New organic compounds detection and potential removal in crude phosphoric acid using waste sludge

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\textbf{ABSTRACT}

Some organic compounds in phosphoric acid are a potential mediator of adverse environmental impacts on soil. This work aims to detect and reduce the content of organic compounds in crude phosphoric acid using waste sludge, from water treatment plants, as a low-cost sorbent. Gas chromatography/mass spectrometry (GC/MS) was used to detect the organic species in crude phosphoric acid, while X-ray fluorescence (XRF), X-ray Diffraction (XRD), scanning electron microscope equipped with energy-dispersive X-ray (SEM/EDAX) and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy were used to characterise waste sludges. Practically, three sludge samples (S1 from El-Marg, S2 from Al-Obour and S3 from El-Sheikh Zayed stations, respectively) were utilised and different factors including shaking time, sorbent dose and phosphoric acid concentration were studied.

The results of GC/MS revealed that crude phosphoric acid contains bis [tert-butyl(dimethyl)silyl] azelaate, dibutyl phthalate and 2,6-di-tert-butyl-4-methylphenol as the main organic species. Moreover, the clay content and the surface charge of sludge strongly affect the removal efficiency of organic species. Kinetic analysis using Lagergren pseudo-first-order, pseudo-second-order, Morris-Weber and Elovich models displays that the sorption process using waste sludges is a chemisorption process. The sorption capacity of the applied three sorbents was 26.3, 23.3 and 22.8 mg/g for S1, S2 and S3, respectively, which indicates that the three sludge samples exhibit potential sorbents for the clarification of phosphoric acid and sequentially to produce green phosphate fertilisers.

\textbf{1. Introduction}

Phosphorus (P) is one of the vital macronutrients required for plant growth as well as human life. Phosphorus was utilised for increasing crop products since the 1950s [1]. The United Nations reported that the world population is expected to become about 9 billion by 2050, and the food demand will increase by 60% for the same period that subsequently will rise the global phosphorus demand [2]. Phosphorus security is considered one of the greatest global sustainability challenges in the twenty-first century [3]. Phosphorus management is very important for sustainable food and agriculture, particularly in food-deficient and phosphorus-scarce countries [4].
Phosphate rock is a non-renewable natural resource that is used to describe phosphate-bearing minerals. Approximately 90% of the phosphate rock production worldwide is utilised in the fertiliser industry, and the other 10% is used in the animal feeds, detergents and chemical industries [5,6]. Phosphate rock sources may be sedimentary origin as in Florida, Jordan, North Africa, and igneous origin as in South Africa, Brazil, Russia, or secondarily metamorphic origin as in India. Phosphate rocks exhibit different chemical, physical and crystallographic characteristics based on its geological history and origin [7].

It is well known that phosphate rocks contain organic compounds as a result of the biological sedimentation of sea organisms [8]. In addition to organic compounds, phosphate rock contains different hazardous elements such as U, Cd and As [7]. Organic compounds as well as other harmful elements are introduced to phosphoric acid and phosphate fertilisers during the acidulation of phosphate rock [7,9]. Most of previous studies reported that the organic compounds in the phosphoric acid mainly consist of humic compounds, aromatics and other saturated and unsaturated fatty acids [10–13]; however, the main organic compounds in wet crude phosphoric acid have not been detected.

Organic compounds present in phosphoric acid have a negative impact on the quality and the quantity of the produced phosphoric acid, whereas they give a dark colour to the produced acid and affect the crystallisation of the phosphogypsum [8,14]. Furthermore, organic compounds result in serious operating problems during the application of liquid–liquid method for the recovery of uranium from phosphoric acid as well as the purification of phosphoric acid, whereas organic compounds accumulate and coagulates heavily at the interfacial area between the phosphoric acid and organic solvent which leads to the losses of the organic solvent and negatively impact on the process economy [12–15]. Also, organic compounds form stable toxic complexes with the harmful elements in the phosphoric acid, which accumulate in the environment as a result of the continuous application of phosphate fertilisers and also transfer to the human body through the food chain [7,8].

Accordingly, the reduction of the organic compound from phosphoric acid is an important process in respect to improve the quality of phosphoric acid and produce eco-friendly fertilisers. Various methods were applied for the reduction of organic compounds from crude phosphoric acid, for example liquid–liquid extraction or sorption [10–14]. Several materials were investigated for achieving this proposes such as clays [14,16] and activated bio-chars [8,13].

Sludge is the waste materials generated from water treatment plant. The production of sludge is expected to be increased shortly as a result of urbanisation and industrial development [17]. The chemical and physical properties of the sludge are varied as a result of the difference in the water treatment technology, hydrogeology and geology of the intake area, as well as the chemical composition of the utilised raw materials [18,19]. The management of sludge could be performed using several methods such as landfilling [20], road surfacing [21] and incineration [22].

Proper management of sludge in an eco-friendly and economical manner is very interesting. Water treatment residuals have great sorption capacities due to their large specific surface area and chemical composition. Accordingly, these residuals have the ability to adsorb heavy metals and metalloids from water [22,23]. Rahmani and Mahvi
investigated the biosorption of cadmium and copper ions from industrial wastewaters using waste activated sludge [24]. Rashad et al., studies the removal of Cd, Pb, Cu and Mn from aqueous solution [17]. The adsorption and desorption capacity of four different metal ions [Cd(II), Cu(II), Ni(II), Zn(II)] using sewage sludge have been evaluated [25]. To the authors knowledge, sludge has never been applied for the purification of industrial phosphoric acid. In this regard, the present work aims to detect the main organic compounds in crude phosphoric acid as well as the application of waste sludge as a sorbent for the retention of organic species through batch investigation in order to produce a purer phosphoric acid suitable for the production of an eco-friendly phosphate fertilisers and reduce the accumulation of sludge in the environment.

2. Experimental procedures

2.1. Materials

Sludge samples designated here as S1, S2 and S3 were collected from three different water treatment stations, namely, El-Marg, Al-Obour and El-Sheikh Zayed, respectively. The samples were washed with double distilled water, left overnight in an oven at 110°C for complete drying, ground in mortar and was ready for further analysis.

Commercial crude phosphoric acid, containing (P₂O₅ = 26.5%, CaO = 0.34%, Fe₂O₃ = 1.1%, F = 0.64%, U(VI) = 40 ppm and organic compounds = 450 ppm) was purchased from Abu Zaabal Company for Fertiliser and Chemical Materials. Shimadzu UV-visible 160 A spectrophotometer was used to determine the content of organic compounds, iron and uranium.

2.2. Characterisation methods

X-ray Fluorescence (XRF) spectroscopy (Axios, sequential WD-XRF spectrometer, PANalytical) was used to determine the chemical composition of sludge samples. The phase composition of sludge samples was determined using X-ray diffraction (XRD, Bruker D8 advance X-ray diffractometer). The patterns were recorded by Cu–Kα radiation with λ of 1.5406 Å and 40 kV tube voltage, 40 mA tube current, 2θ scan range of 4–90°, 0.01° step width and scan speed 0.5°/min. X’Pert High Score TM (version 2.0.1) was used to perform a semi-quantitative analysis of the crystalline phases in the sludge samples [26]. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy (Spectrum Two IR Spectrometer – PerkinElmer, Inc., Shelton, USA) was used to identify the main functional groups of sludge samples. Acquisition conditions were 64 scans and 4 cm⁻¹ resolution in wavenumbers ranging from 4000 to 400 cm⁻¹.

The mean diameter of the sludge particles was determined at 170°, by dynamic light scattering (DLS) (NICOMP 380 ZLS, PSS, Santa Barbara, CA, USA). Also, the zeta potentials of the three samples were measured at 18°. Nitrogen adsorption-desorption measurements were carried out at 77.35 K on a Nova Touch LX⁴ Quantachrome, USA to determine the Brunauer–Emmett–Teller (BET) surface area and relative indices, average pore size (APS) and total pore volume (TPV) adsorption/desorption results also measured using Barrett, Joyner and Halenda (BJH) method. Before measurement, samples were kept in a desiccator until testing. All samples were charged in 9 mm cell tube with detected
weight for degassing process at 200°C for 6 h under low pressure 10^{-3} \text{ mbar}. After degassing, the cells let to cool until room temperature with back filling with nitrogen. Samples were cooled with liquid nitrogen and analysed by measuring the volume of gas (N_2) adsorbed at specific pressures. The pore volume was taken from the adsorption branch of the isotherm at P/P_0 = 0.995 assuming complete pore saturation.

Gas chromatography/mass spectrometry (GC/MS) HP5890 Series II Gas Chromatograph, HP 5972 Mass Selective Detector and Agilent 6890 Series Autosampler (Agilent Technologies, USA) was used to identify the chemical constituents of crude phosphoric acid solution. A Supelco MDN-55 30 m × 0.25 mm capillary column with a 0.5 μm film thickness was used with helium as the carrier gas at a flow rate of 1.0 mL/min. The GC oven temperature was programmed at an initial temperature of 40°C for 5 minutes, then heated up to 140°C at 5°C/min and held at 140°C for 5 min, then heated to 280°C at 9°C/min and held for five additional minutes. Injector and detector temperatures were set at 250°C. Mass spectrometry was run in the electron impact mode (EI) at 70 eV. The identification of the chemical constituents was determined by their GC retention times, retention indices and interpretation of their mass spectra and confirmed by mass spectral library search using the National Institute of Standards and Technology (NIST) database with those of authentic samples or published data [27]. The retention indices were calculated for all the volatile constituents using a homologous series of C8-C20 n-alkanes.

2.3. Sorption methodology

The three sludge samples were investigated for the sorption of organic species from crude phosphoric acid (4.5 M) in batch technique. All tests were achieved in polyethylene type using a thermostatic shaking water bath. The influence of reaction time, sludge amount of addition, and phosphoric acid concentration on the removal percent has been examined. In detail, 0.4 g of the sorbent has been shaken with 40 mL of liquid phase at 298 ± 1 K for 24 h. The adsorption experiments have been conducted in duplicates, and the mean values ≤ 4% relative errors were accepted for the performed experiments. After equilibration, the sludge was removed from the phosphoric acid. The concentration of organic compounds in crude acid has been measured using a spectrophotometer at 418 nm [8].

The following equations have been applied to figure out the impact of the main variables on the removal efficiency of organic compounds from industrial phosphoric acid:

\[ E(\%) = \frac{1 - C_e}{C_o} \times 100 \]  

\[ q_e = C_o - C_e \frac{V}{m} \]  

where \( C_o \) and \( C_e \) are the organic materials concentration (mg L^{-1}) before the adsorption and at equilibrium, respectively, \( q_e \) (mg g^{-1}) is the amount of organic materials sorbet, \( V \) is the volume of phosphoric acid (L), and \( m \) is the mass of the sludge (g).
3. Results and discussions

3.1. Characterisation of sludge samples

3.1.1. Physical characterisation
Particle size distributions of different sludge samples were investigated to examine the mean particle size and polydispersity index of Gaussian distribution. The samples S1, S2 and S3 are measured, and the bell shape distribution forms are clearly detectable in Figure 1a. The mean particle sizes for S1, S2 and S3 are 1725, 748 and 755 nm, respectively. In addition, the polydispersity index was laid between 0.2 and 0.5 that indicated to unimodal particle size with narrow distributions [28]. Selected sludges were directly measured without further treatment like grinding or burning. Big clusters of sludge with accumulated inorganic and organic substance resulted from Nile River were present in range 0.7 to 1.7 µm. Neither big particles of sludge nor excellent polydispersity indices were pointed to homogenised particle size [29,30].

Zeta potential has a great affect in the stability of dispersed solution from sludge in aqueous medium. The average zeta potentials of sludge over 11 measurements for each sample were illustrated in Figure 1b. Investigated sludge samples S1, S2 and S3 by DLS measurements with mean zeta potential $-5.55$, $-27.93$ and $-34.14$ mV, respectively. In addition, the average mobilities of dispersed particles were $-0.39$, $-2.02$ and $-2.38$ M. U. for S1, S2 and S3, respectively. Previous results indicated to the stability of samples S2 and S3 is higher than S1 with low mobility and low zeta potential. The separation of organic compounds was dependent on the fast precipitation of sludge during physical adsorption mechanism.

![Graphs](image-url)

**Figure 1.** (a) Particle size distribution of WTS samples. (b) Zeta potential of different WTS samples. (c) Shows the complete adsorption-desorption isotherm of nitrogen gas for three sludge samples.
The surface area is one of the unique phenomena related to the particle size with inverse proportions [31].

Surface area measurement with related indices for sludge samples is tabulated in Table 1. The complete adsorption/desorption isotherm branches of nitrogen gas on dry degassed sludge power were applied to calculate BET values 19, 94 and 102 m$^2$/g for sludge samples S1, S2 and S3, respectively. The adsorption indices were indicated to perfect trend of measured points with correlation coefficient $\approx$1 as first-order equation of linear relationship as shown in Figure 1c.

The average pore size for sludge samples is in the range from 1.99 to 2.86 nm, and the largest pore size ranges from 290 nm up to 484 nm. In addition, the pore per volume calculations were presented in the range 206e-2 to 1.3e-1. These results can be indicated to the availability to adsorbed organic contaminants in a wide range of size and variability to trap adsorbed materials in relative to suitable volume and size.

The particle size results have a great agreement with confirmation to each other’s through increasing the surface area with decreasing particle size from S3, S2 to S1. Overall, the physical characterisation measurements are verified the stability, size and surface area for sludge samples as mentioned theoretically and previous research [29,32,33].

### 3.2. Chemical characterisation

The chemical composition of sludge samples is presented in Table 2. The XRF analysis shows that silica and alumina are the main oxides of the three sludges due to the precipitated clay. Figure 2 shows the FTIR spectra of the three sludge samples. In all spectra, the bands at 3400 cm$^{-1}$ and 1630 cm$^{-1}$ are related to the stretching and bending vibrations of –OH group of the interlayer water molecule, respectively.

| Sample | BET m$^2$/g | Average pore size APS, nm | Total Pore volume TPV, cc/g | Pores smaller than nm |
|--------|-------------|--------------------------|----------------------------|-----------------------|
| SM     | 19.6398     | 2.86                     | 2.6845e-002                | 290.26                |
| SO     | 94.2146     | 1.99                     | 8.4197e-002                | 324.56                |
| SSZ    | 102.804     | 2.08                     | 1.3403e-001                | 484.86                |

| Chemical composition | S1  | S2  | S3  |
|----------------------|-----|-----|-----|
| SiO$_2$              | 45.48 | 49.93 | 39.03 |
| Al$_2$O$_3$          | 14.60 | 14.75 | 13.97 |
| Fe$_2$O$_3$          | 4.63  | 3.35  | 4.09  |
| CaO                  | 4.93  | 4.86  | 8.31  |
| MgO                  | 0.98  | 0.56  | 0.72  |
| Na$_2$O              | 0.83  | 1.22  | 1.13  |
| K$_2$O               | 1.72  | 1.43  | 1.59  |
| BaO                  | 1.85  | 1.58  | 1.69  |
| TiO$_2$              | 3.69  | 2.33  | 3.44  |
| P2O5                 | 1.45  | 1.08  | 1.63  |
| SO$_3$               | 2.99  | 2.13  | 4.45  |
| L.O.I                | 16.85 | 16.78 | 19.95 |
The band located at 1070 cm\(^{-1}\) assigned to T-O-Si (T = Si or Al) asymmetric stretching. Other significant bands are related to symmetric stretching of Si-O-Si and bending of Si-O are located at around 800 cm\(^{-1}\) and 455 cm\(^{-1}\), respectively. The presence of such bands confirms the mineralogical analysis about the presence of aluminosilicate phases in sludge samples. Furthermore, the peak around 1400 cm\(^{-1}\) is likely attributed to carbonate species, while the peaks at 2900 cm\(^{-1}\) and 2985 cm\(^{-1}\) correspond to stretches of C-H carbons of organic species in S2 sludge.

The results of XRD, Figure 3, indicated the presence of feldspar-type minerals, quartz, clay minerals (illite, kaolinite and chlorite), carbonate minerals (calcite, aragonite and
dolomite) as main crystalline phases as well as mica, anhydrite, apatite and other minerals as minor phases. The related semi-quantitative data are presented in Table 3. It is well known that the clay mineral content and the charge on clay surface play an important role in the efficient sorption of organic compounds [34,35]. As shown, the total clay content in S1 is higher than that in S2 and S3, while the feldspar content is much lower. Moreover, the quartz content in S1 and S2 is much higher than that in S2.

The surface structure of sludge samples is observed by SEM and presented in Figure 4. The figure reveals the presence of the rod-like shape, open structure of meso-size pores and similar amorphous structures.

### 3.3. Detection of organic constituent in crude phosphoric acid

The accumulation of organic compound as well as potentially toxic elements in the environment has become a global concern. Continuous application of phosphate fertilisers will increase the accumulation of the organic compounds and other hazardous to the ecosystems. Therefore, the detection of the main organic compounds in crude phosphoric acid is important for a successive process for the removal of these contaminants.

The obtained results in Figure 5 clear that the main organic compounds in crude phosphoric acid are mainly composed of three components: azelaic acid (diTBDMS: (Bis [tert-butyl (dimethyl)silyl) azelaate), butylated hydroxytoluene (2,6-di-tert-butyl-4-methylphenol) and dibutyl phthalate.

Azelaic acid, diTBDMS, is a saturated dicarboxylic acid that belongs to the class of organic compounds known as medium-chain fatty acids. It has the following formula and molecular weight: C_{18}H_{44}O_4Si_2 and 416.74 g/mol [36]. 2, 6-Di-tert-butyl-4-methylphenol (Butylated hydroxytoluene) is a lipophilic organic compound with a chemical formula of C_{15}H_{24}O and a molecular mass of 220.35 g/mol [37]. Butylated hydroxytoluene (BHT) is a member of the alkyl phenols broad group, which has been widely used as an antioxidant food additive. BHT is rapidly decomposed forming different metabolites in the environment such as in water and soils [38]. BHT is hardly biodegradable and, therefore, the bioaccumulation of BHT and its derivatives exhibits high toxicity to aquatic organisms, and they are considered as a human health risk from a food safety point of view. The BHT and its metabolites are on the undesirable substances list ‘Danish Environmental Protection Agency’ [38,39].

| Phase       | S1   | S2   | S3   |
|-------------|------|------|------|
| Quartz      | 18.2 | 18.5 | 8.1  |
| Feldspar    | 32.7 | 42.4 | 40.8 |
| Illite      | 16.4 | 13.9 | 12.0 |
| Kaolinite   | 4.9  | 4.2  | 5.1  |
| Chlorite    | 5.4  | 3.3  | 3.0  |
| Calcite     | 1.3  | 2.2  | 8.6  |
| Aragonite   | 3.4  | 3.6  | 3.9  |
| Dolomite    | 1.6  | 1.1  | 1.8  |
| Anhydrite   | 2.7  | 1.5  | 2.3  |
| Mica        | 3.5  | 1.2  | 2.5  |
| Apatite     | 3.1  | 2.3  | 3.5  |
| Others      | 6.8  | 5.8  | 8.4  |
Figure 4. SEM-EDAX of sludge samples (a) S1, (b) S2 and (c) S3.

Figure 5. The main organic components in the crude phosphoric acid.
Dibutyl phthalate (DBP) is a phthalate ester with the following formula and molecular mass: \( \text{C}_{16}\text{H}_{22}\text{O}_{4} \) and 278.34 g/mol [40]. Dibutyl phthalate is a ubiquitous environmental contaminant that is used widely as plasticiser in modern agricultural production due to wastewater irrigation, and the common applications of agricultural chemicals [41]. The U. S. Environmental Protection Agency classified the Dibutyl phthalate as an endocrine disruptor chemical and environmental pollution, which means that the distribution of DBP through the soil poses threats to both the environment and the human food chain [42].

3.4. Sorption investigation

The following section discusses the application of three sludge wastes for the clarification of crude phosphoric acid in order to obtain a proper acid for clean fertilisers. The impact of shaking time, phosphoric acid concentration and sludge amount of addition, as main variables, on the organic compounds adsorption percent have been tested. The sorption isotherms, as well as kinetics, have been performed in order to provide useful data required for the scale-up experiments and the process design.

3.4.1. Effect of shaking time

Several experiments were achieved to investigate the impact of reaction time in the range of 1–120 min on organic species sorption from commercial phosphoric acid (4.5 M) using different sludge wastes. In detail, the three waste sludge has been shaken with crude phosphoric acid with sorbent dose of 10.0 g/L, shaking speed of 150 rpm and room temperature.

The variation of organic compounds adsorption percent as a function of shaking time has been illustrated in Figure 6. From the data, it is evident that the sorption of organic species from industrial phosphoric acid by the three sludge is a fast reaction, whereas the reaction equilibrium is obtained after 30 min for the three sorbents. In addition, the three

![Figure 6](image_url). Organic matter sorption efficiency as a function of shaking time.
sorbent exhibit the same sorption performance, whereas the sorption reaction consists of two stages: the first stage starts from 1 to 30 min and is characterised by a high adsorption rate of reaction. Numerically, organic compounds sorption efficiency increased from 19.0 to 54.0% for S1, from 13.1 to 48.0% for S2 and 17.8% to 48.4% for S3, as the shaking time increased from 1 to 30 min, respectively. This behaviour may be due to the presence of free active sites on the surface of the waste sludge [43,44].

The second stage shows a slow rate of reaction, whereas the organic compounds sorption percent is slightly varied from about 54.0% to 58.5% for S1, from 48.0% to 51.7% for S2 and from 48.4% to 50.7% for S3 as the shaking time increase from 30 to 120 min. This performance may be due to that most of the sorbent surface active sites were occupied; therefore, organic compounds molecules need more time for the diffusion and reaction with the inside active groups [43,44]. This was consistent with other previous reports [8,45–47]. To ensure that complete equilibrium was attained, other subsequent experiments were performed at 120 min.

3.4.2. Influence of phosphoric acid concentration
To investigate the impact of phosphoric acid concentrations ranging from 4.5 to 8.0 M on the sorption of organic compounds using different waste sludge sorbents, a set of experiments were achieved at 120 min reaction time, 100 rpm stirring speed and 25 ± 1°C. The collected data has been illustrated in Figure 7 as a relation between organic compounds sorption % and phosphoric acid molarity. The exhibited data declare that the increase in phosphoric acid concentration has the same impact on the sorption behaviour of the three investigated waste sludge sorbents. In detail, organic compounds sorption efficiency has drastically reduced from 59.0% to 30.2% for S1, from 52.3% to 26.0% for S2 and from 50.7% to 22.9% for S3 sorbent as the phosphoric acid concentration increased from 4.5 to 8.0 M.

This behaviour could be attributed to that as the phosphoric acid molarity increases, the number of phosphoric acid molecules increases which, in turn, increases the coverage

![Figure 7](image-url)  
**Figure 7.** Organic matter sorption efficiency as a function of phosphoric acid concentration.
of the surface active sites of the sorbent particles by the excess acid molecules and in turn decreases the sorption capability of the sorbent. Also, the increase of acid molarity results in the increase of the acid bulk density, which effects negatively on the diffusion of the organic compounds molecules to the sorbent surface [8,48].

3.4.3. Effect of sorbent dose

Figure 8 explores the impact of S1, S2 and S3 waste sludge amount of addition on the reduction of organic compounds from industrial phosphoric acid. In detail, the sorbent amount of addition covers the range from 0.5 to 20 g/L; however, the other controlling conditions were kept at a phosphoric acid concentration of 4.5 M, room temperature, 100 rpm stirring speed and 120 min shaking time, to optimise the required sorbet dose for maximum organic compounds removal. It is obvious that the organic compounds adsorption percent increases by increasing the three waste sludge sorbents’ amount of addition. This performance may be attributed to the existence of more active reaction sites as the sorbent dose increases [13,49].

Numerically, the organic compounds sorption changed from 16.2% to 71.5% for S1, from 11.0% to 61.7% for S2 and from 13.5% to 59.1% for S3 sorbent as the waste sludge dose increased from 0.5 to 20.0 g L⁻¹. It is worth noted that the sorption capacity of the investigated three waste sludge sorbents negatively impacted by the increase in the sorbent amount of addition. Specifically, the sorption capacity, qe value, decreased from 145.6 to 16.1 mg/g for S1, from 99.0 to 13.9 mg g⁻¹ for S2 and from 121.5 to 13.3 mg g⁻¹ for S3 as the sorbent dose increased from 0.5 to 20.0 g L⁻¹. This performance could be attributed to the sorbent active sites were not freely available for binding with organic compounds molecules, and the low concentration of organic compounds species could not meet the adsorption capacities of adsorbents, and thereby decreased the qe [13,49]. This result is consistent with studies applying alum sludge and sewage sludge for wastewater treatment [46,50].
3.5. The uptake kinetics

The uptake kinetics is important in the solid–liquid reactions for better understanding the rate of reaction and the possible adsorption mechanism. In this section, the kinetics of OM removal from industrial phosphoric acid using S1, S2 and S3 waste sludge were performed. Accordingly, the equations of the following kinetic models, namely, pseudo-first-order, pseudo-second-order, Elovich and Weber and Morris kinetic models (Eq. (3), Eq. (4), Eq. (5) and Eq. (6) respectively) have been applied to the adsorption data as shown in Figures 9–12, respectively [51,52]. The values of the kinetic model constants have been calculated and displayed in Table 4. The coefficient of correlation ($R^2$) was employed to figure out the best kinetic equation for describing the resin–metal ions interaction.

$$Log(q_e - q_t) = Log q_e - \left( \frac{K_1}{2.303} \right) t$$  (3)

$$\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \left( \frac{1}{q_e} \right) t$$  (4)

$$q_t = \frac{1}{\beta} \ln (q_\beta) + \frac{1}{\beta} \ln t$$  (5)

$$q_t = K_{id} t^{0.5} + C$$  (6)

Where $q_t$ is the sorption capacity at time $t$ (mg g$^{-1}$); $K_1$ is the rate constant of the pseudo-first-order sorption (min$^{-1}$), $t$ is time (min); $K_2$ is the rate constant of the pseudo-second-order kinetics (g/mg min); $\beta$ is referred to the surface coverage extension and the activated energy for chemisorption and $\alpha$ (mg/g.min) is the initial adsorption rate; $K_{id}$ is intraparticle diffusion rate constant (mg/g.min$^{1/2}$); $C$ is the initial adsorption (mg g$^{-1}$).

![Figure 9. Lagergreen plot for organic matter sorption using WTS.](image-url)
The experimental data have been analysed using the Pseudo-first-order equation as explored in Figure 9. The Figure obvious that the relation between Log(qe-qt) vs time yields straight lines with poor correlation coefficient which indicated that the organic compounds sorption process is not fitted well with the Lagergren equation. In many cases in the literature, Lagergren kinetic model was commonly is not fitting well for the whole reaction times; however, it is applicable only for describing the initial stage of the sorption processes [45].

The pseudo-second-order reaction equation (McKay equation) was examined to fit the obtained results as shown in Figure 10. It is obvious that the relation between t/qt as
a function of sorption time gives an excellent linear relationship with a correlation coefficient equal to 0.99 for the investigated three waste sludges. Besides, the experimental sorption capacity $q_{e_{\text{exp}}}$ for S1, S2 and S3 sorbents is consistent with the calculated sorption capacity $q_{e_{\text{cal}}}$ This evidences that the pseudo-second-order kinetic equation could successfully describe the organic compounds sorption from crude phosphoric acid using S1, S2 and S3 sludge. This suggests the chemisorption mechanisms for
organic matter sorption process [8, 44]; however, appropriate clarification could be declared when considering the thermodynamic parameters of the sorption process [44]. The presence of surface functional groups on the surface of the applied waste sludge sorbents could enhance efficient electron transfer or electron sharing between the surface groups and organic pollutants. These results are consistent with other previous reports [8, 10, 45, 47].

The half-equilibrium time, $t_{1/2}$ (h), and the initial adsorption rate, $h$ (mol/g.h) for S1, S2 and S3 waste sludge sorbents were calculated from equations 1 and equation presented in [13]. The explored results in Table 4 reveal that S2 sludge has the highest half-equilibrium time (5.3), while S3 has the lowest value (3.6). Nevertheless, S1 and S3 sorbents have the greatest initial adsorption rate (6.69 and 6.55 mol/g.h), and S2 sorbent has the lowest value (4.6 mol/g.h). The sorption capacity at equilibrium for the three applied sludge sorbents could rank as the following S1 > S2 > S3. It is worth noted that the S3 sorbent has the highest surface area (m²/g) followed by S2 (m²/g) and then S1 sorbent (m²/g), even though S3 sorbent exhibits the lowest sorption capacity and S1 shows the highest organic compounds sorption capacity. This means that the synergistic effect of the sorbent surface area is not the only parameter that controls the sorption process; however, there are other parameters that may exhibit anti-synergistic effects such as the net charge of the sorbent surface. From the zeta potential analysis for the applied three sorbents, it is clear that S2 and S3 have a highly negative surface (−27.9 and −34.2 mV, respectively), which in turn results in the repulsion between the sorbent particles and the formation of unstable complexes with the organic compounds species. However, S1 has a much lower surface charge (−5.6 mV) which means that it could produce more stable complexes with organic compounds.

The mathematical treatment of the obtained results using Elovich equation has been performed to figure out where the organic compounds adsorption process is chemical adsorption in nature or not. The plot of ln t versus qt, Figure 11, explores straight lines with a good correlation coefficient (about 0.95) for S1, S2 and S3 waste sludge sorbent. This confirms that the organic compounds adsorption from crude phosphoric acid using S1, S2 and S3 is a chemisorption process, and the adsorption rate is exponentially dependent on the number of available adsorption sites in the applied sorbents [47]. Table 4 declares that the initial adsorption rate for S1, S2 and S3 sorbents is 31.6, 14.9 and 32.8 mg/g.min, respectively. It is worth noted that the initial sorption rate value (α) obtained from Elovich model has the same trend as the initial sorption rate (h) obtained from McKay equation, whereas $S1 \approx S3 > S2$. Nevertheless, α values are 4–5 times greater than h values.

Despite pseudo-second order and Elovich kinetic models have successfully described the nature of the organic compounds sorption process as a chemisorption reaction; however, they could not give clear information regarding the organic compounds adsorption mechanism. In the solid–liquid reactions, the sorption kinetics could be controlled by numerous diffusion mechanisms: resistance to bulk diffusion, film diffusion and intraparticle diffusion. Mainly, the resistance to film diffusion is active at the beginning of the sludge sorbents and liquid phosphoric acid. Also, by applying sufficient velocity for mixing the sludge sorbents and phosphoric acid, the effect of the resistance to bulk diffusion could be overlooked. Thus, the resistance to intraparticle diffusion is the main controlling step. Accordingly, the obtained experimental results have been analysed
using the Morris-Weber model as shown in Figure 12. The model constants were evaluated from the plot of $q_t$ as a function of $t_{0.5}$ and presented in Table 4. Figure 12 displays two regions (multi-linear relationship) for S1, S2 and S3 sorbents, which means that the intraparticle diffusion is not the only mechanism that controls the organic compounds sorption process. This may be due to the rate of transfer of the organic compounds molecules is not the same in both sorption stages; initial and final which clears the effect of the boundary layer [53].

Table 4 evident that the first stage of the organic compounds adsorption process is characterised by low boundary layer effect and in turn high sorption rate for the applied three sorbents, which confirm the fast reaction. The reason beyond that may be the presence of available surface active sites, which result in the external surface adsorption [8,53]. On the contrary, the second stage is characterised by a low absorption rate and high boundary layer effect for S1, S2 and S3 sludge, which could be attributed to the saturation of most sludge surface sites; accordingly, the intraparticle diffusion (IPD) begins. In this regard, it could be indicated that the sorption of organic species from commercial phosphoric acid using S1, S2 and S3 sewage sludge is controlled by the combination of external surface adsorption and intraparticle diffusion as rate-controlling steps [8,45].

The adsorption capacity of S1, S2 and S3 sludge sorbents has been compared with other adsorbents that applied for the same purpose, removal of organic compounds recovery from crude phosphoric acid and exhibited in Table 5. The revealed data declare that the utilized three sorbents; S1, S2, and S3 possess organic compounds sorption capacity within the given sorbents from literature which is obvious that these sewage sludges could be applied for the clarification of crude phosphoric acid.

3.6. The sorption isotherm

The sorption isotherm is an essential factor for the plant design and improving the adsorption system. Accordingly, Freundlich and Langmuir isotherm models were applied for analysing the obtained equilibrium results. The coefficient of correlation ($R^2$) has been applied for testing the fitting of the obtained data to the isotherm equations. The linear

| Table 5. The experimental capacity of investigated sludge samples compared with the sorption capacity of other sorbents for organic matter recovery from phosphoric acid. |
|---------------------------------|------------------|----------------|
| Sorbent Type                   | Sorption Capacity, (mg/g) | Reference      |
| Low quartz kaolinite (Ball clay)| 11.7             | [21]           |
| High quartz kaolinite (Kaolin clay)| 5.7               |                |
| Raw bentonite clay (RBC)       | 17.2             | [18]           |
| Raw grey clay (RGC)            | 15.0             | [9]            |
| Natural bentonite              | 24.0             |                |
| Sulphuric acid activated bentonite | 27.7             |                |
| Hydrochloric acid activated bentonite | 17.3           |                |
| Blank bio-char (BC)            | 33.6             | [1]            |
| Hydrochloric acid activated bio-char (HAC) | 53.7    |                |
| Nitric acid activated bio-char (NAC) | 47.9         |                |
| Sludge El Sheikh Zaid (SSZ)    | 22.8             | Present work   |
| Sludge Al Obour (SO)           | 23.3             |                |
| Sludge El Marg (SM)            | 26.3             |                |
form of Freundlich and Langmuir isotherm models has commonly expressed equations 7 and 8, respectively [54]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$  \hspace{1cm} (7)

$$\frac{C_e}{q_e} = \frac{1}{K_f q_m} + \frac{C_e}{q_m}$$  \hspace{1cm} (8)

where $K_F$ (L/mg) is corresponding to the sorption capacity, and $n$ refers to the sorption intensity. $q_m$ (mg. g$^{-1}$) is the maximum sorption capacity of the sorbent, and $K_L$ (L.mg$^{-1}$) is the equilibrium constant which refers to the energy of adsorption and reflects the affinity of resin towards the organic compounds.

The isotherm parameters of Freundlich model have been evaluated from the illustration of $\ln q_e$ as a function of $\ln C_e$, Figure 13, and presented in Table 6. Nevertheless, the parameters of Langmuir model were obtained from the Figure of $C_e/q_e$ as a function of $C_e$ and displayed in Table 6.

The explored results in Figures 13 and 14 as well as Table 6, declare that only Freundlich isotherm plot gives a straight line with a perfect correlation coefficient (about 0.98) for all investigated sorbents. This indicates that the organic compounds adsorption from crude dihydrate phosphoric acid using S1, S2 and S3 waste sludge is fitting Freundlich isotherm model, which means a heterogeneous sorption system.

![Figure 13. Freundlich model plot for organic matter sorption using different WTS samples.](image)

| Table 6. Isotherm constants of Freundlich and Langmuir isotherm models. |
|-----------------------------|-----------------|-----------------|-----------------|
| Model                      | $S1$            | $S2$            | $S3$            |
| Freundlich isotherm $n$    | 1.3             | 1.6             | 1.1             |
| $K_F$ (mg/g)               | 0.4             | 0.7             | 0.1             |
| $R^2$                      | 0.98            | 0.98            | 0.98            |
| Langmuir isotherm $Q_m$ (mg/g) | 140.8           | 70.4            | 333.3           |
| $b$ (L/mg)                 | 0.01            | 0.97            | 0.01            |
| $R^2$                      | 0.84            | 0.96            | 0.3             |
with different active sites. Furthermore, Table 6 shows that $n > 1$ for the applied three waste sludge sorbents which obvious that the sorption is a physical process [55–57].

4. Conclusions

Bis [tert-butyl(dimethyl)silyl] azelaate, 2,6-Di-tert-butyl-4-methylphenol and Dibutyl phthalate compounds have been detected as the main organic compounds in crude phosphoric acid. Waste sludge, namely, S1, S2 and S3, has been successfully utilised for the clarification of crude phosphoric acid. The main variables that affect the organic compounds sorption efficiency such as: shaking time, sorbent dose and phosphoric acid concentration were studied. The revealed data declare that the adsorption reaction is fast, whereas the reaction equilibrium has been reached after 30 min for the three investigated sorbents. The sorbent does have positive impact on the sorption percent on the other hand the phosphoric acid concentration has negative influence. The sorption kinetics has been performed using pseudo-first-order, pseudo-second-order, Elovich and Weber-Morris kinetic models. The displayed results explore that the S1, S2 and S3 sorbent exhibit chemisorption reaction. S1 waste sludge exhibits the highest sorption capacity, while S3 shows the lowest sorption capacity.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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