Al-Azhar Bulletin of Science

Volume 34 | Issue 3 Article 7

2023
Section: Chemistry

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How to Cite This Article

Helal, Abdel-Rahman M.; Sultan, Mohamed E.; Bakry, Ahmed Rabea; and Khalil, Hazem F. (2023) "REMOVAL OF ORGANIC MATTER FROM ABU-TARTUR PHOSPHORIC ACID USING GLAUCONITE: A COMPARATIVE STUDY WITH SOME INDUSTRIAL-USED ADSORBENTS," *Al-Azhar Bulletin of Science*: Vol. 34: Iss. 3, Article 7.
DOI: https://doi.org/10.58675/2636-3305.1658

ORIGINAL ARTICLE

# Removal of Organic Matter from Abu-Tartur Phosphoric Acid using Glauconite: a Comparative Study with some Industrial-used Adsorbents

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## Abstract

**Wet-process phosphoric acid (WPPA) is considered the main source for the production of phosphate fertilizer around the world, it is produced by the reaction between sulfuric acid as a leaching agent and phosphate ore rocks. The produced acid contains various contaminants such as iron, magnesium, aluminum, cadmium, and organic matter. So the elimination of the organic matter very an essential stage for the production of purified phosphoric acid. Glauconite ore is present in the Abu-Tarture region nearly to the production site of phosphoric acid. For that no cost for the purification of the produced phosphoric acid and for the first time, glauconite is used in the purification of phosphoric acid. Treatment of phosphoric acid was studied at various parameters such as adsorbent type, adsorbent dose, temperature, and phosphoric acid concentration. The phosphoric acid can be measured before and after treatment by Spectrophotometer, volumetric titration methods, and atomic absorption Spectroscopy. The used glauconite is characterized by radiography diffraction (XRD), elemental analysis by atomic absorption spectroscopy, and particle size analysis. The obtained results for organic carbon removal efficiency in the case of glauconite as adsorbent was 63.36 % which may be an excellent adsorbent compared with acid-activated bentonite and sodium montmorillonite. This work aims to study the organic matter removal by glauconite as a novel adsorbent material in phosphoric acid purification and compare its results experimentally with the most industrial adsorbent materials such as acid-activated bentonite and sodium montmorillonite. The experimental data exhibited that glauconite promising for this purpose because it is a natural material and a reduction in expensive methods for the elimination of organic matter from phosphoric acid.**

*Keywords:* Acid-activated bentonite, Glauconite, Organic matter removal, Phosphoric acid, Sodium montmorillonite

## 1. Introduction

Phosphoric acid ($H_3PO_4$) can be manufactured by various methods. The ultimate common processes are thermal and wet. The thermal process usually contains a very low amount of impurities, but it high expensive technique and notwithstanding. The wet process is the most frequently used at an industrial scale. The wet process occurs through a reaction between mineral acids and phosphate rock. The mineral acids can be selected from the following acids: hydrochloric acid (HCl), nitric acid ($HNO_3$), and sulphuric acid (H2SO4). The farthest common acid used for the process is sulfuric acid [1]. The obtained phosphoric acid by the wet process included multiple ionic impurities such as nickel, copper, fluoride, sulfate, and iron. In addition to the presence of organic matter like humic substances (humic acid and fulvic acid) and hazardous like that (organic matter, copper,

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Received 2 September 2023; revised 11 October 2023; accepted 12 October 2023.
Available online 27 December 2023

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*https://doi.org/10.58675/2636-3305.1658*

cadmium, mercury, …. etc) [2]. The above impurities affect the concentration and the grade of the final output. Therefore around 95 % of the wet-process phosphoric acid (WPPA) is directly used in the agricultural field as fertilizer [3]. WPPA was used in phosphate fertilizer and many industrial domestic products, metal surface cleaners and catalysts, and also as an ingredient for food, and cosmetics. The primary source of WPPA is phosphate rock which has the common form $Ca_{10}(PO_4)_6\ X_2$, anywhere X: $F^-$, $Cl^-$, $OH^-$. Phosphoric acid is produced from two types of phosphate rocks, sedimentary rocks, and igneous rocks, but sedimentary rocks are used more than igneous rocks. The phosphoric acid store was valued at USD 4.85 billion in the year 2019. The component annual growth rate (CAGR) of phosphoric acid is expected to be 3.9 % from 2020 to 2030 [4,5]. Removing organic matter, heavy metals, and all impurities is crucial when developing a simple and reduction in expenses method for WPPA purification. Through the acidification step, some of the carbonaceous material present in the phosphate ore is transformed into humic acids and related organic compounds generally referred to as humates. The organic matter included in the acid may associated with the organic solvent to form constant foams, preventing phase settling, or simply by forming cross layers and organic phases, denaturing part of the solvent. So elimination of these organics seems to be an essential step for the production of purified phosphfigoric acid. The organic matter can be found as colloidal suspension and soluble forms, the colloidal parts are coagulated and deposited with gypsum precipitation through the aging of phosphoric acid, while the soluble parts remain beyond in phosphoric acid.

Many research techniques have been used to remove organic matter from WPPA like ion exchange [6], precipitation [7], membrane process like electrolysis, reverse osmosis and nanofiltration [8], adsorption on activated carbon [9], crystallization [10], extraction with chelating or impregnated resins [11], and concentration or addition of additives [12]. These methods have been widely used but they have disadvantages such as high operating and waste treatment costs, high consumption of reagents, and formation of a huge amount of sludge [13]. Though, it leads to their high cost and sometimes not availability, their use is not compatible as it should be. So a reduction in expenses for alternative technologies or adsorbents for the treatment of impurities such as metals and organic matter which present in WPPA during manufacturing is necessary [14]. Various natural materials (as adsorbents) were tested such as polymeric materials and activated carbon [15]. Clay materials are one of the natural sources that can be used as ion exchangers for the elimination of heavy metals from water due to it is low cost [16]. Activated clays such as activated bentonite are used to remove organic matter from WPPA [17]. The reverse osmosis (RO) membrane is another technique used to remove organic materials and solid materials [18]. Glauconite is a naturally occurring, green sand that is the name given to sediments rich in the bluish-green to greenish-black mineral known as glauconite with low cost and is more effective when compared with another method [19]. In our research, we used the adsorption method in the study of removing organic matter from phosphoric acid with natural glauconite. The cost-effectiveness of glauconite use can be attributed to the availability of this raw material in Egypt compared with the traditional adsorbents in addition to using it without any chemical treatment. Glauconite is a naturally occurring mineral that has a granular appearance, it is hydrous iron potassium silicate, and it has been used in various applications, such as agriculture, and removing heavy metals from water and wastewater. It is used with surface coating by manganese as filter media for removing soluble lead and zinc from water [20]. This article examines simple and reduction in expenses methods for reducing the organic matter by local raw material (glauconite) from WPPA to provide environmentally acceptable phosphate-based fertilizers and other industrial applications. Using glauconite ore to reduce the organic matter in phosphoric acid and comparing the findings with the most traditionally used adsorbents such as activated bentonite acid-activated bentonite and alkali-activated bentonite was studied.

## 2. Materials and methods

### 2.1. Materials

We utilized analytical grade (A.R) chemicals and reagents without any further purification in our experiments. For preparing and diluting aqueous solutions, double-distilled water was used. The chemicals used, along with their names, molecular structures, and sources, are listed in Table 1. We have provided the chemical analysis of phosphate ore obtained from the New Valley (Abu-Tartur) open-cast in Table 2. The $CaO/P_2O_5$ weight ratio was found to be 1.48, which is lower than 1.6. This lower value of the ratio is advantageous for the production of phosphoric acid as it results in lower sulfuric acid consumption during processing.

*Table 1. The used chemicals, molecular structure, and sources in this work.*

| Name, molecular structure | Mol. Wt.[a] | Grade | Source |
|---|---|---|---|
| Sulfuric acid, $H_2SO_4$ | 98.08 | G.R | European |
| Nitric acid, $HNO_3$ | 63.01 | G.R | Merck, Germany |
| Hydrochloric acid, HCl | 36.46 | G.R | Scharlau, Spain |
| Ammonium molybdate, $(NH_4)$ $6Mo_7O_{24}.4H_2O$ | 1235.9 | G.R | Merck, Germany |
| Ammonium meta vanadate, $NH_4VO_3$ | 116.98 | G.R | Merck, Germany |
| Ortho-phosphoric acid, $H_3PO_4$ | 98 | G.R | European |
| Potassium dihydrogen phosphate, $KH_2PO_4$ | 141.97 | G.R | Merck, Germany |
| Ammonium Ferrous sulfate hexahydrate, $(NH_4)_2Fe(SO_4)_2$ $6H_2O$ | 392.14 | GR | Belgium |
| Potassium Dichromate, $K_2Cr_2O_7$ | 294.19 | ACS | Merck, Germany |
| Barium diphenylamine sulfonate indicator, $C_{24}H_{20}BaN_2O_6S_2$ | 633.90 | AR | Merck, Germany |

[a] Mol. Wt, molecular weight.

*Table 2. Chemical analysis of New Valley (Abu-Tartur) open-cast phosphate ore.*

| Components | Wt., % | Components | ppm |
|---|---|---|---|
| $P_2O_5$ | 29.16 | Pb | 15 |
| $Al_2O_3$ | 1.40 | Co | 8 |
| MgO | 0.61 | Cd | 2 |
| $Fe_2O_3$ | 3.95 | Mn | 315 |
| CaO | 43.31 | V | 50 |
| Loss on ignition | 7.05 | As | 35 |
| $K_2O$ | 0.15 | Cu | 17 |
| $Na_2O$ | 0.90 | Cr | 40 |
| $SiO_2$ | 4.05 | Zn | 105 |
| Organic matter | 0.13 | Ba | 70 |
| $SO_3$ | 4.00 | Ni | 35 |
| F | 2.95 | Cl | 700 |
| $CO_2$ | 4.55 | | |

*Table 3. Characteristics of the working acid produced from New Valley (Abu-Tartur) open-cast phosphate ore.*

| Components | DPA[a], wt. % | CPA[b], wt. % |
|---|---|---|
| $P_2O_5$ | 27.5 | 44.20 |
| $Al_2O_3$ | 0.43 | 0.89 |
| MgO | 0.31 | 0.54 |
| $Fe_2O_3$ | 2.90 | 3.35 |
| CaO | 0.05 | 0.10 |
| Organic matter | 0.066 | 0.103 |
| $SO_4^{-2}$ | 2.61 | 3.31 |
| $K_2O$ | 0.0029 | 0.003 |
| $Na_2O$ | 0.020 | 0.022 |
| $F^-$ | 1.45 | 0.89 |
| $SiO_2$ | 0.19 | 0.22 |
| Components | Trace elements (ppm) | Trace elements (ppm) |
| Co | 5 | 8 |
| Ni | 37.35 | 63.25 |
| V | 46.66 | 79.60 |
| Cu | 22.80 | 35.70 |
| Ba | 8 | 13.50 |
| Zn | 155 | 280 |
| Cr | 33.0 | 55.45 |
| Mn | 210 | 360 |

[a] DPA = Diluted phosphoric acid.
[b] CPA=Concentrated phosphoric acid.

However, the high concentration of Ferric oxide ($Fe_2O_3$) content reduces the filtration rate. We have also provided the chemical analysis of phosphoric acid produced from open-cast phosphate ore in Table 3.

(Tonsil optimum 210 FF or bleaching Earth) is acid-activated bentonite which is used in a wide application for purification processes. It is manufactured by acidic activation of calcium bentonite. Acid-activated bentonite is a fine, yellowish-grey powder that appears with a highly porous inner structure and a multitude of acids on its surface. Acid-activated bentonite possesses an outstanding adsorptive capacity for polar compounds via chemisorption and acid catalysis. The particle size of acid-activated bentonite is characterized by sieve analysis of the dry powder; the following average values have been determined for the various sieve in Table 4. The chemical composition of acid-activated bentonite was determined for determining the components in the form of oxides, as illustrated in Table 5.

Sodium montmorillonite bentonite with a commercial name, AccoForm WT is supplied as a free-flowing powder with a high-purity grade of sodium montmorillonite, selectivity mined, consisting of micronized particles. AccoForm WT is specifically produced to be used as drainage, detention, and

*Table 4. The particle size distribution of acid-activated bentonite and glauconite by sieve analysis.*

| Materials | >150 μm | >100 μm | >63 μm | >45 μm | >25 μm |
|---|---|---|---|---|---|
| Acid-activated bentonite, % | 5 | 17 | 29 | 40 | 60 |
| Glauconite, % | 7 | 19 | 30 | 43 | 61 |

*Table 5. The Chemical analysis of activated bentonite and glauconite.*

| Components,% | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $Na_2O$ | $K_2O$ | L.O.I[a] |
|---|---|---|---|---|---|---|---|---|
| Acid-activated bentonite | 66.8 | 14.20 | 3.70 | 1.10 | 2.30 | 0.80 | 2.20 | 8.0 |
| Glauconite | 62.49 | 10.58 | 10.40 | 1.84 | 3.34 | 0.10 | 2.63 | 6.16 |

[a] L.O.I: loss of ignition.

formation aid in the manufacture of various paper grades as microparticle agents. The best performance is achieved when used in combination with a medium to high molecular weight cationic flocculant. AccoForm WT can be used also for process and waste-water treatment and sludge treatment (i.e., de-inking and waste-water treatment) as a coagulant in combination with both cationic and anionic for coagulation purposes. AccoForm WT can be used also for fresh-water treatment in equipment as accelerators. AccoForm WT is a completely natural product, obtained through simple thermo-mechanical activation and milling of cave extracts, is fully complies with FDA regulations, allows slurries to be prepared that are nearly neutral and do not give rise to corrosion in make-up units, pumps, and pipes, is a 100 % active content product and is therefore very cost-effective, is widely unaffected by cationic demand and $p^H$ changes. It's a very high specific surface in dispersion, ranking up to 750–800 $m^2/g$. The application of AccoForm WT depends on the required function. Glauconite is a mixed-layer mineral composed of smectite and glauconitic mica they are potassium-rich dioctahedral phyllosilicates that generally become in the form of rounded grains. Glauconite works as a cation exchanger. In this work, the glauconite was supplied from the New Valley region (Abu-Tartur) without any treatment in the rock and then converted to powder form before use in the organic matter treatment of phosphoric acid. The present minerals in glauconite can be investigated by radiography diffraction (XRD) as graphically illustrated in Fig. 1 and their quantities are shown in Table 6.

### 2.2. Production of untreated phosphoric acid from phosphate rock

The preparation of untreated phosphoric acid (30 % $P_2O_5$) according to Al-Fariss T.F. et al. [21], is comprised of the following stages: (a) First, add the stereometric amount of sulphuric acid to the grounded phosphate rock to produce phosphoric acid with concentration about 20 % as $P_2O_5$ which is called a recycled acid. (b) Acidulation step: a certain calculated amount of 20 % $P_2O_5$ acid was put in the

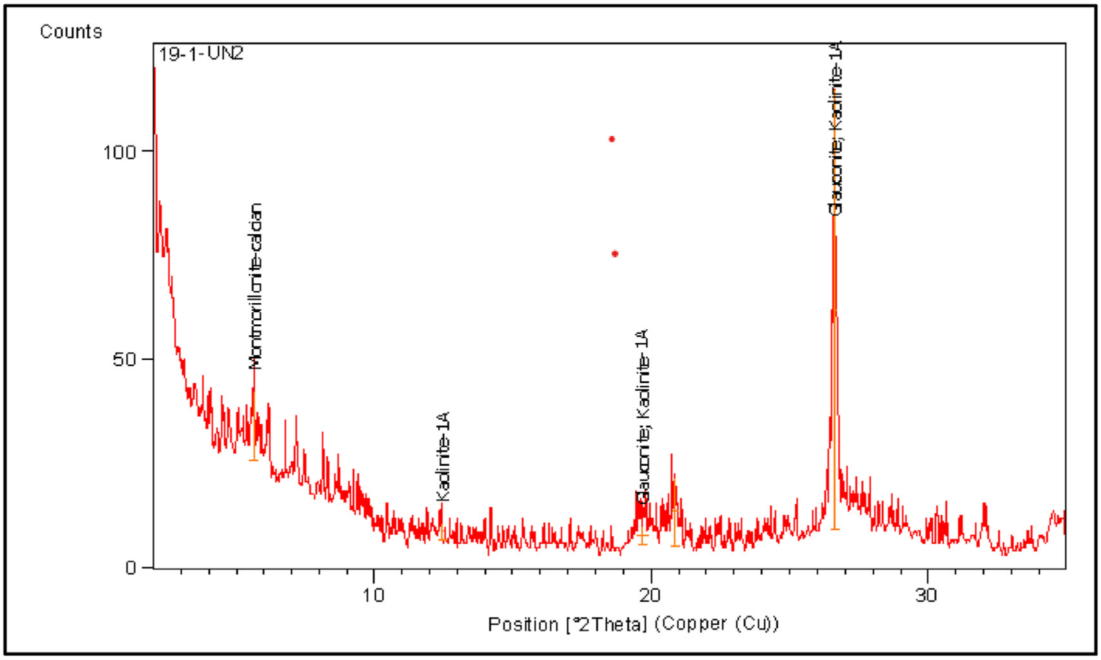

*Fig. 1. Radiography diffraction analysis of glauconite sample.*

*Table 6. Radiography diffraction analysis of the working glauconite.*

| Ref. code | Minerals name | Chemical formula | Semi Quant [%] |
|---|---|---|---|
| 00-000-0466 | Glauconite | (K, Na) $(Fe^{+3}$, Al, Mg$)_2$ (Si, Al$)_4$ $O_{10}(OH)_2$ | 80 |
| 00-058-2028 | Kaolinite-Al | $Al_2Si_2O_5$ $(OH)_4$ | 4 |
| 00-058-2008 | montmorillonite | $CaO_2$ (Al, Mg$)_2$ $Si_4O_{10}(OH)_2.xH_2O$ | 16 |

reactor (100 ml covered beaker) as a recycled acid that was placed in an automatically controlled thermostat adjusted at 70 °C, and an additional amount of phosphate rock was added gradually using vibrating rock feeder for 1 h while constant mechanical stirring at 450 rpm (cover of the beaker to avoid loss of solution by evaporation) to avoid blinding i.e. coating of the phosphate rock particles with rapidly formed gypsum crystals and hence preventing further reaction. Sulfuric acid was added continuously for 1 h using the peristaltic dosing pump. Figure 2 shows the acidulation process. (c) Filtration step: the produced suspension was immediately filtered under suction using a Buchner funnel and polypropylene filter cloth. The gypsum cake was washed three times by calculated amounts of wash I (~10 % $P_2O_5$), wash II (~5 % $P_2O_5$), and wash III (water).

## 3. Methods

### 3.1. Analytical procedures

Several batches of experiments were conducted to partially purify materials. The particle size was determined through sieve analysis of the dry powder. The organic carbon was analyzed by the volumetric method; which was one of the most used on the industrial scale. Through, a great number of tests were necessary to determine the end-point (Pale green to green), (Walkley-Black procedure) [22]. The $P_2O_5$ content of a sample was determined by measuring the light absorbed at 420 nm by a solution containing the yellow molybdivanadophosphoric acid complex [23], (Spectrophotometer method), The fluoride content was determined by ion selective electrode (Thermo Scientific PH/ISE meter Orion Star A 214), Sulfur oxide and silicon oxide determined by gravimetric method, Organic matter and loss of ignition in case of the solid sample determined by calcination method used Muffle furnace L9/13/B410 (0–1300 °C) and the other cations in the medium are detected with Atomic Absorption Spectroscopy (AA7000). Radiography diffraction (XRD) analysis was done by PAN analytical XRD equipment model X'Pert PRO with Secondary Monochromator, Cu-radiation (l = 1.542 Å) at 45 K V., 35 M A. and scanning speed 0.04°/second were used. The diffraction peaks between 2θ = 2 and 60, corresponding spacing (d, Å), and relative intensities (I/Io) were obtained. The diffraction charts and relative intensities are obtained and compared with ICDD files.

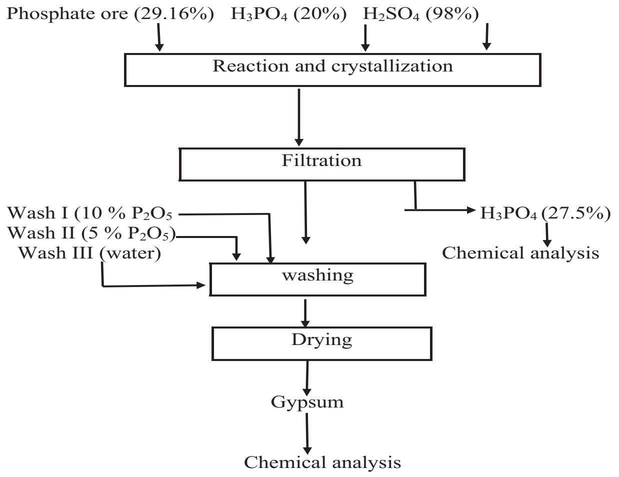

*Fig. 2. The preparation steps for untreated phosphoric acid.*

### 3.2. Removal of organic matter with the different adsorbents

The adsorbent was utilized at concentrations between 8.67 and 14.67 g/l of crude acid WPPA under the following operational parameters: agitation speed of 350 rpm, contact time of 60 min, and temperatures of 25, 40, and 50 °C. After reaching equilibrium, the mixture was allowed to settle, and the supernatant acid was filtered to remove solid particles.

## 4. Results and discussion

### 4.1. Removal of organic matter with the activated bentonite

#### 4.1.1. Effect of acid-activated bentonite content and the concentration of phosphoric acid on the organic matter removal efficiency

The study investigated how different amounts of bentonite affected the reduction efficiency of organic matter, using doses ranging from 8.67 to 14.67 g/l of PA. The experiment also included two concentrations of untreated phosphoric acid (27.50

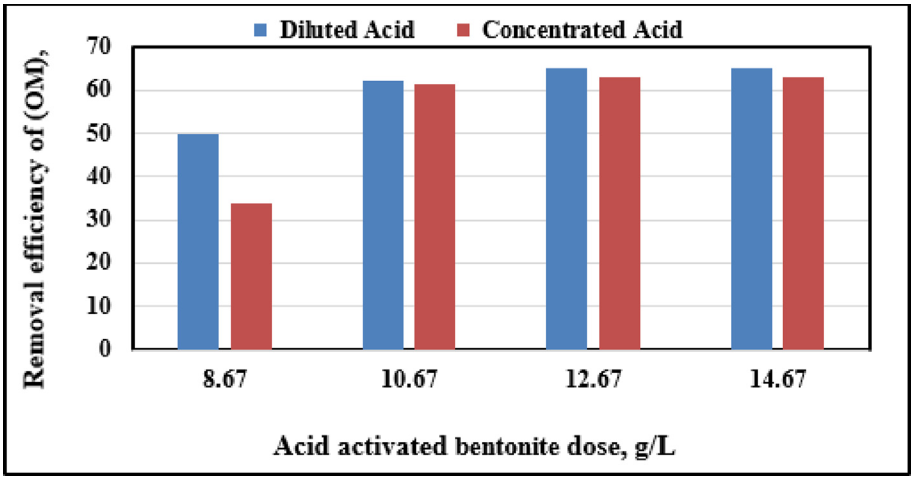

*Fig. 3. Removal efficiency of organic matter by the different doses of acid-activated bentonite and different concentrations of phosphoric acid.*

and 44.20 % $P_2O_5$), as shown in (Fig. 3). The temperature was kept constant at 25 °C, with stirring at 350 r.p.m, and a contact time of about 60 min. The results showed that increasing the dose of acid-activated bentonite up to 12.67 g/l led to an increase in organic matter removal efficiency, followed by a slight decrease for 14.67 g/l samples. The best results were obtained for the 12.67 g dose, the removal efficiencies were 65.15 % for diluted acid and 63.11 % in the case of concentrated acid. However, the increasing dose caused practically stable adsorption of organic matter because of the attainment of equilibrium between the adsorbate and adsorbent [24]. The results clarify that the adsorption performance is decreased by increasing the concentration of phosphoric acid. This could be attributed to the alkaline nature of bentonite [25], which neutralizes the high acidity of phosphoric acid as well as decreases the viscosity of the diluted phosphoric acid (DPA) which enables the particles of surface bentonite to spread and penetrate more easily through dilute medium [26].

### *4.1.2. Effect of temperature son organic matter removal efficiency in case of DPA*

Studying the effect of the various temperatures 25, 40, and 50 °C on the removal efficiency of organic matter for both the DPA by acid-activated bentonite. The selection of diluted phosphoric acid for several temperatures was done after comparing the diluted and concentrated acids in the above section. The effect of temperature on the organic matter adsorption onto bentonite from phosphoric acid 27.50 % $P_2O_5$ was studied at three different temperatures 25, 40, and 50 °C, with different amounts of bentonite = 8.67, 10.67, 12.67, and 14.67 g/L of DPA. Figure 4 presents the obtained data as related to organic matter adsorption efficiency % and temperatures. The obtained results indicate that the removal percentage of organic matter decreased

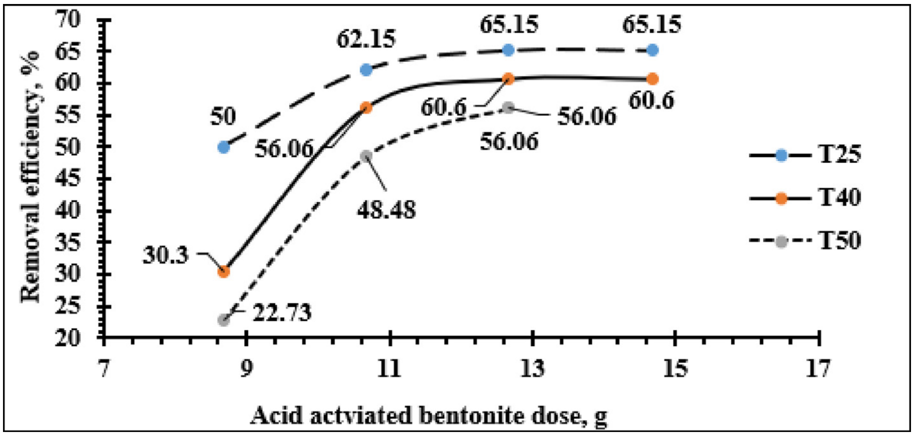

*Fig. 4. Removal efficiency of organic matter at different temperatures and doses.*

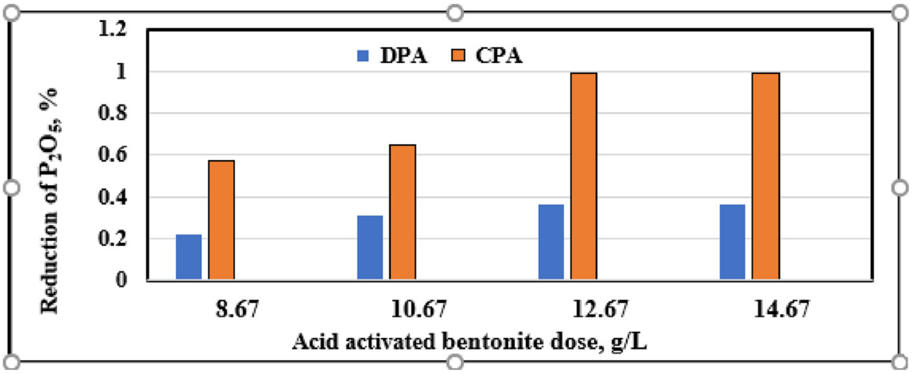

*Fig. 5. Effect of acid-activated bentonite dose on $P_2O_5$ reduction for diluted phosphoric acid and concentrated phosphoric acid.*

with increasing temperatures, these results are a fact that conform to the physical adsorption hypothesis [27].

### 4.1.3. *Effect of acid-activated bentonite dose on $P_2O_5$ reduction for DPA and CPA*

Study the effect of the amount of bentonite dose, the evolution of the reduction of $P_2O_5$% was followed (8.67–14.67 g/L of PA), other parameters ware remained constant at temperature =(25 °C), the concentration of phosphoric acid = 27.50 and 44.20 % $P_2O_5$ and the stirring time = 60 min. Figure 5 present the obtained data as the relation between the reduction of $P_2O_5$% and the amount of added bentonite, the data illustrate that the $P_2O_{5\%}$ is still constant with a small decrease in the case of DPA and the case of CPA the reduction of $P_2O_{5\%}$ increases more than in case of DPA [28].

### 4.1.4. *Effect of different temperatures on $P_2O_5$ reduction for DPA*

Study the effect of temperatures on the reduction of $P_2O_5$ percent in the case of filter phosphoric acid 27.50 % $P_2O_5$ was studied at three different temperatures, 25, 40, and 50 °C, with different amounts of bentonite = 8.67, 10.67, and 12.67 g/L of PA, stirring time = 60 min, agitation sped = 350 rpm. Figure 6 presents the obtained data as the relation between the reduction of $P_2O_5$ percent and temperatures. The obtained results indicate that the reduction of $P_2O_5$ percent increases with increasing temperatures, these results may lead to the formation of Lehr, 's salt [$2FeKH_{14}(PO_4)_8.4H_2O$], which is easily formed by heating [28].

## 4.2. *Removal of organic matter with sodium montmorillonite bentonite*

### 4.2.1. *Effect of sodium montmorillonite bentonite content and the concentration of phosphoric acid on the organic matter removal efficiency*

The effect of sodium montmorillonite bentonite dose on removal efficiency of organic matter was studied at different concentrations (8.67, 10.67, 12.67, and 14.67 g/l of PA), other parameters were remained constant at temperature 25 °C, stirring

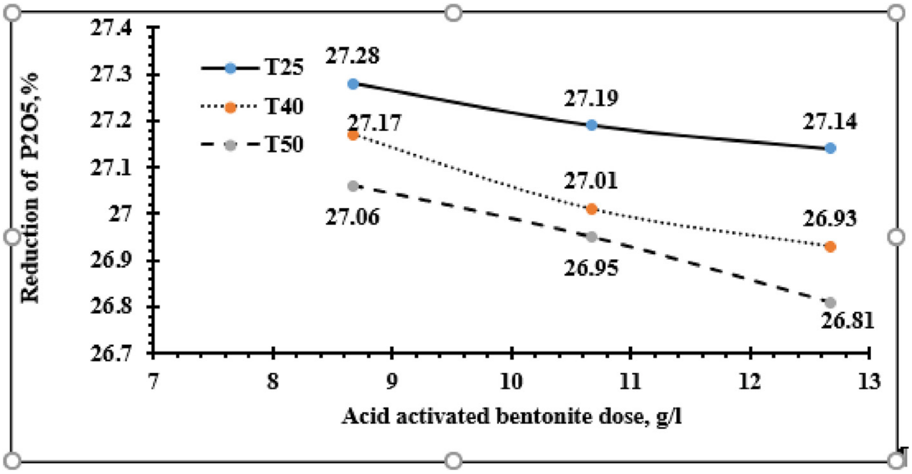

*Fig. 6. Study the effect of temperature on the reduction of $P_2O_5$ percent in the case of filter acid as a function of the temperature difference.*

time = 60, the concentration of phosphoric acid = 27.50 and 44.20 % as $P_2O_5$ for DPA and CPA, respectively. Figure 7 presents the obtained data as the relation between organic matter removal efficiency percent and the amount of sodium montmorillonite added to bentonite. The results illustrate that the organic matter removal efficiency increased by increasing the dose of sodium montmorillonite. This increase can be attributed to the increase in the surface area and adsorption function sites [29]. The best removal efficiency results for organic matter were obtained for 12.67 g/l samples which are given 56.06 % in the case of DPA and 53.39 % in the case of CPA. However, the increasing dose caused practically stable adsorption of organic matter because of the attainment of equilibrium between the adsorbate and adsorbent [24]. The experimental results clear that the adsorption efficiency is decreased by increasing the concentration of phosphoric acid. This may be due to the decrease in the viscosity of the acid by dilution in case low concentration of phosphoric acid, which enables the particles of surface adsorbent to spread and penetrate more easily through a dilute medium. On the other hand, the more viscous acid solutions lead to scaling of the adsorbent particles on the walls of the container during shaking and hence decrease the available surface area of the adsorbent even when using a high shaking speed [26].

### 4.2.2. *Effect of temperature on organic matter removal efficiency in case of DPA*

The effect of temperatures on the organic matter adsorption by sodium montmorillonite bentonite for DPA was studied at 25, 40, and 50 °C, with different amounts of Sodium montmorillonite bentonite = 8.67, 10.67, 12.67, and 14.67 g/l of PA, stirring time = 60 min, and agitation speed = 350 rpm. Figure 8 indicates that, the obtained data for organic matter removal efficiency, Sodium montmorillonite bentonite dose, and temperatures. The obtained results indicate that the removal percentage of organic matter decreased with increasing temperatures, these results in a fact that conformed to the physical adsorption hypothesis [27], and the decreasing removal percentage of organic matter with increasing temperatures indicates an exothermic adsorption process. Adsorption is an exothermic process. Heat is released whenever molecules are adsorbed on the surface. So, the rate of adsorption decreases whenever the temperature increases. This is because when the temperature increases the kinetic energy of adsorbed molecules gets increased and they overcome the electrostatic force of attraction by the adsorbent surface and by increasing temperature the breakdown between links increases [30]. The work at low temperatures leads to a decrease in the consumption of energy which leads to a decrease in the cost of the purification process.

### 4.2.3. *Effect of sodium montmorillonite bentonite dose on $P_2O_5$, %reduction for DPA and CPA*

The effect of the amount of sodium montmorillonite dose on the reduction of $P_2O_5$, % was estimated at different concentrations within the range 8.67–14.67 g/l of PA, other parameters were fixed at temperature, 25 °C, two concentrations of phosphoric acid 27.50 and 44.20 % $P_2O_5$ for DPA and CPA, respectively, and the stirring time 60 min. Figure 9 illustrates that, the obtained results for

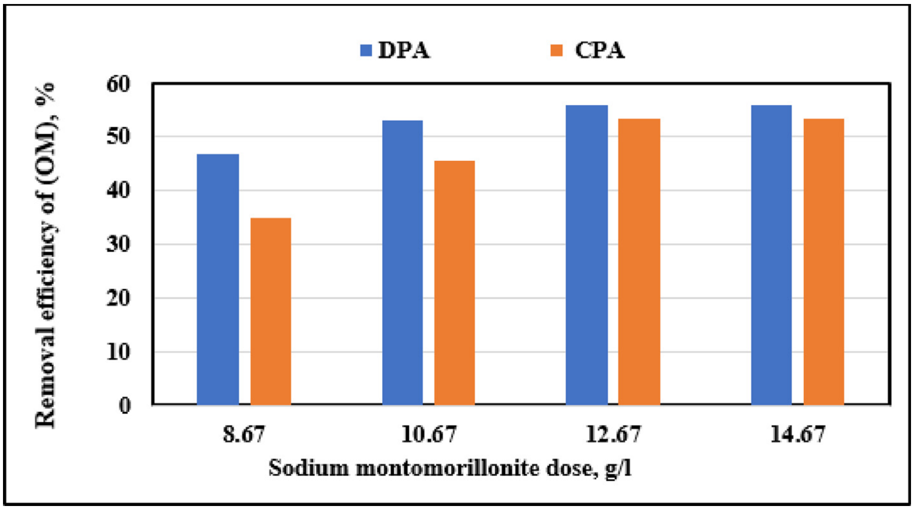

Fig. 7. Removal efficiency of organic matter by different doses of sodium montmorillonite bentonite and different concentrations of phosphoric acid (diluted phosphoric acid and concentrated phosphoric acid).

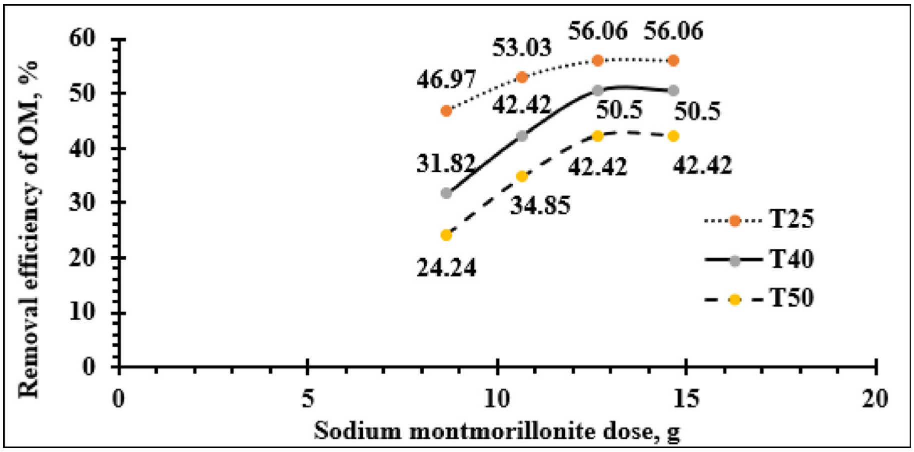

*Fig. 8. Removal efficiency of organic matter at different temperatures and doses.*

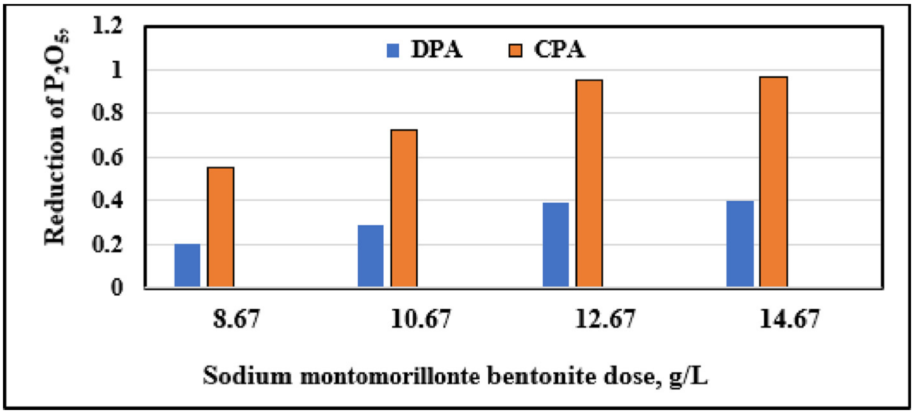

*Fig. 9. Effect of sodium montmorillonite bentonite dose on $P_2O_5$, % reduction for diluted phosphoric acid and concentrated phosphoric acid.*

$P_2O_5$% reduction. The data clear that the $P_2O_{5\%}$ is still constant at different doses of sodium montmorillonite in the case of DPA of about (0.1 %). On the other hand, the rate of $P_2O_5$ reduction in the case of CPA given high reduction values compared with DPA which may be related to the high concentration of CPA causing sedimentation and crystallization of some phosphate salts [28].

### *4.2.4. Effect of different temperatures on $P_2O_5$ reduction for DPA*

The effect of temperatures on the reduction of $P_2O_5$, % in the case of DPA was studied at three different temperatures 25, 40, and 50 °C with different amounts of sodium montmorillonite of 8.67, 10.67, and 12.67 g/l, stirring time; 60 min and agitation speed; 350 rpm. Figure 10 shows the obtained data as the relation between the reduction of $P_2O_5$ percent, and temperatures. The obtained results indicate that the reduction of $P_2O_5$ increases with increasing temperatures, these results may lead to the formation of Lrhr's salt $[2FeKH_{14}(PO4)_8.4H_2O]$, which is easily formed by heating [28].

## *4.3. Removal of organic matter with glauconite*

### *4.3.1. Effect of glauconite content and the concentration of phosphoric acid on the organic matter removal efficiency*

Evaluation of the removal efficiency of organic matter with different amounts of glauconite was studied at concentrations from 8.67 to 14.67 g/l and concentration of phosphoric acid = 27.50 % DPA and 44.20 % $P_2O_5$ CPA, other parameters ware remained constant such as temperature at 25 °C and the stirring time about 60 min. Figure 11 shows the obtained data as the relation between organic matter removal efficiency and the amount of added glauconite. The results illustrate that the organic matter reduction efficiency increased by increasing the dose of introduced Glauconite, this increase can be attributed to the increase in the surface area and

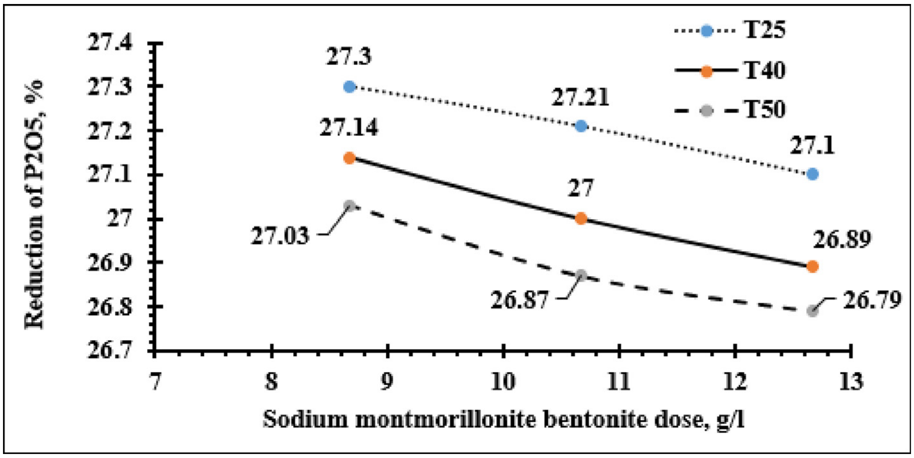

*Fig. 10. Study the effect of temperature on the reduction of P2O5 percent in the case of diluted phosphoric acid as a function of the temperature difference.*

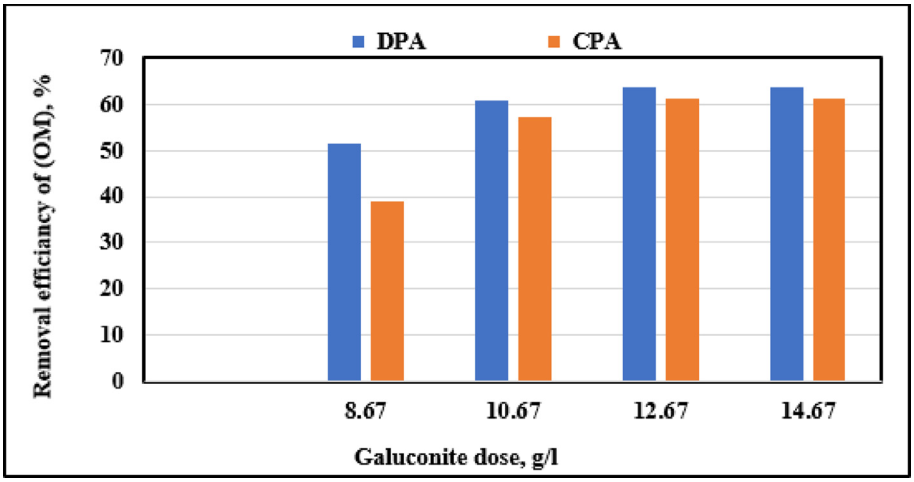

*Fig. 11. Removal efficiency of organic matter by a different dose of glauconite and different concentrations of phosphoric acid.*

adsorption function sites. The mechanisms and specific properties by which glauconite effectively removes organic matter from phosphoric acid. Glauconite is characterized by high availability, low cost, and thermal and radiation resistance, in addition, it has molecular adsorption and ion exchange properties. The manifestation of the ion exchange capacity of glauconite, by analogy with other aluminosilicate minerals, is due to the following factors: the presence of a negative uncompensated charge in the structural cell of glauconite resulting from the substitution of tetravalent silicon with trivalent aluminum or divalent magnesium in the crystal lattice of the mineral, the presence on the side faces of crystals of the glauconite OH-groups attached to the silicon atoms, a hydrogen cation, which may react under certain conditions. Molecular adsorption of glauconite is the penetration of electrolyte solutions into the free cavities of the crystalline structure present in this mineral, with simultaneous and equivalent adsorption of cations and anions from the electrolyte solutions. Also, glauconite has a generally irregular structure and contains various bent and curled crystals that form numerous mesopores, which significantly raises the adsorption ability [29]. For the glauconite dose, (12.67 g/l), the removal efficiency results were 63.63 % in the case of DPA which is regarded as the best result, and 61.16 % in the case of CPA. However, increasing of dose caused practically stable adsorption of organic matter because of the attainment of equilibrium between the adsorbate and adsorbent which does not affect the organic carbon removal efficiency [24]. Therefore 12.67 g/l of phosphoric acid is the best-chosen dose. The experimental results clear that the adsorption efficiency is decreased by increasing the concentration of phosphoric acid. This may be due to the decrease in the viscosity of the acid by dilution in case low concentration of phosphoric acid, which enables the particles of surface glauconite to spread and penetrate more easily through a dilute medium [26]. On the other hand, the more viscous acid solutions lead to scaling of the glauconite particles on the walls of the container and hence decrease the available surface area of the glauconite even when using a high shaking speed. So it is preferred to work practically on the acid with a concentration (27 % $P_2O_5$ to 30 % $P_2O_5$), the purification process for organic matter removal is directly applied to the crude phosphoric acid after the filtration process.

#### 4.3.2. Effect of temperature on organic matter removal efficiency in case of DPA

The temperature effect on the organic matter adsorption onto Glauconite from DPA was studied at three different temperatures 25, 40, and 50 °C with different amounts of bentonite = 8.67, 10.67, 12.67 and 14.67 g/l of PA, stirring time; 60 min, agitation speed; 350 rpm. Figure 12 clarifies that, the obtained data concerning organic matter adsorption performance, %, and temperature. The obtained results clear that the removal efficiency of organic matter decreases with increasing temperatures, these results comply with the physical adsorption hypothesis [27]. On the other hand, decreasing the removal percentage of organic matter with increasing temperature indicates an exothermic adsorption process [30].

#### 4.3.3. Effect of the glauconite dose on $P_2O_5$, % reduction for DPA and CPA

The effect of the amount of glauconite dose on the reduction of $P_2O_5$% was studied at 8.67, 10.67, 12.67, and 14.67 g/l of DPA and CPA. Other parameters such as temperature; 25 °C and the stirring time; 60 min. Figure 13 represent the obtained results for $P_2O_5$% reduction and the amount of added glauconite. The data shows that the $P_2O_{5\%}$ is still constant at a low decrease for DPA. On the other hand, the reduction of $P_2O_{5\%}$ in the case of CPA gave higher decreasing values compared with DPA [28]. These obtained results are making with the above results in the case of both acid-activated bentonite and sodium montmorillonite.

#### 4.3.4. Effect of different temperatures on $P_2O_5$ reduction for DPA

The effect of temperature on the reduction of $P_2O_5$ percent in the case of DPA was studied at three different temperatures, 25, 40, and 50 °C, by different amounts of glauconite (8.67, 10.67, 12.67, and 14.67 g/l of DPA, stirring time; 60 min, agitation speed, 350 rpm. Figure 14 presents the obtained data as the relation between the reduction of $P_2O_5$ percent and temperatures. The obtained results indicate that the reduction of $P_2O_5$ percent increases with increasing temperatures, these results may lead to the formation of Lrhr's salt [$2FeKH_{14}(PO4)_8.4H_2O$], which is easily formed by heating [28].

### 4.4. Comparison between acid-activated bentonite, glauconite, and sodium montmorillonite bentonite in the case of DPA for organic carbon removal efficiency

Using of acid activated bentonite, glauconite, and sodium montmorillonite at the following concentrations: 8.67, 10.67, 12.67, and 14.67 g/l of DPA with optimum conditions; agitation speed 350 rpm, contact time 60 min, temperature 25 °C and concentration of phosphoric acid ($P_2O_5$) = 27.50 %. At equilibrium, the blended was left to settle and

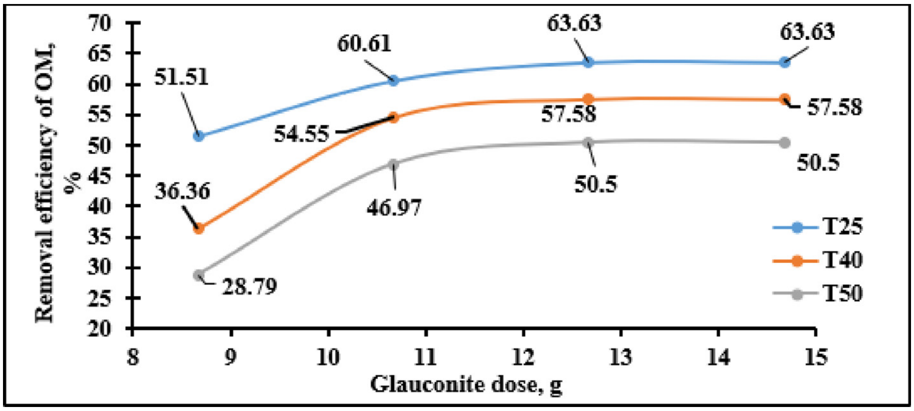

Fig. 12. Removal efficiency of organic matter at different temperatures and doses.

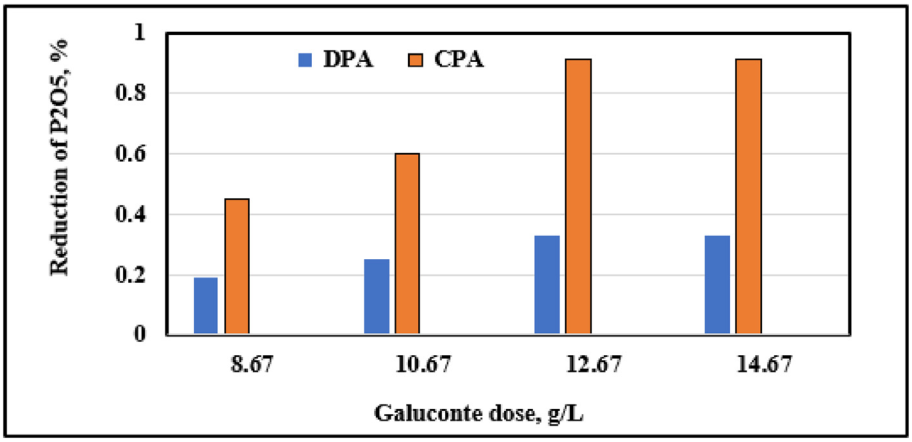

*Fig. 13. Effect of glauconite dose on $P_2O_5$ reduction for diluted phosphoric acid and concentrated phosphoric acid.*

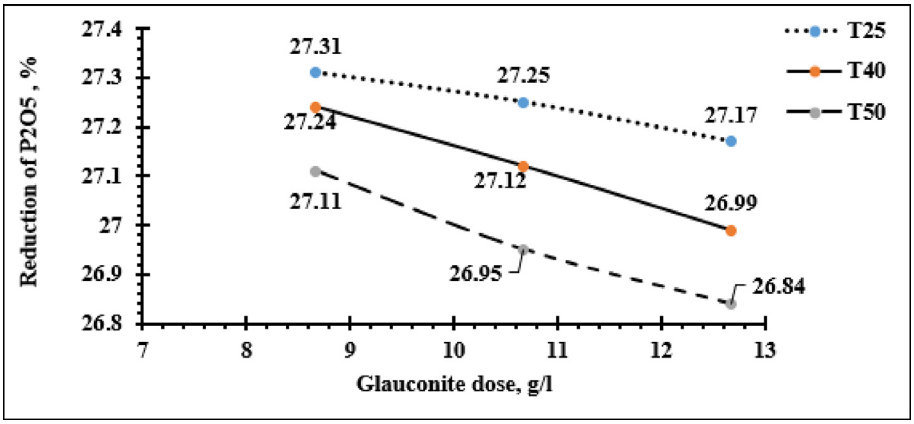

*Fig. 14. Effect of temperature on reduction of $P_2O_5$, % in the case of diluted phosphoric acid as a function of added glauconite.*

supernatant acid was filtered to eliminate all particles. The results in Fig. 15 indicate that the best result for the removal of organic matter efficiency is in the following order: acid-activated bentonite, glauconite, and sodium montmorillonite, respectively. For the concentration of 12.67 g/l of the above adsorbents, the values for organic carbon removal efficiencies were 65.15, 63.63, and 56.06 % for acid-activated bentonite, glauconite, and sodium montmorillonite, respectively.

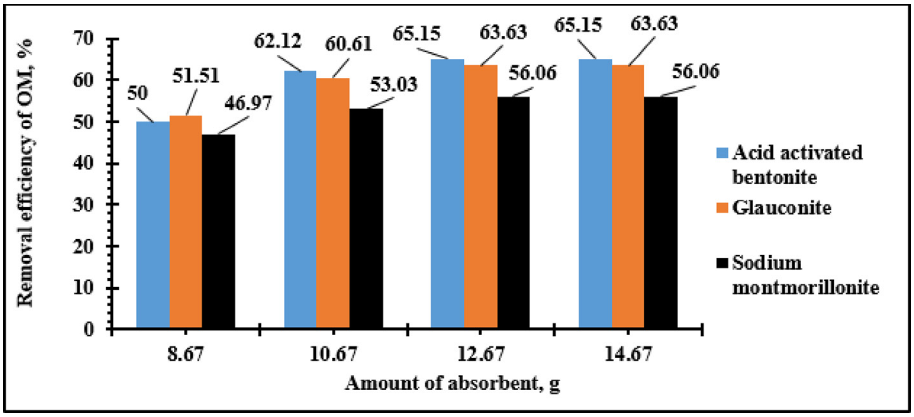

*Fig. 15. Comparison between acid-activated bentonite, glauconite, and sodium montmorillonite bentonite in the case of dilute phosphoric acid.*

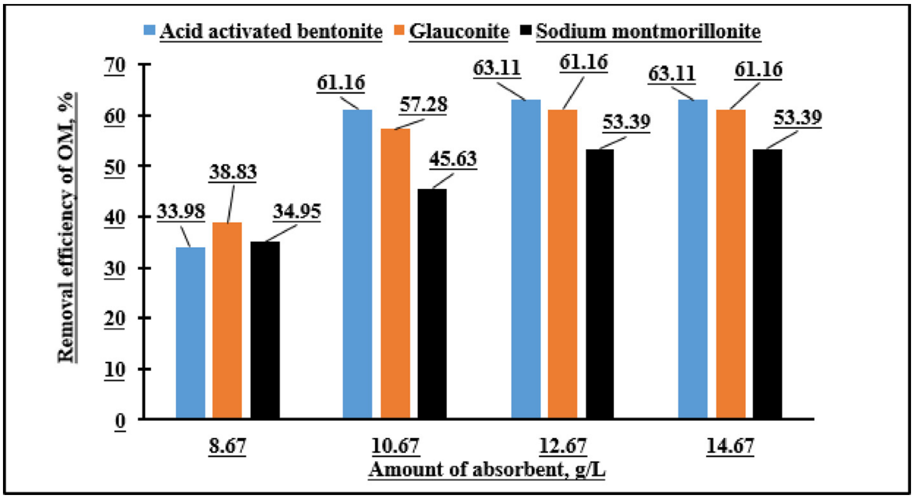

*Fig. 16. Comparison between acid-activated bentonite, glauconite, and sodium montmorillonite bentonite in the case of concentrated phosphoric acid.*

*Table 7. Summary of previous work of treatment of wet-process phosphoric acid to remove or minimize the organic matter.*

| Method of treatment | Removal efficiency, % | Reference |
|---|---|---|
| Treatment of diluted phosphoric acid by acid-activated bentonite | 65.15 | The current work |
| Treatment of diluted phosphoric acid by glauconite | 63.63 | The current work |
| Treatment of diluted phosphoric acid by sodium montmorillonite bentonite | 56.06 | The current work |
| Adsorption of organic matter contained in industrial $H_3PO_4$ onto bentonite: batch-contact time and kinetic study | 60.83 | [31] |
| Purification of phosphoric acid by minimizing iron, copper, cadmium, and fluoride. Reduction of organic carbon (Kaolinite, Vermiculite, and Bentonite) | 17.0, 25.40 and 61.80 | [28] |
| Retention of organic matter contained in industrial phosphoric acid solution by raw Tunisian clay: Kinetic equilibrium study (clay sample illite and smectite) | 14.0 and 18.0 | [32] |
| Adsorption of organic matter from industrial phosphoric acid onto activated bentonite | 47.48 | [27] |
| Phosphoric acid purification through different raw and activated clay (Southern Tunisia) | 52 to 68.46 | [33] |
| Treatment of crude phosphoric acid from some undesirable impurities (Removal of organic matter with Kaolin clay and Ball clay) | 39.0 and 53.6 | [34] |
| Application of acid-activated bentonite for efficient removal of organic pollutants from industrial phosphoric acid: Kinetic and Thermodynamic study | 60.0 | [17] |
| Technological studies on the scrubbing stage during the phosphoric acid purification process for the production of partially purified and highly pure-grade phosphoric acid | 62.20 | [35] |
| Recycling of spent reverse osmosis membranes for a second use in the clarification of wet-process phosphoric acid | 61.0 | [18] |
| Removal of iron from wet-process phosphoric acid using ion exchange method by prompt MTS9570 resin (organic matter removal using activated carbon) | 64.0 | [36] |

### *4.4.1. Comparison between acid-activated bentonite, glauconite, and sodium montmorillonite bentonite in the case of concentrated phosphoric acid*

A pretreatment was undertaken using acid-activated bentonite, glauconite, and sodium montmorillonite at these experiments 8.67–14.67 g of absorbent used for one liter of crude WPPA with optimum conditions; agitation speed = constant stirring (350 rpm), contact time = 60 min, temperature=(25 °C) and concentration of phosphoric acid ($P_2O_5$) = 44.20 % at equilibrium, the mixture was left to settle and supernatant acid was filtered to remove any particles. The results in (Fig. 16) indicate that the best result of removal of organic matter is the following order, acid activated bentonite, glauconite, and sodium montmorillonite, respectively, 65.15, 63.36, and 56.06 % of the organic matter were removed using 12.67 g of acid-activated bentonite, glauconite, and sodium montmorillonite, respectively/liter of crude WPPA.

### *4.5. Summary of previous and present work of treatment of wet-processes phosphoric acid to the removal of organic matter*

By comparison, the current finding for glauconite with the previous studies for organic carbon removal efficiency was 63.36 %. This value is regarded as a positive result in the treatment of phosphoric acid in addition to the availability and low cost of local raw material (glauconite), as shown in Table 7.

## 5. Conclusions

(1) The organic matter removal efficiency for glauconite, sodium montmorillonite, and acid-activated bentonite increased by increasing the dose of all adsorbents up to 12.67 g/l followed by a slight decrease for 14.67 g/l.
(2) The obtained results for all used adsorbents clear that the removal percentage of organic matter decreased with increasing temperatures.
(3) After adsorbent treatment, the reduction in $P_2O_5$% remained constant with a low decrease in the case of DPA. However, in the case of CPA, the reduction in $P_2O_5$% increased more than in the case of diluted phosphoric acid.
(4) The optimum conditions according to this study are summarized as the following: adsorbent concentration of 12.67 g/l, temperature 25 °C, time of agitation speed 1 h, phosphoric acid concentration 27.5 %, agitation speed 350 rpm.

## Conflicts of interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

## Acknowledgements

Many thanks to the soul of Prof. Dr. Mohsen M. Elsabbah Professor of Physical Chemistry, Al-Azhar University, Faculty of Science, Chemistry Department, Cairo, Egypt for their assistance in the experimental work and valuable participation from the first of the work.

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