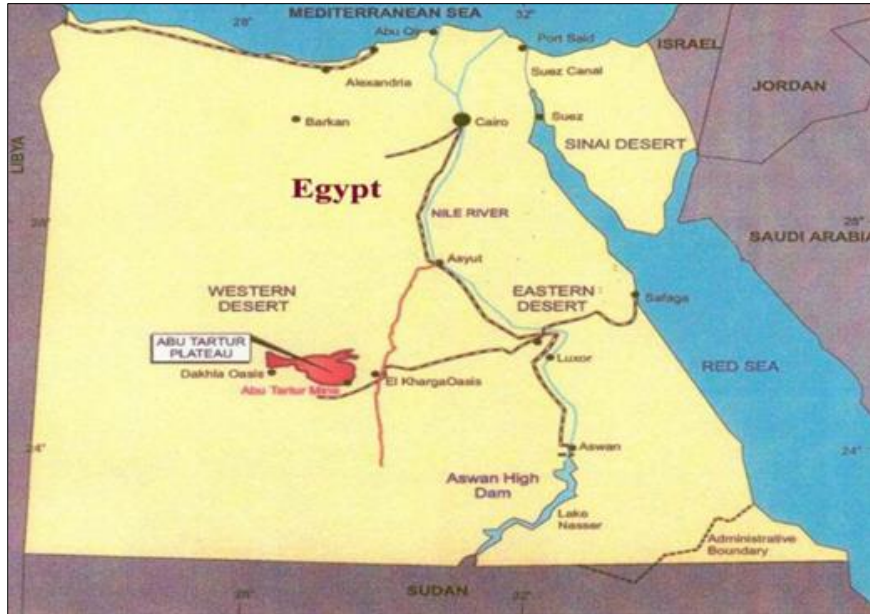


Figure 1 Geographic map of Egypt, Abu Tartur Plateau is highlighted (www.abutarturphosphate.gov.eg)



Figure 2 Glauconite Ore

Table 1 Chemical Composition of Glauconitic grain (after odin 1988)

Deviating results	contents	Oxide
a few higher values indicate quartz admixture	47.5%-50%	SiO ₂
some values up to 15%	3.5%-11%	Al ₂ O ₃
higher values when oxidized	19%-25%	Fe ₂ O ₃
	0.5%-2%	MgO
lower values when	3%-9%	K ₂ O

1.2. Lalite ore (Glauconitic clay)

It exists in abu tartur (new vally governerate) at the top of the phosphate rock, and it's from the comon minerals in the Sedimentary rocks which is rich of potassium (K) especially in Green sand deposits [5,6,7,], Green smooth material from small clay blocks (Figure 3)and it has the ability to get wet with water [8], and its chemical formula is $[K.H_3O(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2.(H_2O)]$ [27]. As the aluminum concentration increases at the expense of the iron

concentration, and The percentage of potassium ranges in glauconite according to XRF analysis between 3%-9 % (Tables 1,2,3 shows the chemical composition of glauconite, bitumen and clay of abu tartur mine) [27,28].



Figure 3 Lalite ore

Table 2 The chemical composition of the bitumen ore is similar to that of abu tartur

Oxides	Beavers Bend Illite	Marblehead Illite	Rock Island Illite	Fithian Illite	"Grundite"
SiO ₂	47.00	52.78	54.09	43.95	47.08
Al ₂ O ₃	23.30	24.90	26.30	21.12	28.05
Fe ₂ O ₃	07.74	00.78	01.50	07.90	08.16
FeO	03.20	01.19	01.49	03.42	nd
MgO	01.70	03.60	02.00	01.50	02.33
CaO	00.17	00.69	00.49	00.84	nil
Na ₂ O	00.14	00.22	00.22	00.32	00.32
K ₂ O	06.69	07.98	06.87	05.90	06.48
H ₂ O+	08.24	06.73	06.89	08.25	nd
H ₂ O-	00.64	02.56	01.32	02.08	nd
Ign. Loss	06.64	06.36	05.79	12.44	07.73
TiO ₂	00.66	01.02	00.68	00.62	nd
P ₂ O ₅	-	-	-	00.70	nd
Total	97.24	99.61	99.43	98.69	100.15

The chemical composition of the bitumen ore which is similar to that of abu Tartur

Table 3 Clay composition

Clay	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	CaO	MgO	K ₂ O	Na ₂ O	Ti ₂ O	MnO	Ign. Loss	Sum
Composition	54.18	14.20	12.11	02.03	02.03	00.68	04.01	04.01	00.04	00.22	00.03	06.56	100.13

2. Material and methods

2.1. Procurement of raw materials

Phosphate rock with a total P₂O₅ content of 22% and illite clay was collected from abu tartur mine–new valley. Phosphate rock and illite clay was ground. H₂SO₄ of purity equals 98% from EFIC assuit. Distilled water was used for

the dilution of the acid. The ground phosphate ore was then mixed with different ratios of ground illite clay to prepare the samples on study. It was initially calculated that a total 40% (70gm) of liquid (acid) is enough to wet a 100 gm. of solid (rock) [29].

2.2. Experimental methods

50 gm of ground phosphate was mixed with 50 gm of ground illite in a beaker Softness of phosphate and green clay from 92% -94%.. Then H_2SO_4 was diluted to 55 bumea by careful addition of distilled water. Now The amount of acid added 60% concentration is 60 grams of acid per 100 grams of (phosphate + green clay) with the help of glass stirrer. The sample then carefully placed in oven at 80oC for one hour before analysis. Other samples of single super phosphate and illite were prepared by using different ratios of phosphate and illite, are shown in (table 1). Two industrial samples were prepared (samples No 2, 3 in (table 4)).

Table 4 Single Super Phosphate with Illite Clay Samples

Sample	Composition
1	50g phosphate rock+60g H_2SO_4 (55 peamu)+50g illite
2	60g phosphate rock+60g H_2SO_4 (55 peamu)+40g illite
3	70g phosphate rock+60g H_2SO_4 (55 peamu)+30g illite
4	75g phosphate rock+60g H_2SO_4 (55 peamu)+25g illite
5	80g phosphate rock+60g H_2SO_4 (55 peamu)+20g illite
6	90g phosphate rock+60g H_2SO_4 (55 peamu)+10g illite

Samples on study (from mixing SSP with illite)

2.3. Product analysis

Standard methods from EFIC Assuit Standards Quality Control Authority were adopted for the analysis of samples to get accurate values of the contents present in samples. Following were the testing procedures adopted to analyze the samples for oxides and potassium.

2.3.1. Test for total P_2O_5 content

Determination of total P_2O_5 content percentage according to Setro method

2.3.2. Test For Potassium Oxide

Determination of potassium oxide percentage according to Determination of potassium oxide in fertilizer method

2.3.3. Test for fluorine

Determination of Fluorine, formation of silicon tetra-fluorine and absorption of the evolved gas in water according to offerman's method

3. Results and discussion

It is noted that glauconite ore (green sand) and elite (green clay) contain a significant percentage of potassium. Potassium along with nitrogen and phosphorus is considered one of the basic elements for the plant, and on a large part of its importance in corps production. Most soils contain large amounts of total potassium (1-2 %) in the form of insoluble mineral components. However, only a fair portion (less than 1 %) is abundant for plants in the soil, as Dissolved potassium and interchangeable potassium. In general, the soil lacks the recoverable potassium + dissolved in the soil and available to the plant. When the levels of recoverable potassium are less than (100-150 ppm), there is a shortage of potassium, which means the necessity of fertilization in order to produce crops that need potassium. And the benefits of potassium for the plant are endless as it is considered a prominent element for the plant to survive.

Table 5 Industrial samples results

Analysis	raw phosphate at 70% with 30% of green clay ore	raw phosphate at 60% with 40% of green clay ore
Moisture	9.9	9.25
Acidity	7.40	8.95
Solable P ₂ O ₅	7.20	6,9
Total P ₂ O ₅	10.52	2.0
Sol. K ₂ O	1.5	1.89
Sol. K ₂ SO ₄	3.35	4.46
Sol.MgO	0.5% – 1.0 %	1.0
(Fe ₂ O ₃ – Al ₂ O ₃) With an average percentage of 2.0% – 5.0 %		

Industrial samples results

Table 6 A fresh glauconite sample has been analyzed

Contents (XRF)	Oxide
46.21	SiO ₂
4.81	Al ₂ O ₃
31.41	Fe ₂ O ₃
2.52	MgO
5.64	K ₂ O
2.00	P ₂ O ₅

Result of analysis of a fresh glauconite sample

Table 7 Fresh illite sample has been analyzed

Volumetric analysis Contents	Contents (XRF)	Oxide
	54.68	SiO ₂
	18.03	Al ₂ O ₃
	7.71	Fe ₂ O ₃
	3.60	MgO
< % 0.7 potassium oxide	4.00	K ₂ O
	0.20	P ₂ O ₅

Result of analysis of a fresh illite sample

Table 8 Fluorine results

Industrial Sample	% Fluorine mg/m ³
100g phosphate + 80g H ₂ SO ₄	16
75g phosphate + 25g illite + 80g H ₂ SO ₄	48

Result of released Fluorine during preparing the sample

3.1. Moisture, acidity, potassium Oxide and P₂O₅ results

Moisture, acidity, potassium Oxide and P₂O₅ results shown in table 9

Table 9 Results of mixed phosphate with Illite Clay

No	Sample	Moisture	Acidity	Sol. P ₂ O ₅	K ₂ O
1	50g phosphate rock+50g illite	5.1%	9.23	5.88%	2.5%
2	60g phosphate rock+40g illite	10.3%	9.23%	6.93%	1.67%
3	70g phosphate rock+30g illite	9%	8.52%	7.7%	1.64
4	75g phosphate rock+25g illite	10.3%	6.4%	8.41%	0.69
5	80g phosphate rock+20g illite	7.12%	5.11	8.92%	0.58
6	90g phosphate rock+10g illite	6.81	6.11	9.89%	Nil

3.2. XRF Analysis results

XRF results of samples on study listed in (table 10).

Table 10 XRF analysis results of samples on study

XRF Sample	50g phosphate rock+50g illite	60g phosphate rock+40g illite	70g phosphate rock+30g illite	75g phosphate rock+25g illite	80g phosphate rock+20g illite
SiO ₂	37.62	36.26	55.7	13.75	24.45
Al ₂ O ₃	13.59	13.15	20.17	4.06	4.96
Fe ₂ O ₃	4.36	4.22	6.51	1.52	1.97
CaO	0.57	0.58	1.14	26.77	22.89
HgO	2.49	2.43	3.71	0.87	1.05
SO ₃	0.95	0.86	0.54	12.23	11.89
Na ₂ O	0.11	0.11	0.18	0.40	0.41
K ₂ O	2.5	1.671	1.64	0.69	0.58
Cl	0	0	0	0	0
TiO ₂	0.17	0.16	0.25	0.22	0.22
P ₂ O ₅	0.26	0.25	0.39	0.28	0.3
Mn ₂ O ₃	0.18	0.18	0.33	7.34	5.89
Cr ₂ O ₃	0.01	0.01	0.02	0.00	0.00
LOI	37.70	39.98	8.42	30.97	24.76

LOI refers to lost of ignition

3.3. XRF of Industrial samples at a 1:1, 7:3 and 6:4 ratios

XRF results of industrial samples listed in (table 11).

Table 11 XRF analysis results of mixing phosphate and green clay is at a 1: 1 ratio sample (industrial sample)

Volumetric analysis Contents	Contents (XRF)	Oxide
	17.89	Si ₂ O
	4.78	Al ₂ O ₃
	4.35	Fe ₂ O ₃
	1.21	MgO
3.2% of Potassium Oxide	2.5	K ₂ O
	6.06	P ₂ O ₅

3.4. FTIR Results

FTIR results of samples on study shown in figures (4, 5, 6, 7, 8, and 9).

3.5. FarIR Results

FarIR results of samples on study shown in figures (10, 11).

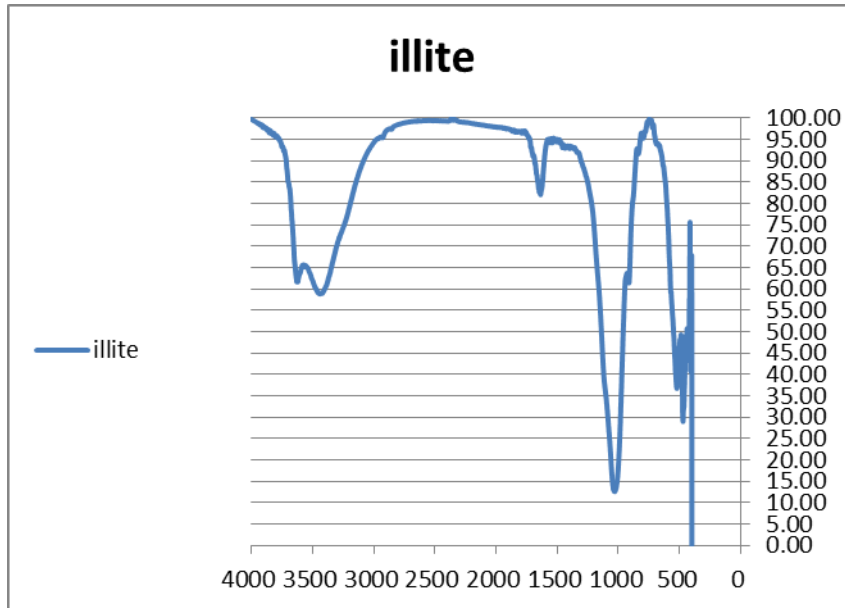


Figure 4 Illite FTIR

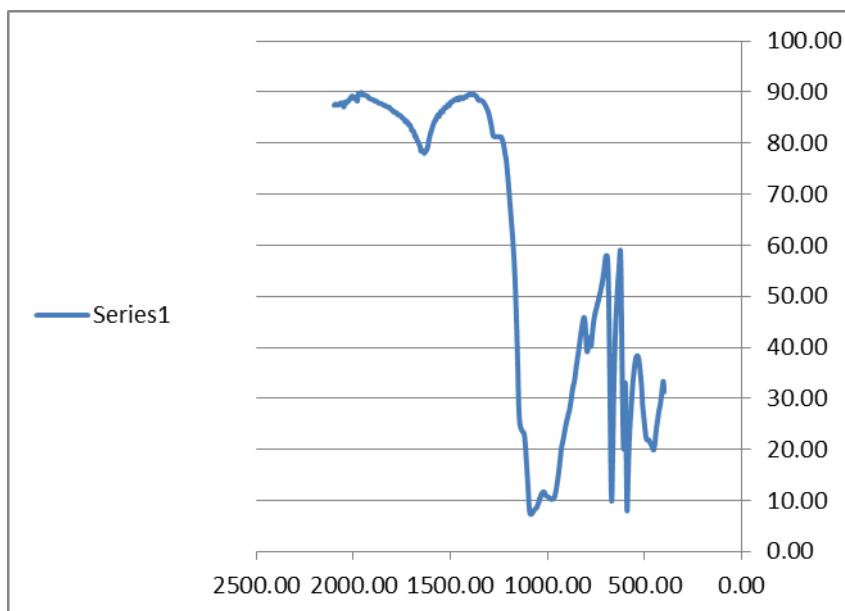


Figure 5 FTIR of single super phosphate without additives

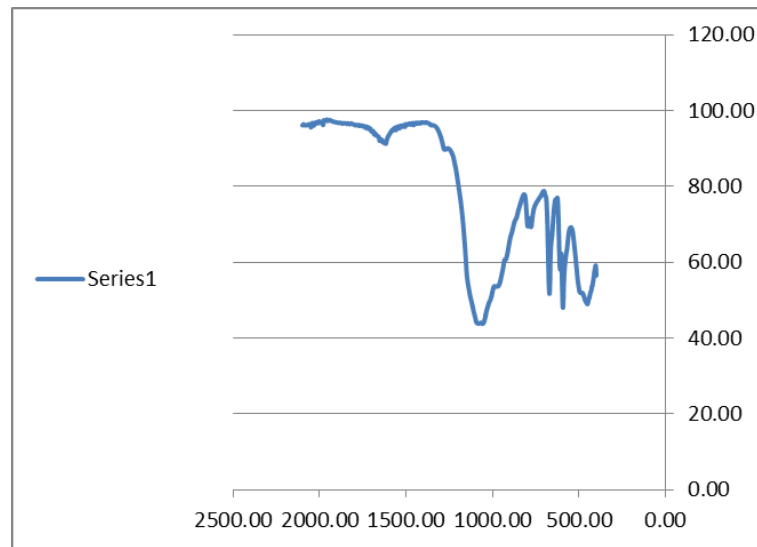


Figure 6 FTIR of (75% phosphate + 25% illite + 80g H₂SO₄) sample.

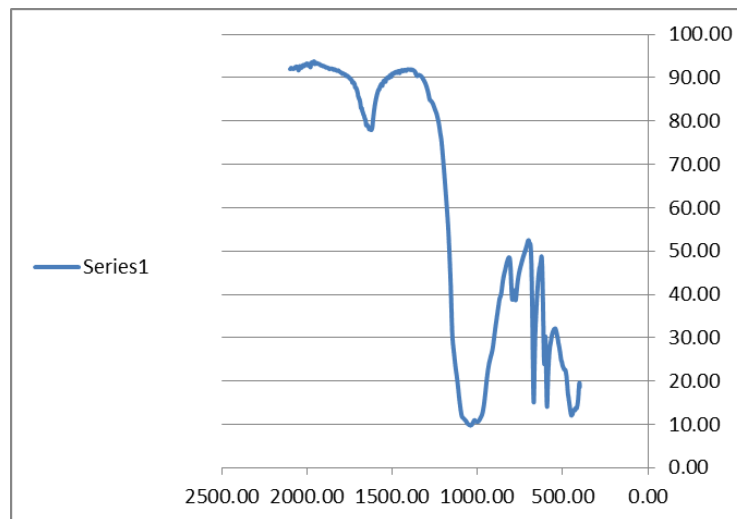
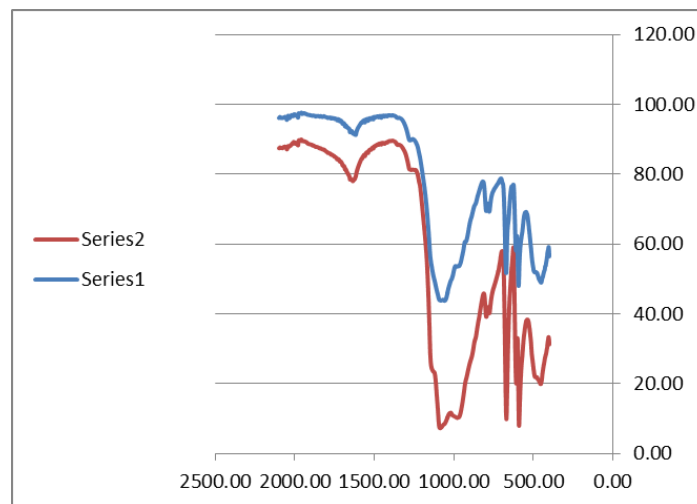


Figure 7 FTIR of (75% phosphate + 25% illite + 80g H₂SO₄) sample.



series1= 100% ph + 0% illite + 80g H; series2= 75g Ph + 25g illite+ 80g H

Figure 8 FTIR

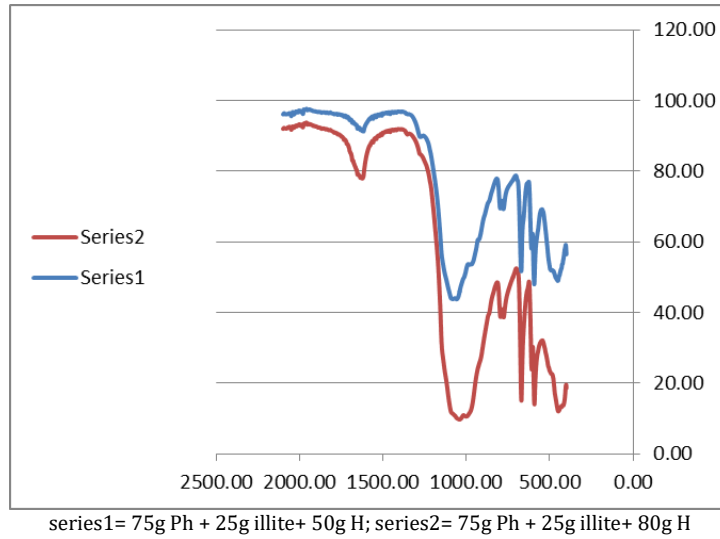


Figure 9 FTIR

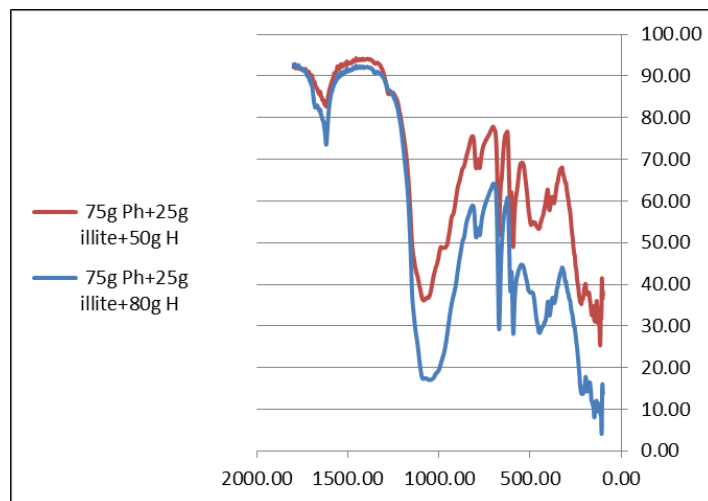


Figure 10 FarIR

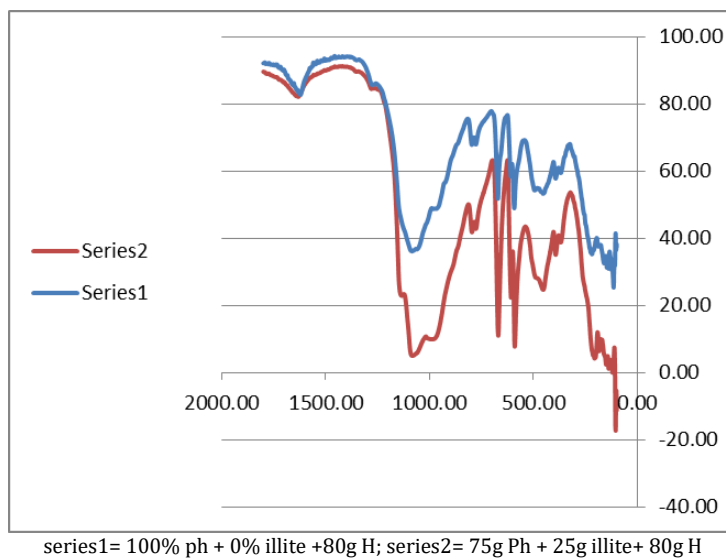


Figure 11 FarIR

3.6. Ramman Results

Ramman results of samples on study shown in figures (12, 13).

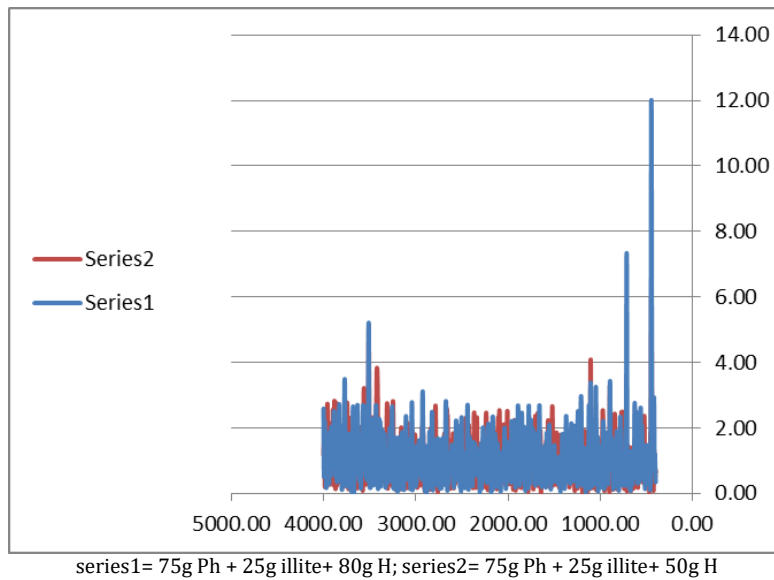


Figure 12 Ramman

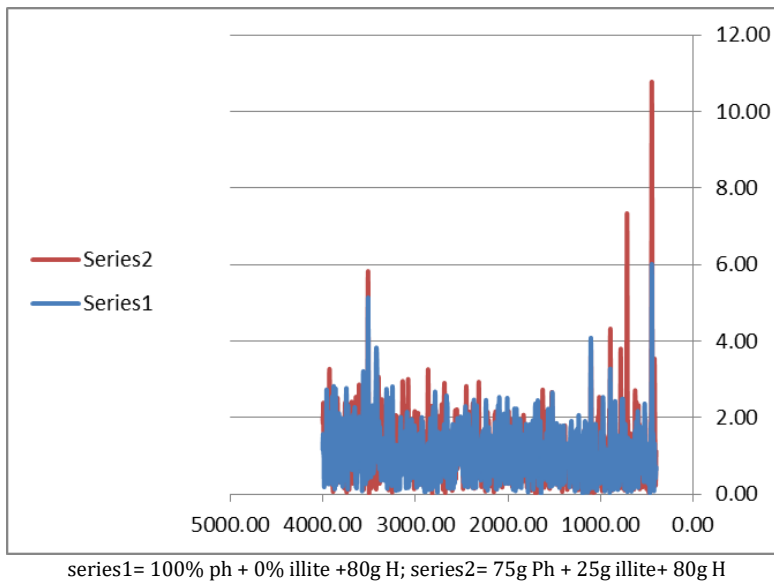


Figure 13 Raman

Using Illite (or Lalite) Clay as an additive to the phosphate rock during preparing single super phosphate resulted in adding new essential elements (as potassium oxide) for the plant in the new prepared fertilizer.

During the addition of potassium (whether ratified or natural) to the phosphate rock during manufacturing the fertilizer, reduces the amount of released florosalysalic acid (which causes very bad odor) so it enhances the fertilizer industry.

4. Conclusion

This study aims to Improving the quality of superphosphate fertilizer resulting from the use of low quality phosphate rock, so we used abotartor phosphate rock 22% and tried some additives like Illite Clay rock by mixing it with phosphate rock at different ratios and was detected from XRF analysis the addition of essential elements for the plant as potassium

oxide , adding potassium as additive reduces the released florosalysalic during manufacturing, which considered a real enhancement for the resulting fertilizer.

Compliance with ethical standards

Acknowledgments

The valuable inputs from colleagues and friends during this review compilation are highly appreciated.

Disclosure of conflict of interest

No conflict of interest.

References

- [1] E D Schall. Superphosphate: it's history, chemistry, and manufacture. Journal of Association of Official Agricultural Chemists. 1965; 48: 1082.
- [2] GLENN CR, ARTHUR MA. Anatomy and origin of a Cretaceous phosphorites-greensand giant, Sedimentology. 1990; 37;123-154.
- [3] SEDIEK KN, AMER AM. Sedimentological and technological studies of Abu Tartur Black Shales, Western Desert, Egypt. Physicochemical Problems of Mineral Processing. 2001; 35: 141-152.
- [4] SOLIMAN, M. A., HABIB, M. E. & AHMED, E. A. Sedimentologic and tectonic evolution of the Upper Cretaceous-Lower Tertiary succession at Wadi Qena, Egypt. Sediment. Geol. 1986; 46, 111-133 .
- [5] AWAD. G. H., GHOBRIAL.M. G. Zonal stratigraphy of the Kharga Oasis Cairo, Egypt Geol,1965; 34; 77.
- [6] BURST, J. F. Glauconite pellets, their mineral nature and applications to stratigraphic interpretations, Bull. Am. Ass. Petrol. Geol. 1958a; 42;310-337.
- [7] BURST, J. F. Mineral heterogeneity in glauconite pellets. Am. Mineral. 1958b; 43; 481-497.
- [8] AMOROSI, A. Glauconite and sequence stratigraphy, a conceptual framework of distribution in siliciclastic sequences. Journal of Sedimentary . 1995;Research B65; 419-425
- [9] NOTHOLT, A. J. G. Phosphorite resources in the Mediterranean (Tethyan) Phosphogenetic Province, A progress report. Sci Géol. Mém., 1985; 77; 9-21.
- [10] MANSOUR HH, KHALLAF AF. Application of textural characteristics for depositional environment interpretation of the Upper Cretaceous-Paleocene east of Idfu-Sibaiya, Nile Valley, Ann. Geol. Surv. Egypt. 1979; 9: 471-497.
- [11] MANSOUR HH, YOUSSEF MM, EL YOUNSI AR. Petrology and sedimentology of the Upper Cretaceous, Paleocene succession northwest of Kharga Oasis, Ann. Geol. Surv. 1979; 9: 471-497.
- [12] M. A.M. Uosif and A. El-Taher. RADIOLOGICAL ASSESSMENT OF ABU-TARTUR PHOSPHATE, WESTERN DESERT EGYPT, Radiation Protection Dosimetry. 2008;130;228-235.
- [13] HASSAN, M. A. & EL-SHALL, H. Glauconitic clay of El Gidida, Egypt, evaluation and surface modification. Applied Clay Science. 2004;27; 219-222 .
- [14] TANTAWY AA, KELLER G, ADATTE T, STINNESBECK W, KASSAB A. SCHULTE P. Maastrichtian to Paleocene depositional environment of the Dakhla Formation, Western Desert, Egypt. sedimentology, mineralogy, and integrated micro- and macrofossil biostratigraphies. , Cretaceous Research. 2001; 22; 795-827.
- [15] HENDRIKS, F., LUGER, P., KALLENBACH, H. & SCHROEDER, J. H. Stratigraphical and sedimentological framework of the Kharga-Sinn El-Kaddab stretch (western and southern part of the Nile Basin), Western Desert, Egypt. Berliner geowiss. Abh. (A). 1984; 50; 117-151
- [16] HERMINA, M. H., GHOBRIAL, M. G. & ISSAWI, B. : The geology of the Dakhla area: Cairo. Egypt Geol. Survey Mineral Resources Dept., 1961;33
- [17] HERMINA, M. H. Geology of the northwestern approaches of Kharga, Cairo, Egypt Geol. 1967; Survey Paper 44; 88p .
- [18] ODIN GS. Green Marine Clays, Oxford (Elsevier). 1988; 22 - 441.

- [19] ODIN GS, FULLAGAR PD. Geological significance of the glauconite facies. In Odin, GS. Green Marine Clays. 1988; 295-332.
- [20] ODIN, G. S. De glauconiarum: Constitutione, origine, aetateque. Thèse d'Etat, Université Pierre et Marie Curie, Paris', 1975. .
- [21] ODIN, G. S. Green Marine Clays. Oxford (Elsevier).1988;22 - 441,
- [22] ODIN, G. S. & FULLAGAR, P. D. : Geological significance of the glauconite facies. In Odin, G. S. Green Marine Clays. , Amsterdam (Elsevier).1988;295-332.
- [23] ODIN, G. S. & LÉTOLLE, R. : Glauconitization and phosphatization environments: A tentative comparison. In Y. K. Bendor (Edit.). Marine Phosphorites. Soc. Econ. Pal. Min. Spec. Publ. 1980;29; 227-237 .
- [24] ODIN, G. S. & MATTER, A. : De glauconiarum origine. Sedimentology. 1981;28; 611-641 .
- [25] HERMINA MH. Geology of the northwestern approaches of Kharga, Egypt Geol. Survey Paper. 1967; 44: 88.
- [26] HERMINA MH, GHOBRIAL MG, ISSAWI B. The geology of the Dakhla area, Egypt Geol. Survey Mineral Resources Dept. 1961; 33.
- [27] S.Ferrari , A.F. Gualtieri .The use of illitic clays in the production of stoneware tile ceramics . Applied Clay Science , 2006;32;73–81.
- [28] Alessandro F. Gualtieri,a * ,Simone Ferrari, Matteo Leoni, Georg Grathoff, Richard Hugo, Mouath Shatnawi, Gianluca Pagliad and Simon Billinged. Structural characterization of the clay mineral illite-1M. Journal of Applied Crystallography ,2008; 10.1107.
- [29] A Hina, M Shahid, T Muhammad, U Muhammad. Enhancement of P2O5 Content in SSP Made from Local Rock Phosphate of Pakistan, International Journal of Innovation and Applied Studies. 2014; 9: 484.