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New Organic Compounds Detection and Potential Removal in Crude Phosphoric Acid using Waste Sludge

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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), and Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy were used to characterize waste sludges. Practically, three sludge samples were utilized 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 Lagregran pseudo-first-order, pseudo-second-order, Morris-Weber, and Elvoich models display that the sorption process using waste sludges is a chemisorption process. Finally, the three sludge samples exhibit potential sorbents for the clarification of phosphoric acid and sequentially to produce green phosphate fertilizers.

Keywords:

Waste sludge; Crude phosphoric acid; Organic species; Sorption

1. Introduction

Phosphorus (P) is one of the vital macronutrients required for plant growth as well as human life. Phosphorus was utilized for increasing crop products since the 1950s (Stewart and Roberts 2012). The United Nations reported that the world population is expected to become about 9 billion by 2050, and the food demand will increases by 60% for the same period that sepsequently will rise the global phosphors demand (FAO 2018). Phosphorus security is considered one of the greatest global sustainability challenges in the twenty-first century (Cordell and White 2014). Phosphorus management is very important for sustainable food and agriculture, particularly in food-deficient and phosphorus-scarce countries (Cordell et al. 2015).

Phosphate rock is a nonrenewable natural resource that is used to describe phosphate-bearing minerals. Approximately 90% of the phosphate rock production worldwide is utilized in the fertilizer industry, and the other 10% is used in the animal feeds, detergents, and chemicals industries (Hellal et al. 2019; Nedelciu et al. 2020). 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 (Fayiga and Nwoke 2016).

It is well known that phosphate rocks contain organic compounds as a result of the biological sedimentation of sea organisms (Taha et al. 2019). In addition to organic compounds, phosphate rock is contains different hazardous elements such as U, Cd, and As (Fayiga and Nwoke 2016). Organic compounds as well as other harmful elements are introduced to phosphoric acid and phosphate fertilizers during the acidulation of phosphate rock (Zhang and Zhang 2010; Fayiga and Nwoke 2016). Most of previous studies reported that the organic compounds in the phosphoric acid mainly consists of humic compounds, aromatics, and other saturated and unsaturated fatty acids (Awwad et al. 2013; Hamza et al.

68 2013; Fawzy et al. 2018; El Naggar et al. 2019), however, , the main organic compounds in wet crude
69 phosphoric acid have not been detected.
70 Organic compounds present in phosphoric acid have a negative impact on the quality and the quantity
71 of the produced phosphoric acid whereas they give a dark color to the produced acid and affect the
72 crystallization of the phosphogypsum (Singh et al. 2016; Taha et al. 2019). Furthermore, organic
73 compounds result in serious operating problems during the application of liquid-liquid method for the
74 recovery of uranium from phosphoric acid as well as the purification of phosphoric acid, whereas organic
75 compounds accumulates and coagulates heavly at the interfacial area between the phosphoric acid and
76 organic solvent which leads to the losses of the organic solvent and negatively impact on the process
77 economy (Dissanayake and Chandrajith 2009; Awwad et al. 2013; Singh et al. 2016; El Naggar et al.
78 2019). Also, organic compounds forms stable toxic complexes with the harmful elements in the
79 phosphoric acid, which accumulate in the environment as a result of the continuous application of
80 phosphate fertilizers and also transfer to the human body through the food chain (Fayiga and Nwoke
81 2016; Taha et al. 2019).
82 Accordingly, the reduection of the organic compound from phosphoric acid is an important process in
83 respect to improve the quality of phosphoric acid and produce eco-friendly fertilizers. Various methods
84 were applied for the reduction of organic compounds from crude phosphoric acid for example liquid-
85 liquid extraction or sorption (Awwad et al. 2013; Hamza et al. 2013; Singh et al. 2016; Fawzy et al.
86 2018; El Naggar et al. 2019). Several materials were investigated for achieving this proposes such as
87 clays (Hamza et al. 2015; Singh et al. 2016) and activated bio-chars (El Naggar et al. 2019; Taha et al.
88 2019).
89 Sludge is the waste materials generated from water treatment plant. The production of sludge is expected
90 to be increased shortly as a result of urbanization and industrial development (Rashed 2018). The
91 chemical and physical properties of the sludge are varied as a result of the difference in the water

92 treatment technology, hydrogeology, and geology of the intake area, as well as the chemical composition
93 of the utilized raw materials (Evuti and Lawal; Wołowiec and Bajda 2017). The management of sludge
94 could be performed using several methods such as landfilling (Grassi et al. 2012), road surfacing
95 (Jamshidi et al. 2012), and incineration (Yu and Zhong 2006).
96 Proper management of sludge in an eco-friendly and economical manner is very interesting. Sludge has
97 good sorption properties (Yu and Zhong 2006). Recently, sludge has been utilized for the elimination of
98 heavy metals from wastewater (Ragheb 2018; Rashed 2018; Wołowiec et al. 2019; Bogusz et al. 2019).
99 However, sludge has never been applied for the purification of industrial phosphoric acid. In this regard,
100 the present work aims to detect the main organic compounds in crude phosphoric acid as well as the
101 application of waste sludge as an efficient sorbent for the retention of organic species through batch
102 investigation in order produce eco-friendly phosphate fertilizers and reduce the accumulation of sludge
103 in the environment.

104 **2. Experimental procedures**

105 **2.1. Materials**

106 Sludge samples designated here as S1, S2, and S3, were collected from three different water treatment
107 stations namely El-Marg, Al-Obour, and El-Sheikh Zayed, respectively. The samples were washed with
108 double distilled water, left overnight in an oven at 110 °C for complete drying, and finally left for cooling
109 in a desiccator for further analysis.
110 Commercial crude phosphoric acid, containing (P_2O_5 = 26.5%, CaO = 0.34%, Fe_2O_3 = 1.1%, F = 0.64%,
111 U(VI) = 40 ppm and organic compounds = 450 ppm) was purchased from Abu Zaabal Company for
112 Fertilizer and Chemical Materials. Shimazu UV-visible 160 A spectrophotometer was used to determine
113 the content of organic compounds, iron and uranium.

114 **2.2. Characterization 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 (Degen et al. 2014). 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 LX^4 Quantachrome, USA to determine the Brunauer–Emmett–Teller (BET) surface area. Before measurement, samples were kept in a desiccator until testing. Samples were cooled with liquid nitrogen and analyzed 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/Po = 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 crud phosphoric acid solution. A Supelco MDN-5S 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 (Shahat et al. 2011). The retention indices were calculated for all of 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 teqniche. All tests were achieved in polyethylene type using a thermostatic shaking water bath. The influence of reaction time, sludge amount of addition, phosphoric acid concentration on the removal percent have been examined. In details, 40 mL of liquid phase has been shaken with 0.4 g of the sorbent at 298 ±1 K for 24 hrs. 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 (Taha et al. 2019).

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:

$$E\ \% = \frac{1 - C_e}{C_o} X100\% \dots\dots (1)$$

$$q_e = C_o - C_e X \frac{V}{m} \dots\dots (2)$$

where Co and Ce are the OM concentration (mg L^{-1}) before the adsorption and at equilibrium, respectively, qe (mg g^{-1}) is the amount of OM sorbet, V is the volume of phosphoric acid (L), and m is the mass of the sludge (g).

3. Results and Discussions

3.1. Characterization of sludge samples

3.1.1. Physical characterization

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 were measured and the bell shape distribution forms were clearly detectable in **Fig. 1a**. The mean particle sizes for S1, S2 and S3 are 1725, 748 and 755 nm, respectively. In addition, the poly dispersity index was laid between 0.2 and 0.5 that indicated to unimodal particle size with narrow distributions (Ibrahim and Voit 2009). 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 presence in range 0.7 to 1.7 µm. neither big particles of sludge nor excellent polydispersity indices were pointed to homogenized particle size (Ahmed et al. 2019; Meawad and Ibrahim 2019).

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 **Fig. 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 are higher than S1 with low mobility and low zeta potential. The separation of organic compounds was depending on the fast precipitation of sludge during physical adsorption mechanism.

The surface area is one of unique phenomena related to the particle size with inverse proportions (Ibrahim et al. 2018). Surface area measurement with related indices for sludge samples were tabulated in Table 1. The isotherm branch of nitrogen gas on dry degassed sludge power with adsorption trend were applied to calculate BET values 19, 94 and 102 m^2/g for sludge sample S1, S2 and S3, respectively. The adsorption indices were indicated to perfect trend of measured points with correlation coefficient ≈1 as first order equation of linear relationship. The particle size results have a great agreement with confirmation to each other's through increasing the surface area with decreasing of particle size from

S3, S2 to S1. Overall, the physical characterization measurements are verified the stability, size and surface area for sludge samples as mentioned theoretically and previous research (Ibrahim et al. 2016; Meawad and Ibrahim 2019; Abdelraof et al. 2020).

3.1.2. Chemical characterization

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. **Fig. 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. 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, **Fig. 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 minerals content and the charge on clay surface play an important role in the efficient sorption of organic compounds (Lützow et al. 2006; Setia et al. 2014). 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 are much higher than that in S2.

3.2. Detection of organic constituent in crude phosphoric acid

The accumulation of organic compound as well as potentially toxic elements in the environment has becomes a global concern. Continuous application of phosphate fertilizers 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 **Fig.4** clear that the main organic compounds in crude phosphoric acid is 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: C21H44O4Si2 and 416.74 g/mol (Wheeler et al. 2000). 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 (US National Library of Medicine 2020). 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 (Ryssel et al. 2015). BHT is hardly biodegradable and therefore the bioaccumulation of BHT and its derivatives exhibit 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" (Norwegian Scientific Committee for Food Safety 2009; Ryssel et al. 2015).

Dibutyl phthalate (DBP) it is a phthalate ester with the following formula and molecular mass: $C_{16}H_{22}O_4$ and 278.34 g/mol (2020). Dibutyl phthalate is a ubiquitous environmental contaminant that is used widely as plasticizer in modern agricultural production due to wastewater irrigation, and the common applications of agricultural chemicals (He et al. 2015). The U.S. Environmental Protection Agency classified the Dibutyl phthalate as an endocrine disruptor chemical and an environmental pollutant,

233 which means that the distribution of DBP through the soli poses threatens to both the environment as
234 well as the human food chain (Bui et al. 2016).

235 **3.3. Sorption investigation**

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

241 ***3.3.1. Effect of shaking time***

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

246 The variation of organic compounds adsorption percent as a function of shaking time has been illustrated
247 in **Fig.5**. From the data, it is evident that the sorption of organic species from industrial phosphoric acid
248 by the three sludge is a fast reaction whereas the reaction equilibrium is obtained after 30 min for the
249 three sorbents. In addition, the three sorbent exhibit the same sorption performance whereas the sorption
250 reaction consists of two stages; the first stage starts from 1 to 30 min and is characterized by a high
251 adsorption rate of reaction. Numerically, organic compounds sorption efficiency increased from 19.0 to
252 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
253 30 min respectively. This behavior may be due to the presence of free active sites on the surface of the
254 waste sludge (Zhang et al. 2015; Taha et al. 2018). The second stage shows a slow rate of reaction
255 whereas the organic compounds sorption percent is slightly varied from about 54.0 to 58.5% for S1,
256 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

257 min. This performance may be due to that most of the sorbent surface active sites were occupied,
258 therefore organic compounds molecules need more time for the diffusion and reaction with the inside
259 active groups (Zhang et al. 2015; Taha et al. 2018). This was consistent with other previous reports
260 (Nawar et al. 2015; Ait Ahsaine et al. 2017; Ali et al. 2019; Taha et al. 2019). To ensure that complete
261 equilibrium was attained, other subsequent experiments were performed at 120 min.

262 ***3.3.2. Influence of phosphoric acid concentration***

263 To investigate the impact of phosphoric acid concentrations ranging from 4.5 to 8.0 M on the sorption
264 of organic compounds using different waste sludge sorbents, a set of experiments were achieved at 120
265 min reaction time, 100 rpm stirring speed, and 25 ±1 ^{o}C. The collected data has been illustrated in **Fig.**
266 **6** as a relation between organic compounds sorption % and phosphoric acid molarity. The exhibited data
267 declare that the increase in phosphoric acid concentration has the same impact on the sorption behavior
268 of the three investigated waste sludge sorbents. In details, organic compounds sorption efficiency has
269 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
270 S3 sorbent as the phosphoric acid concentration increased from 4.5 to 8.0 M. This behavior could be
271 attributed to that as the phosphoric acid molarity increases, the number of phosphoric acid molecules
272 increases which, in turn, increase the coverage of the surface active sites of the sorbent particles by the
273 excess acid molecules and in turn decrease the sorption capability of the sorbent. Also, the increase of
274 acid molarity results in the increase of the acid bulk density which effects negatively on the diffusion of
275 the organic compounds molecules to the sorbent surface (Morsy and Hussein 2012; Taha et al. 2019).

276 ***3.3.3. Effect of sorbent dose***

277 **Fig.7** explores the impact of S1, S2, and S3 waste sludge amount of addition on the reduction of organic
278 compounds from industrial phosphoric acid. In details, the sorbent amount of addition covers the range
279 from 0.5 to 20 g/L however, the other controlling conditions were kept at a phosphoric acid concentration
280 of 4.5 M, room temperature, 100 rpm stirring speed, and 120 min shaking time, to optimize the required

281 sorbet dose for maximum organic compounds removal. It is obvious that the organic compounds
282 adsorption percent increases by increasing the three waste sludge sorbents' amount of addition. This
283 performance may be attributed to the existence of more active reaction sites as the sorbent dose increases
284 (Zou et al. 2017; El Naggar et al. 2019). Numerically, The organic compounds sorption changed from
285 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
286 sludge dose increased from 0.5 to 20.0g L^{-1}. It is worth noted that, the sorption capacity of the
287 investigated three waste sludge sorbents negatively impacted by the increase in the sorbent amount of
288 addition. Specifically, the sorption capacity, qe value, decreased from145.6 to 16.1 mg/ g for S1, from
289 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
290 to 20.0 g L^{-1}. This performance could be attributed to the sorbent active sits were not freely available for
291 binding with organic compounds molecules, and the low concentration of organic compounds species
292 could not meet the adsorption capacities of adsorbents, and thereby decreased the qe (Zou et al. 2017; El
293 Naggar et al. 2019). This result is consistent with studies applying alum sludge and sewage sludge for
294 wastewater treatment (Nawar et al. 2015; Abo-El-Enein et al. 2017).

295 **3.4. The uptake kinetics**

296 The uptake kinetics is important in the solid-liquid reactions for better understanding the rate of reaction
297 and the possible adsorption mechanism. In this section, the kinetics of OM removal from industrial
298 phosphoric acid using S1, S2, and S3 waste sludge were performed. Accordingly; the equations of the
299 following kinetic models namely; pseudo-first-order, pseudo-second-order, Elvoich, and Weber and
300 Morris kinetic models (Eq. (3), Eq. (4), Eq. (5) and Eq. (6) respectively) have been applied to the
301 adsorption data as shown in **Figs. 8-11**, respectively (Kim and Kim 2019; Kang and Kim 2019). The
302 values of the kinetic model constants have been calculated and displayed in Table 4. The coefficient of
303 correlation (R^2), was employed to figure out the best kinetic equation for describing the resin- metal ions
304 interaction.

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

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) t \ldots\ldots (4)$$

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

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

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

The experimental data have been analyzed using the Pseudo-first order equation as explored in **Fig. 8**. The Figure obvious that the relation between Log (qe-qt) vs time yield 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 applicable only for describing initial stage of the sorption processes (Ait Ahsaine et al. 2017). The Pseudo-second order reaction equation (McKay equation) was examined to fit the obtained results as shown in **Fig. 9**. 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 sludge. Besides, the experimental sorption capacity qe exp for S1, S2, and S3 sorbents is consistent with the calculated sorption capacity qe cal. This evidence that the Pseudo-second order kinetic equation could be successfully describe the organic compounds sorption from crude phosphoric acid using S1, S2, and S3 sludge. This means that the organic compounds sorption process is chemisorption and there is electron transfer or electron sharing between the applied waste

sludge sorbents and the organic compounds species (Taha et al. 2018, 2019). This results in consistent with other previous reports (Hamza et al. 2013; Ait Ahsaine et al. 2017; Ali et al. 2019; Taha et al. 2019). 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 (El Naggar et al. 2019). 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 worth noted that the S3 sorbent has the highest surface area (m^2/g) followed by S2 (m^2/g) and then S1 sorbent (m^2/g) even though, S3 sorbent exhibits the lowest sorption capacity and S1 show 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 be 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, **Fig. 10**, explore 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 (Ali et al. 2019). Table 4 declares that the initial adsorption rate for S1, S2, and S3 sorbents are 31.6, 14.9, and 32.8 mg/g.min

respectively. It is worth noted that, the initial sorption rate value (α) obtained from Elvoich model has the same trend as the initial sorption rate (h) obtained from McKay equation whereas S1 ≈ S3 > S2. Nevertheless, α values are 4-5 times greater than h values.

Despite Pseudo-second order and Elovich kinetic models have been successfully described the nature of the organic compounds sorption process as a chemisorption reaction however, they could not give clear information regards to the organic compounds adsorption mechanism. In the solid-liquid reactions, the sorption kinetics could be controlled with 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 analyzed using the Morris-Weber model as shown in **Fig. 11**. The model constants were evaluated from the plot of qt as a function of t0.5 and presented in Table 4. **Fig. 11** 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 proces. 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 (Wu et al. 2009). Table 4 evident that the first stage of the organic compounds adsorption process is characterized 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 avialable surface active sites which result in the external surface adsorption (Wu et al. 2009; Taha et al. 2019). On the contrary, the second stage is characterized 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

375 phosphoric acid using S1, S2, and S3 sewage sludge is controlled by the combination of external surface
376 adsorption and intraparticle diffusion as rate-controlling steps (Ait Ahsaine et al. 2017; Taha et al. 2019).
377 The adsorption capacity of S1, S2 and S3 sludge sorbents has been compared with other adsorbents that
378 applied for the same purpose, removal of organic compounds recovery from crude phosphoric acid, and
379 exhibited in Table 5. The revealed data declare that the utilized three sorbents; S1, S2 and S3 possess
380 organic compounds sorption capacity within the given sorbents from literature which obvious that these
381 swage sludges could be applied for the clarification of crude phosphoric acid.

382 **3.5. The sorption isotherm**

383 The sorption isotherm is an essential factor for the plant design and improving the adsorption system.
384 Accordingly, Freundlich and Langmuir isotherm models were applied for analyzing the obtained
385 equilibrium resluts. The coefficient of correlation (R^2) has been applied for testing the fitting of the
386 obtained data to the isotherm equations. The linear form of Freundlich and Langmuir isotherm models
387 have commonly expressed equations 1 and 2, respectively (Hussein and Taha 2013):

388 $$\log q_e = \log K_F + \frac{1}{n}\log C_e \dots\dots (7)$$

389 $$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \dots\dots (8)$$

390 where K_f (L/ mg) is corresponding to the sorption capacity, and n refers to the sorption intensity. q_m (mg.
391 g^{-1}) is the maximum sorption capacity of the sorbent, and k_L (L. mg^{-1}) is the equilibrium constant which,
392 refers to the energy of adsorption and reflects the affinity of resin towards the organic compounds.
393 The isotherm parameters of Freundlich model have been evaluated from the illustration of ln qe as a
394 function of ln Ce, **Fig. 12**, and presented in Table 6. Nevertheless, the parameters of Langmuir model
395 were obtained from the Figure of Ce/qe as a function of Ce and displayed in Table 6.
396 The explored results in **Figs. 12 and 13** as well as Table 6, declare that only Freundlich isotherm plot
397 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 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 (Dacrory et al. 2020; Masoud 2020).

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 utilized 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, Elvoich, and Weber-Morris kinetic models. The displayed results explore that the S1, S2 and S3 sorbent exhibit chemisorption reaction. S1 waste sludge exhibit the highest sorption capacity, while S3 shows the lowest sorption capacity.

5. Declarations

5.1. Ethics approval and consent to participate

Not applicable

5.2. Consent for publication

Not applicable

5.3. Availability of data and materials

All data generated or analysed during this study are included in this published article.

5.4. Competing interests

The authors declare that they have no competing interests.

5.5. Funding

The authors did not receive support from any organization for the submitted work.

The authors have no relevant financial or non-financial interests to disclose.

5.6. Authors' contributions

All authors have equal contributions in the established of the research ides, experimental part, characterization, and explanation of results and shared in writing and revise the manuscript.

6. References

Abdelraof M, Ibrahim S, Selim MH, Hasanin M (2020) Immobilization of L-methionine γ-lyase on different cellulosic materials and its potential application in green-selective synthesis of volatile sulfur compounds. J Environ Chem Eng 8:. https://doi.org/10.1016/j.jece.2020.103870

Abo-El-Enein SA, Shebl A, Abo El-Dahab SA (2017) Drinking water treatment sludge as an efficient adsorbent for heavy metals removal. Appl Clay Sci 146:343–349. https://doi.org/10.1016/j.clay.2017.06.027

Ahmed HM, Abdellatif MM, Ibrahim S, Abdellatif FHH (2019) Mini-emulsified Copolymer/Silica nanocomposite as effective binder and self-cleaning for textiles coating. Prog Org Coatings 129:52–58. https://doi.org/10.1016/j.porgcoat.2019.01.002

Ait Ahsaine H, Zbair M, El Haouti R (2017) Mesoporous treated sewage sludge as outstanding low-cost adsorbent for cadmium removal. Desalin Water Treat 85:330–338. https://doi.org/10.5004/dwt.2017.21310

Ali MM, Attia AA, Taha MH, et al (2019) Application of acid activated bentonite for efficient removal of organic pollutants from industrial phosphoric acid: Kinetic and thermodynamic study. In: SPE Middle East Oil and Gas Show and Conference, MEOS, Proceedings

Awwad NS, El-Nadi YA, Hamed MM (2013) Successive processes for purification and extraction of phosphoric acid produced by wet process. Chem Eng Process - Process Intensif 74:69–74. https://doi.org/10.1016/j.cep.2012.11.009

Bogusz A, Oleszczuk P, Dobrowolski R (2019) Adsorption and desorption of heavy metals by the sewage sludge and biochar-amended soil. Environ Geochem Health 41:1663–1674. https://doi.org/10.1007/s10653-017-0036-1

Bui TT, Giovanoulis G, Cousins AP, et al (2016) Human exposure, hazard and risk of alternative plasticizers to phthalate esters. Sci. Total Environ. 541:451–467

Cordell D, Turner A, Chong J (2015) The hidden cost of phosphate fertilizers: mapping multi-stakeholder supply chain risks and impacts from mine to fork. Glob Chang Peace Secur 27:323–343. https://doi.org/10.1080/14781158.2015.1083540

Cordell D, White S (2014) Life's bottleneck: Sustaining the world's phosphorus for a food secure future. Annu. Rev. Environ. Resour. 39:161–188

Dacrory S, Haggag ESA, Masoud AM, et al (2020) Innovative synthesis of modified cellulose derivative as a uranium adsorbent from carbonate solutions of radioactive deposits. Cellulose 27:7093–7108. https://doi.org/10.1007/s10570-020-03272-w

Degen T, Sadki M, Bron E, et al (2014) The high score suite. In: Powder Diffraction. pp S13–S18

Dissanayake CB, Chandrajith R (2009) Phosphate Mineral Fertilizers, trace metals and human health. J. Natl. Sci. Found. Sri Lanka 37:153–165

El Naggar AMA, Ali MM, Abdel Maksoud SA, et al (2019) Waste generated bio-char supported co-nanoparticles of nickel and cobalt oxides for efficient adsorption of uranium and organic pollutants from industrial phosphoric acid. J Radioanal Nucl Chem 320:741–755. https://doi.org/10.1007/s10967-019-06529-2

Evuti AM, Lawal M Recovery of coagulants from water works sludge: A review. researchgate.net

FAO (2018) Feeding nine billion in 2050. In: Rome. http://www.fao.org/news/story/en/item/174172/icode/. Accessed 17 Nov 2020

Fawzy MM, Farag NM, Amin AS (2018) Treatment of Crude Phosphoric Acid from Some Undesirable Impurities. J Basic Environ Sci 5:204–216

Fayiga AO, Nwoke OC (2016) Phosphate rock: Origin, importance, environmental impacts, and future roles. Environ. Rev. 24:403–415

Grassi M, Kaykioglu G, Belgiorno V, Lofrano G (2012) Removal of Emerging Contaminants from Water and Wastewater by Adsorption Process. pp 15–37

494 Hamza W, Chtara C, Benzina M (2013) Retention of organic matter contained in industrial phosphoric
495 acid solution by raw Tunisian clays: Kinetic equilibrium study. J Chem 2013:.
496 https://doi.org/10.1155/2013/218786
497 Hamza W, Chtara C, Benzina M (2015) Characterization and application of Fe and iso-Ti-pillared
498 bentonite on retention of organic matter contained in wet industrial phosphoric acid (54 %): kinetic
499 study. Res Chem Intermed 41:6117–6140. https://doi.org/10.1007/s11164-014-1726-2
500 He L, Gielen G, Bolan NS, et al (2015) Contamination and remediation of phthalic acid esters in
501 agricultural soils in China: a review. Agron. Sustain. Dev. 35:519–534
502 Hellal F, El-Sayed S, Zewainy R, Amer A (2019) Importance of phosphate pock application for
503 sustaining agricultural production in Egypt. Bull Natl Res Cent 43:. https://doi.org/10.1186/s42269-
504 019-0050-9
505 Hussein AEM, Taha MH (2013) Uranium removal from nitric acid raffinate solution by solvent
506 immobilized PVC cement. J Radioanal Nucl Chem 295:709–715. https://doi.org/10.1007/s10967-
507 012-2158-3
508 Ibrahim S, Abdel Rehim M, Turky G (2018) Dielectric study of polystyrene/polycaprolactone
509 composites prepared by miniemulsion polymerization. J Phys Chem Solids 119:56–61.
510 https://doi.org/10.1016/j.jpcs.2018.03.030
511 Ibrahim S, Abdelfattah I, Soliman O (2016) Environmental recycling of compact disc using industrial
512 wastewater. Der Pharm Lett 8:207–214
513 Ibrahim S, Voit B (2009) Synthesis and characterization of well-defined block copolymers by combing
514 controlled radical and cationic polymerization. In: Macromolecular Symposia. pp 59–66
515 Jamshidi M, Jamshidi A, Mehrdadi N (2012) APPLICATION OF SEWAGE DRY SLUDGE IN
516 CONCRETE MIXTURES
517 Kang HJ, Kim JH (2019) Adsorption Kinetics, Mechanism, Isotherm, and Thermodynamic Analysis of

518 Paclitaxel from Extracts of Taxus chinensis Cell Cultures onto Sylopute. Biotechnol Bioprocess Eng
519 24:513–521. https://doi.org/10.1007/s12257-019-0001-1
520 Kim YS, Kim JH (2019) Isotherm, kinetic and thermodynamic studies on the adsorption of paclitaxel
521 onto Sylopute. J Chem Thermodyn 130:104–113. https://doi.org/10.1016/j.jct.2018.10.005
522 Lützow M V., Kögel-Knabner I, Ekschmitt K, et al (2006) Stabilization of organic matter in temperate
523 soils: Mechanisms and their relevance under different soil conditions - A review. Eur. J. Soil Sci.
524 57:426–445
525 Masoud AM (2020) Sorption behavior of uranium from Sulfate media using purolite A400 as a strong
526 base anion Exchange resin. Int J Environ Anal Chem.
527 https://doi.org/10.1080/03067319.2020.1763974
528 Meawad A, Ibrahim S (2019) Novel bifunctional dispersing agents from waste PET packaging materials
529 and interaction with cement. Waste Manag 85:563–573.
530 https://doi.org/10.1016/j.wasman.2019.01.028
531 Morsy AMA, Hussein AEM (2012) Retention of Uranium from Liquid Waste Soiution onto. Arab Conf
532 Peac use At Energy
533 Nawar N, Ahmad ME, Said WM El, et al (2015) Adsorptive Removal of Phosphorous from Wastewater
534 Using Drinking Water TreatmentAlum Sludge (DWTAS) as Low Cost Adsorbent Citation. Am J
535 Chem Appl 2:7985
536 Nedelciu CE, Ragnarsdóttir KV, Stjernquist I, Schellens MK (2020) Opening access to the black box:
537 The need for reporting on the global phosphorus supply chain. Ambio 49:881–891.
538 https://doi.org/10.1007/s13280-019-01240-8
539 Norwegian Scientific Committee for Food Safety (2009) Opinion of the Panel on Food Additives,
540 Flavourings, Processing Aids, Materials in Contact with Food and Cosmetics of the Norwegian
541 Scientific Committee for Food Safety

542 Ragheb S (2018) Removal of Heavy Metals from Wastewater Using Sewage Sludge Ash (SSA) as
543 Adsorbent. SSRN Electron J. https://doi.org/10.2139/ssrn.3164094
544 Rashed MN (2018) Heavy Metals Removal from Wastewater by Adsorption on Modified Physically
545 Activated Sewage Sludge. Arch Org Inorg Chem Sci 1:.
546 https://doi.org/10.32474/aoics.2018.01.000102
547 Ryssel ST, Arvin E, Lützhøft HCH, et al (2015) Degradation of specific aromatic compounds migrating
548 from PEX pipes into drinking water. Water Res 81:269–278.
549 https://doi.org/10.1016/j.watres.2015.05.054
550 Setia R, Rengasamy P, Marschner P (2014) Effect of mono- and divalent cations on sorption of water-
551 extractable organic carbon and microbial activity. Biol Fertil Soils 50:727–734.
552 https://doi.org/10.1007/s00374-013-0888-1
553 Shahat AA, Ibrahim AY, Hendawy SF, et al (2011) Chemical composition, antimicrobial and antioxidant
554 activities of essential oils from organically cultivated fennel cultivars. Molecules 16:1366–1377.
555 https://doi.org/10.3390/molecules16021366
556 Singh DK, Mondal S, Chakravartty JK (2016) Recovery of Uranium from Phosphoric Acid: A Review.
557 Solvent Extr Ion Exch 34:201–225. https://doi.org/10.1080/07366299.2016.1169142
558 Stewart WM, Roberts TL (2012) Food security and the role of fertilizer in supporting it. In: Procedia
559 Engineering. pp 76–82
560 Taha MH, Abdel Maksoud SA, Ali MM, et al (2019) Conversion of biomass residual to acid-modified
561 bio-chars for efficient adsorption of organic pollutants from industrial phosphoric acid: an
562 experimental, kinetic and thermodynamic study. Int J Environ Anal Chem 99:1211–1234.
563 https://doi.org/10.1080/03067319.2019.1618459
564 Taha MH, El-Maadawy MM, Hussein AEM, Youssef WM (2018) Uranium sorption from commercial
565 phosphoric acid using kaolinite and metakaolinite. J Radioanal Nucl Chem 317:685–699.

https://doi.org/10.1007/s10967-018-5951-9

US National Library of Medicine (2020) Butylated hydroxytoluene | C15H24O - PubChem

Wheeler DL, Chappey C, Lash AE, et al (2000) Database resources of the National Center for Biotechnology Information. Nucleic Acids Res. 28:10–14

Wołowiec M, Bajda T (2017) Current stage of knowledge relating to the use ferruginous sludge from water treatment plants-a preliminary review of the literature. MINERALOGIA 48:39–45. https://doi.org/10.1515/mipo-2017-0010

Wołowiec M, Komorowska-Kaufman M, Pruss A, et al (2019) Removal of heavy metals and metalloids from water using drinking water treatment residuals as adsorbents: A review. Minerals 9

Wu FC, Tseng RL, Juang RS (2009) Initial behavior of intraparticle diffusion model used in the description of adsorption kinetics. Chem Eng J 153:1–8. https://doi.org/10.1016/j.cej.2009.04.042

Yu L, Zhong Q (2006) Preparation of adsorbents made from sewage sludges for adsorption of organic materials from wastewater. J Hazard Mater 137:359–366. https://doi.org/10.1016/j.jhazmat.2006.02.007

Zhang M, Zhang H (2010) Co-transport of dissolved organic matter and heavy metals in soils induced by excessive phosphorus applications. J Environ Sci 22:598–606. https://doi.org/10.1016/S1001-0742(09)60151-0

Zhang R, Chen C, Li J, Wang X (2015) Preparation of montmorillonite@carbon composite and its application for U(VI) removal from aqueous solution. Appl Surf Sci 349:129–137. https://doi.org/10.1016/j.apsusc.2015.04.222

Zou Y, Wang X, Wu F, et al (2017) Controllable Synthesis of Ca-Mg-Al Layered Double Hydroxides and Calcined Layered Double Oxides for the Efficient Removal of U(VI) from Wastewater Solutions. ACS Sustain Chem Eng 5:1173–1185. https://doi.org/10.1021/acssuschemeng.6b02550

(2020) National Center for Biotechnology Information, PubChem Compound Summary for CID 3026,

590 Dibutyl phthalate. In: Natl. Cent. Biotechnol. Inf.
591 https://pubchem.ncbi.nlm.nih.gov/compound/Potassium-ion.
592

Figures

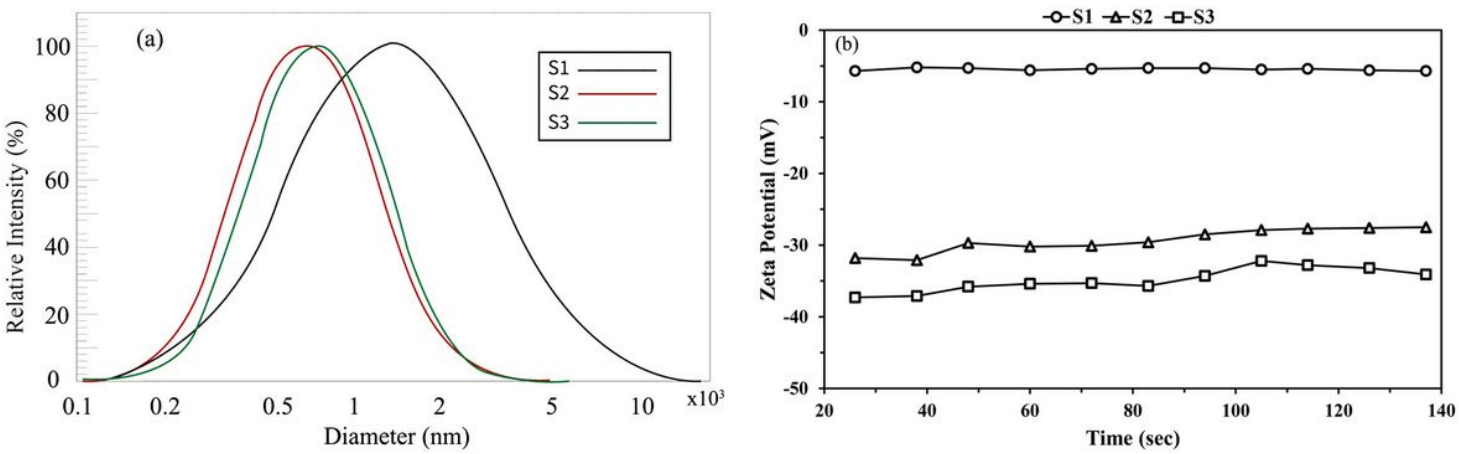

Figure 1

a: Particle size distribution of WTS samples. b: Zeta potential of different WTS samples.

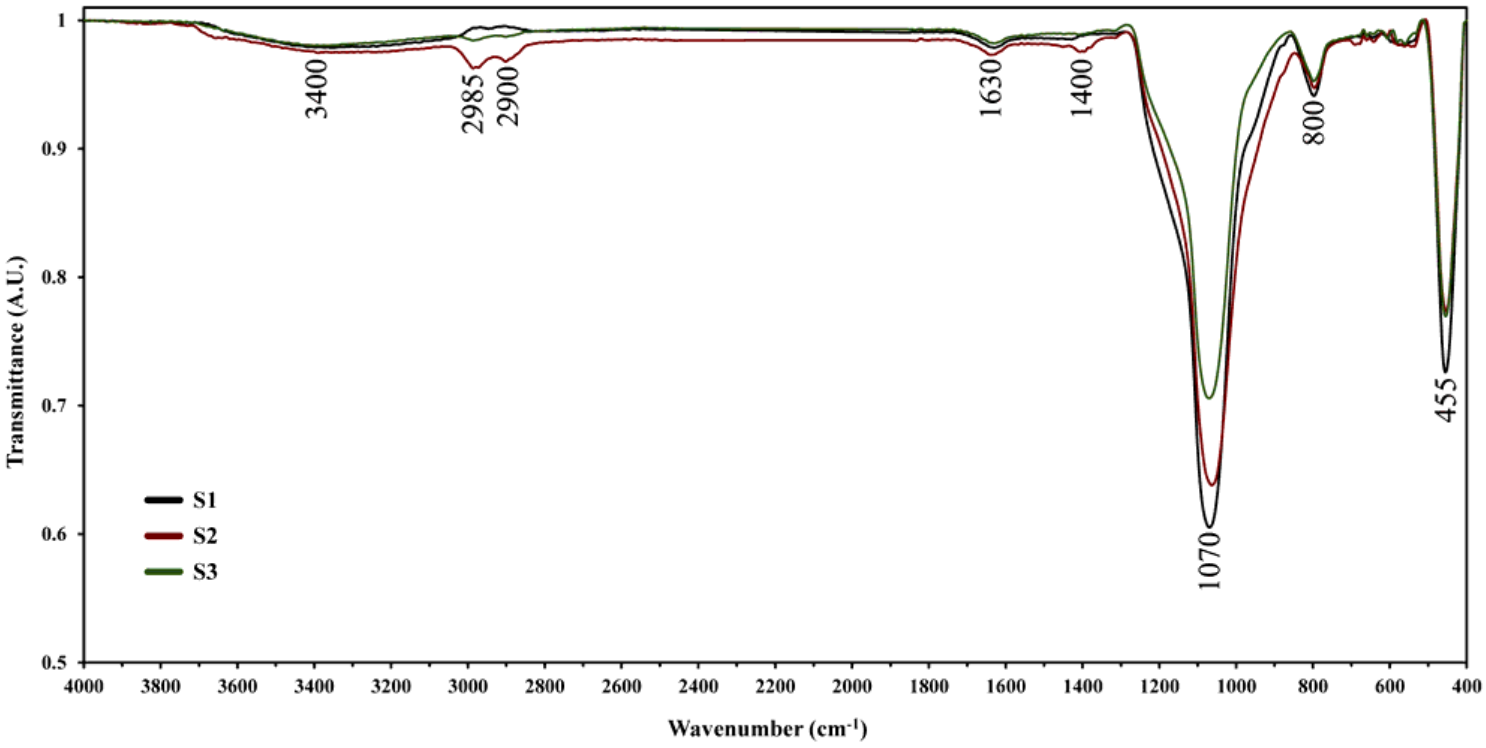

Figure 2

FTIR spectra of WTS samples.

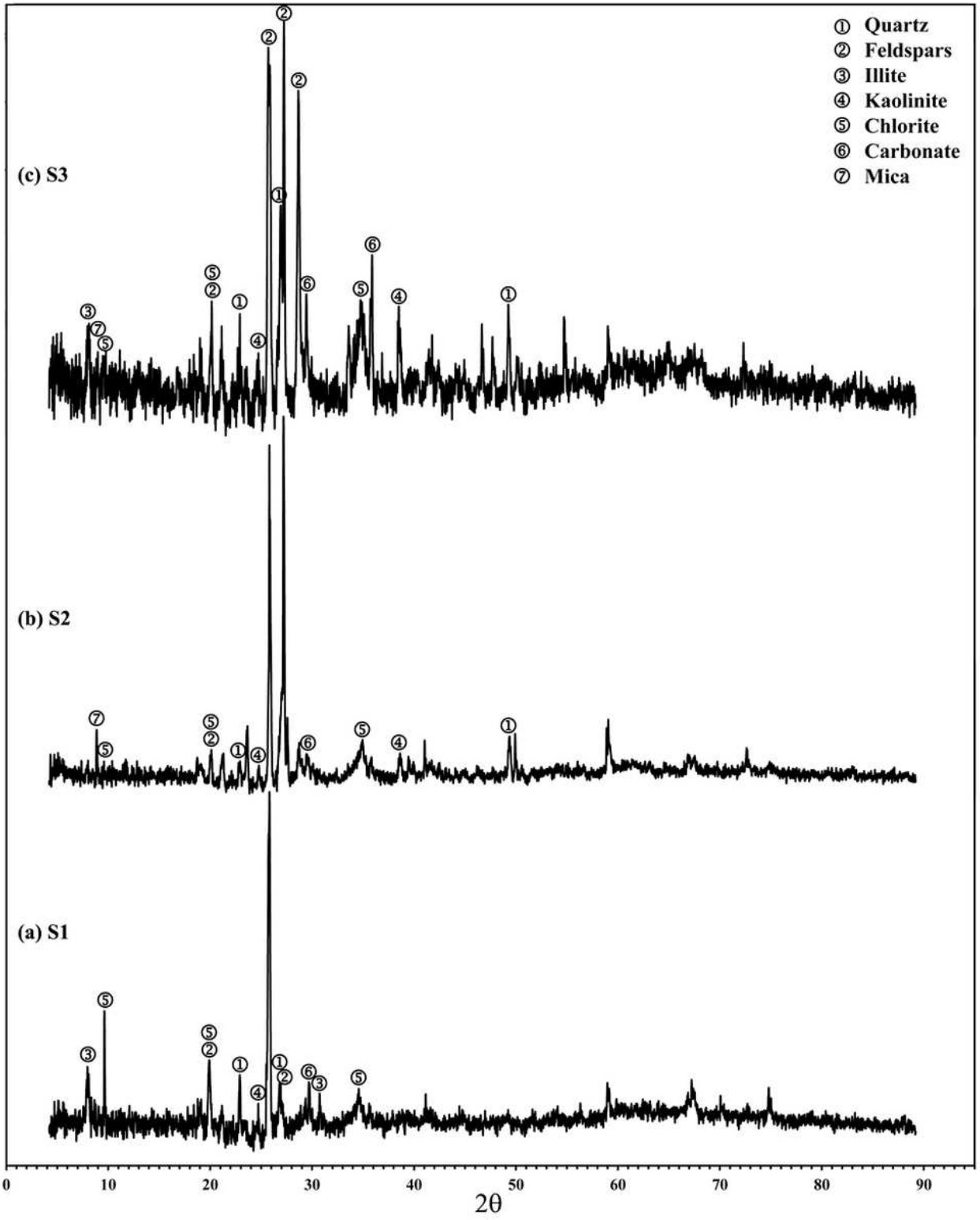

Figure 3

X-ray diffraction patterns of WTS samples.

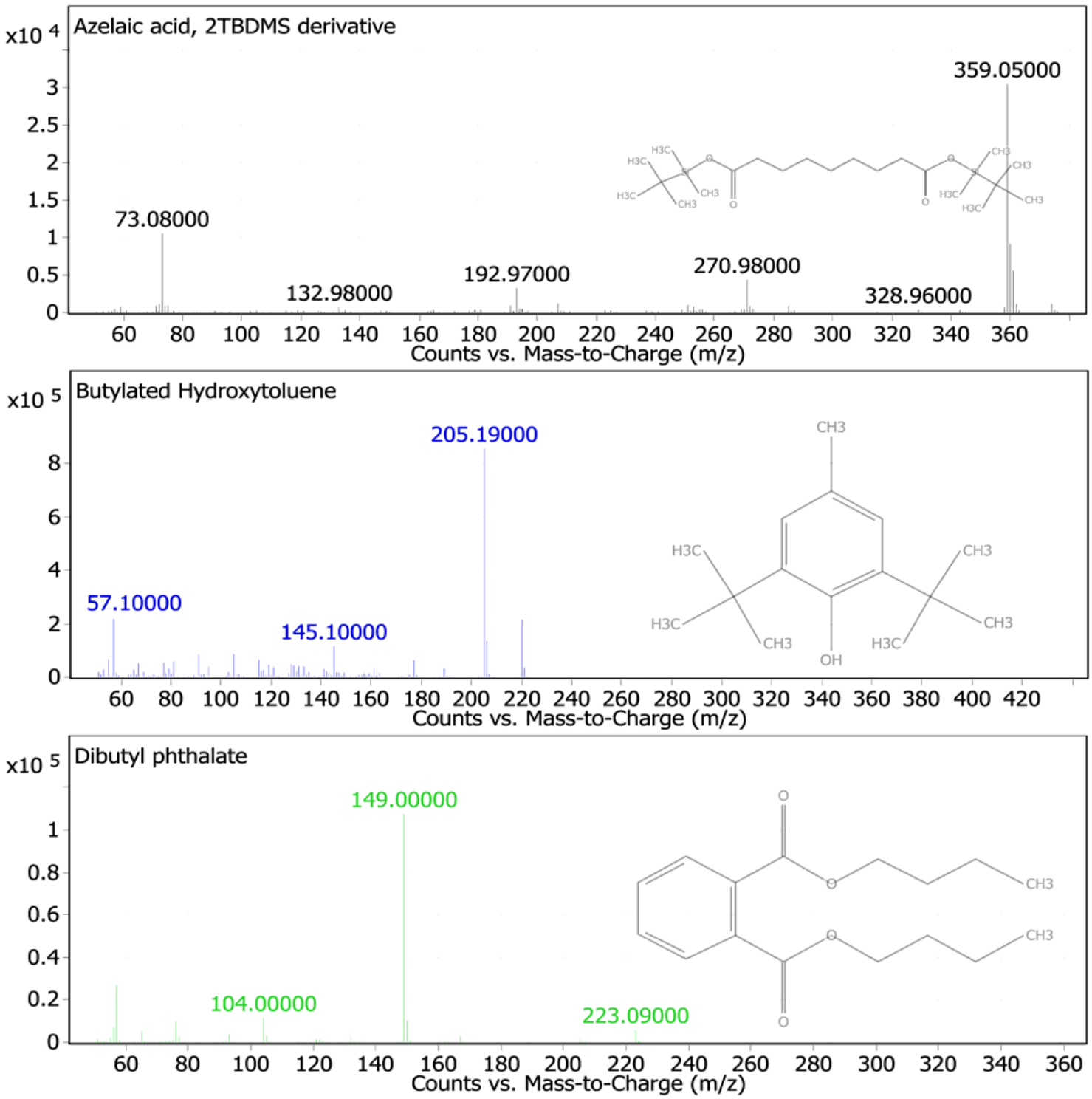

Figure 4

The main organic components in the crude phosphoric acid

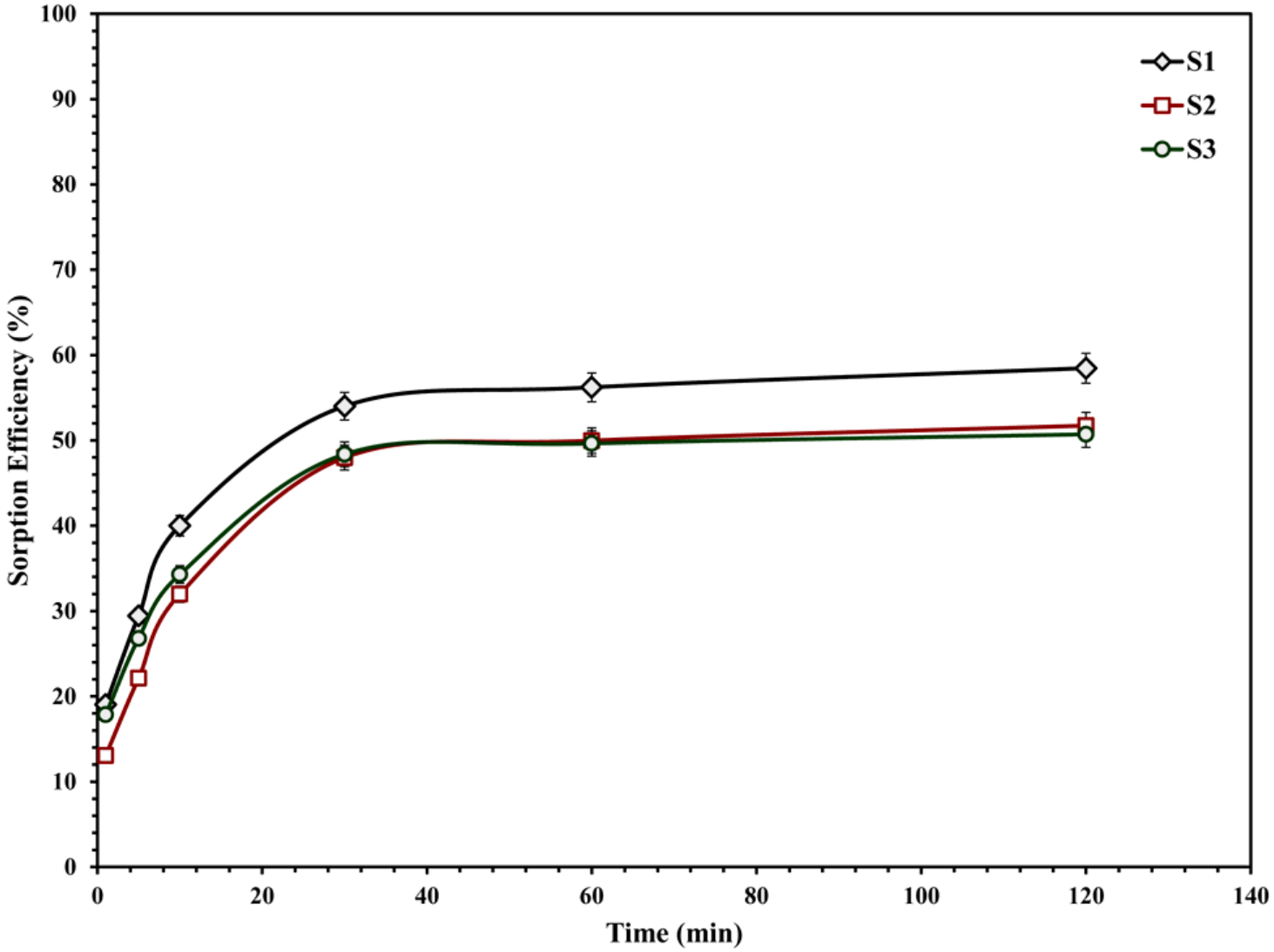

Figure 5

Organic matter sorption efficiency as a function of shaking time.

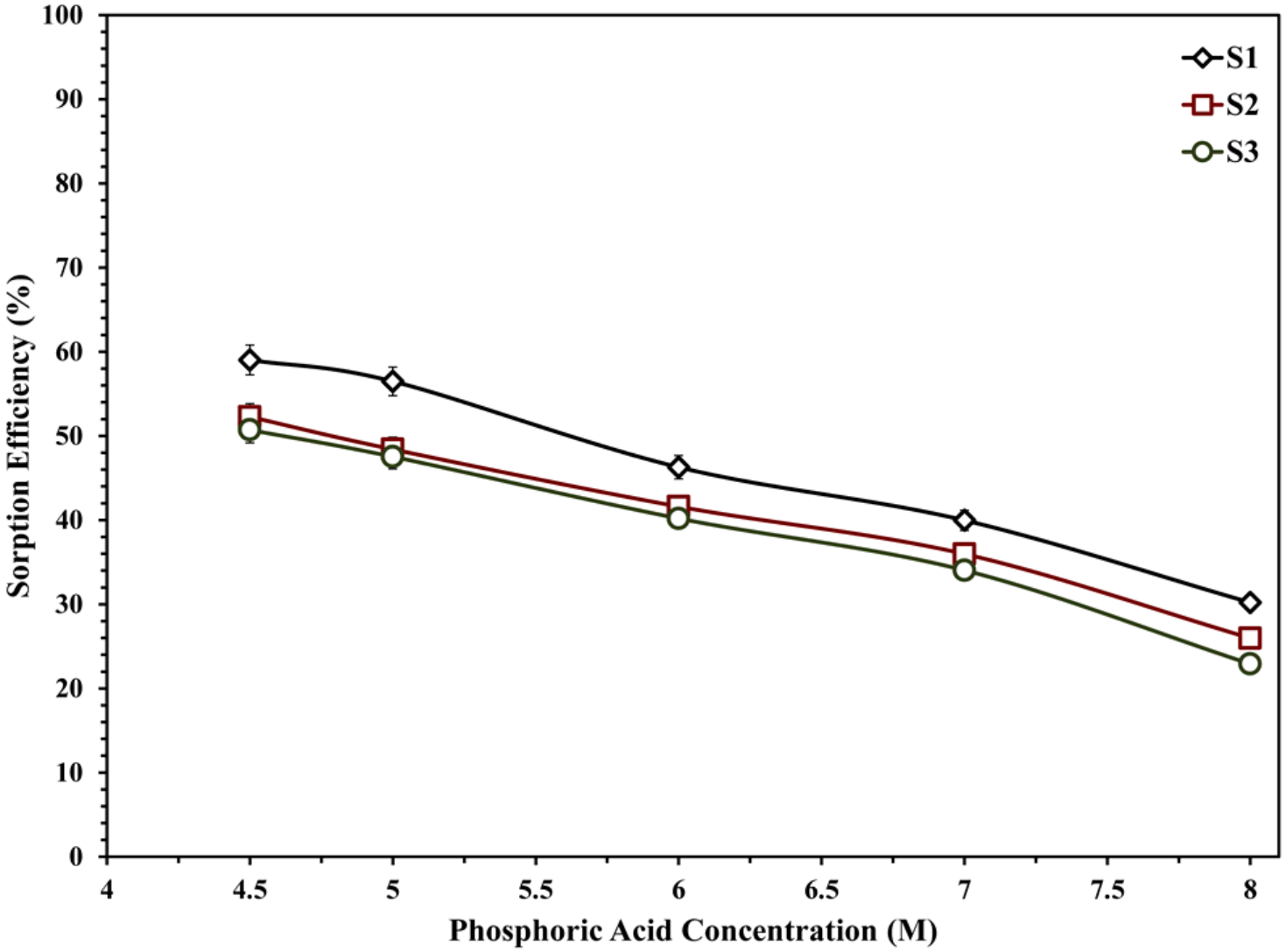

Figure 6

Organic matter sorption efficiency as a function of phosphoric acid concentration.

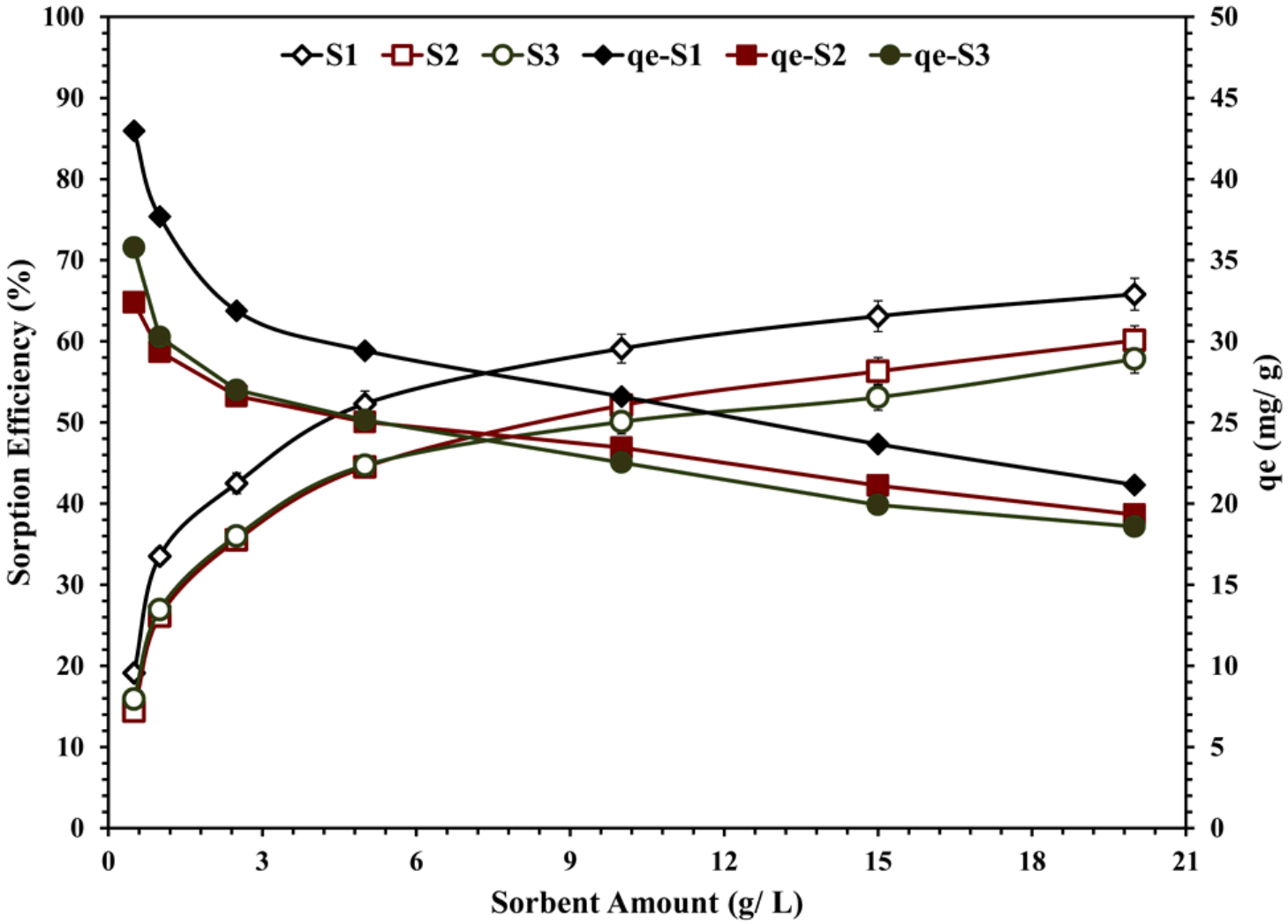

Figure 7

Organic matter sorption efficiency as a function of sorbent amount of addition.

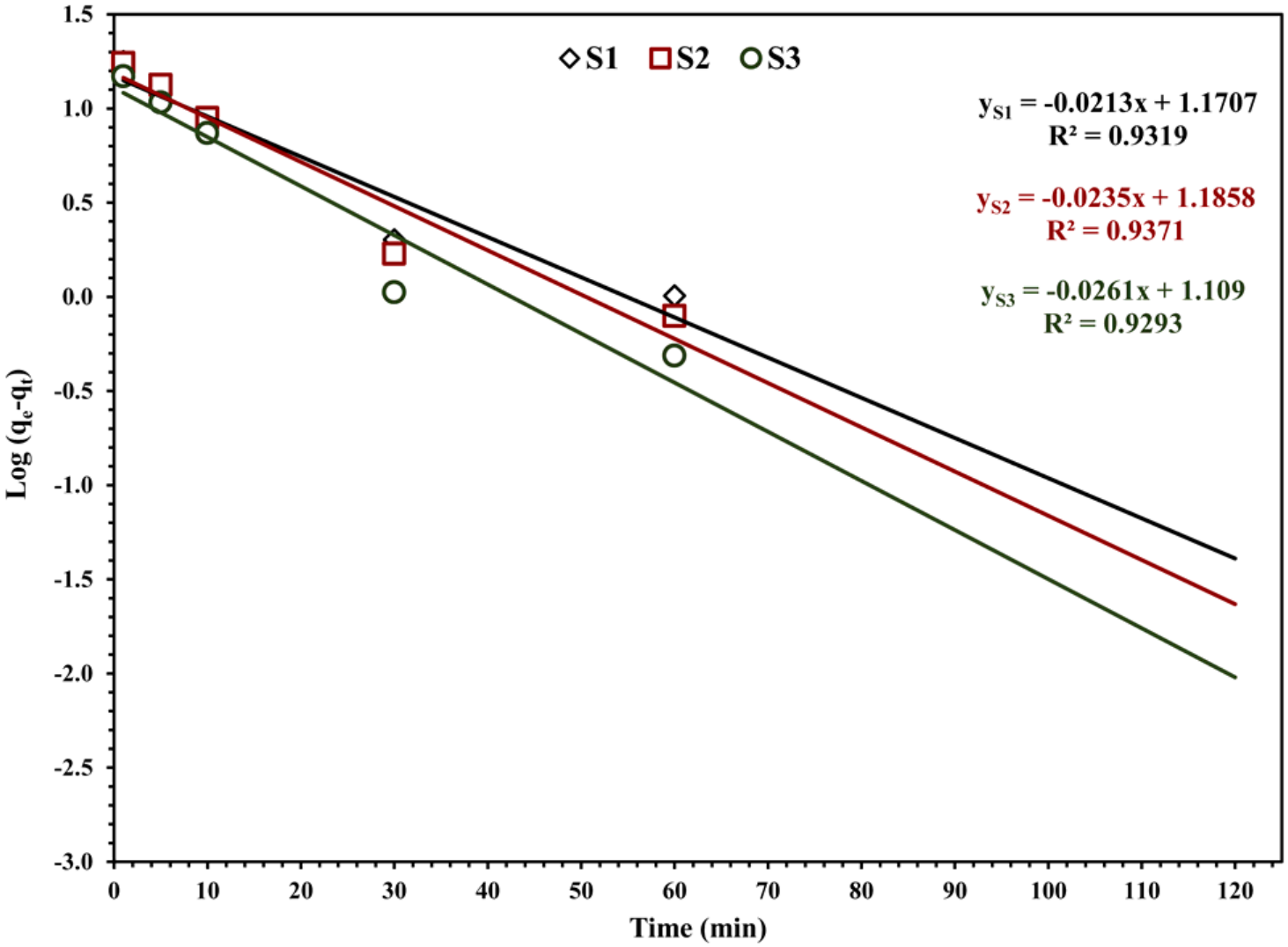

Figure 8

Lagergreen plot for organic matter sorption using WTS.

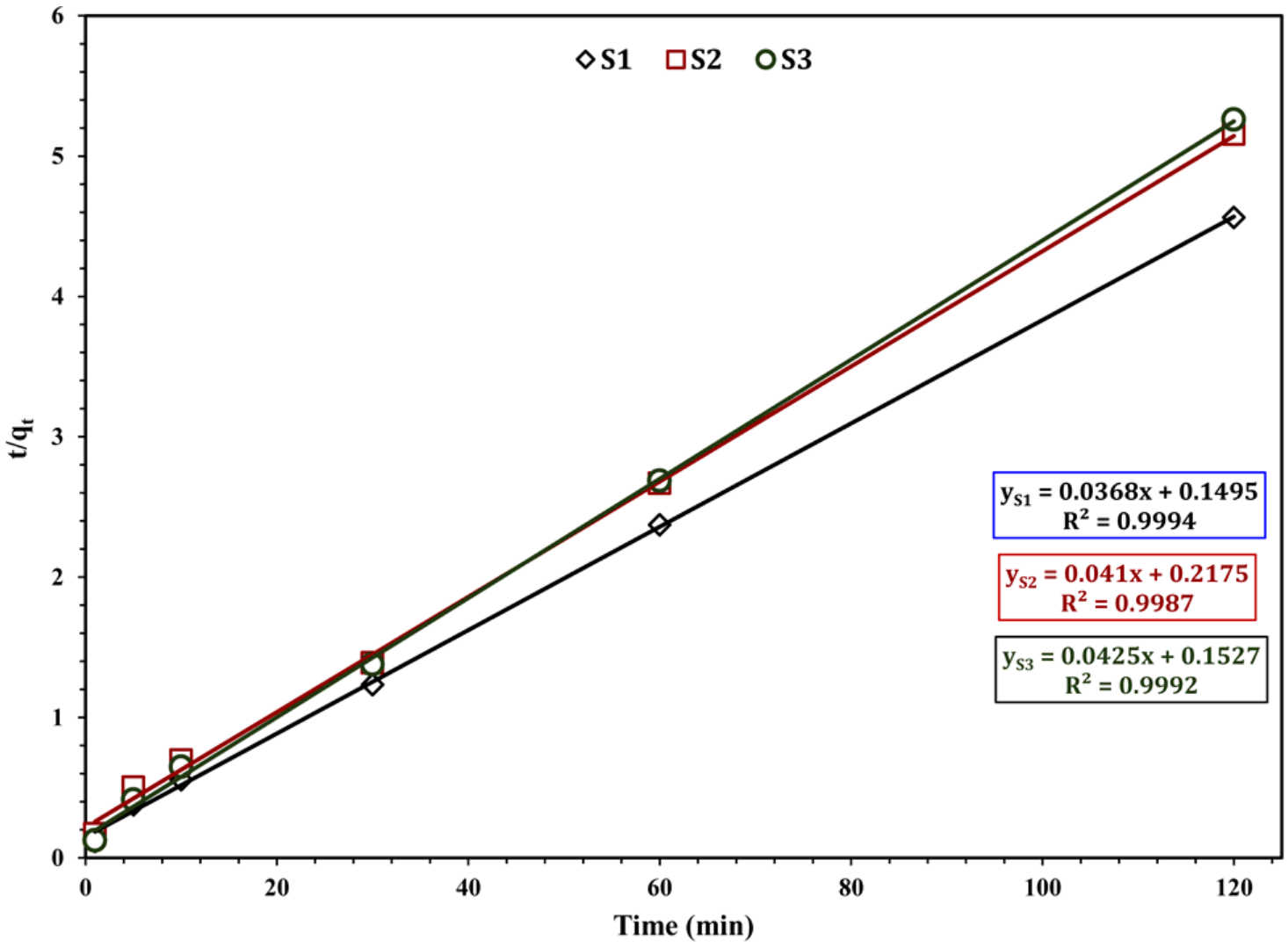

Figure 9

Pseudo second-order plot for organic matter sorption using WTS.

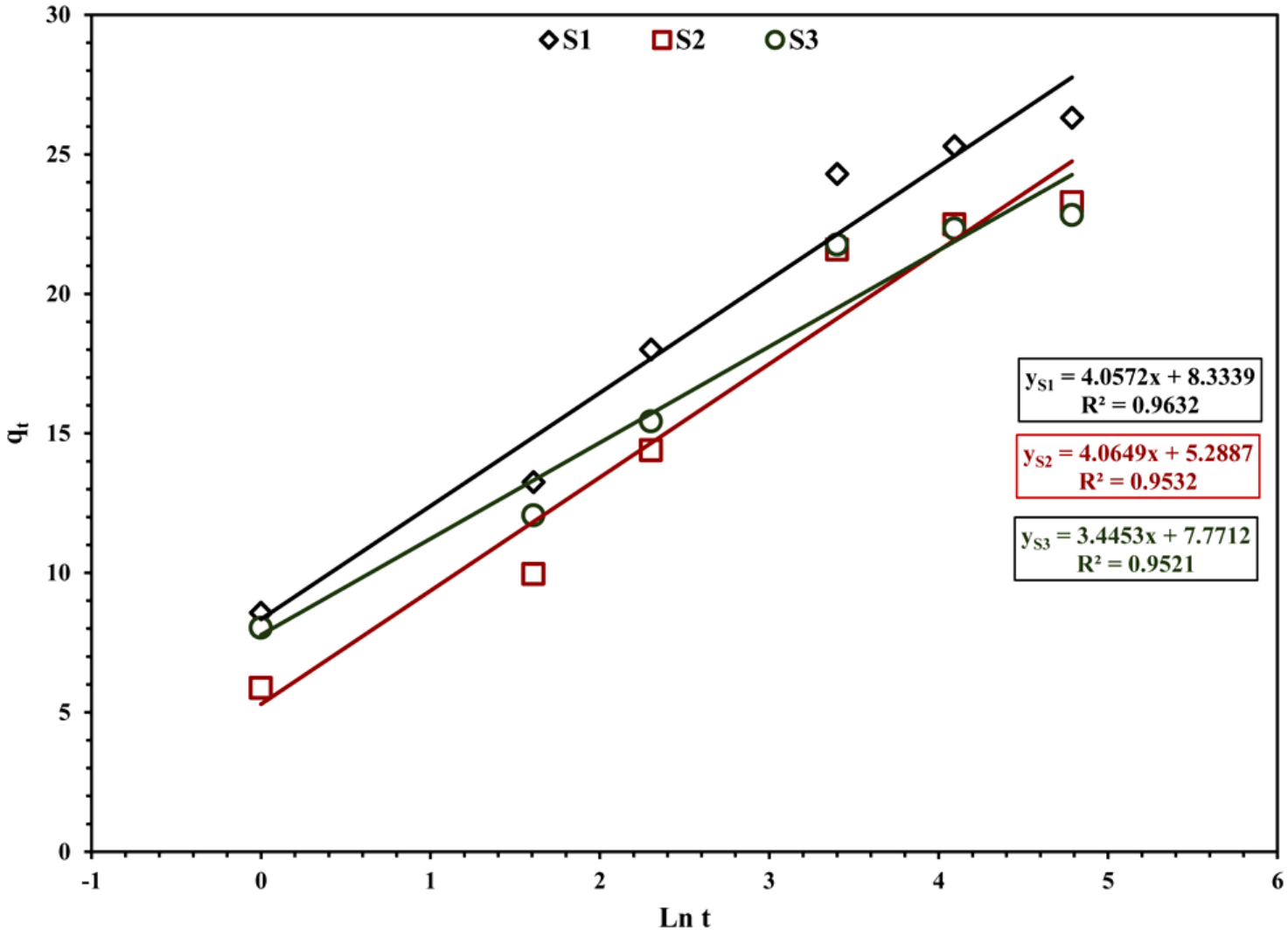

Figure 10

Elovich model plot for organic matter sorption using WTS.

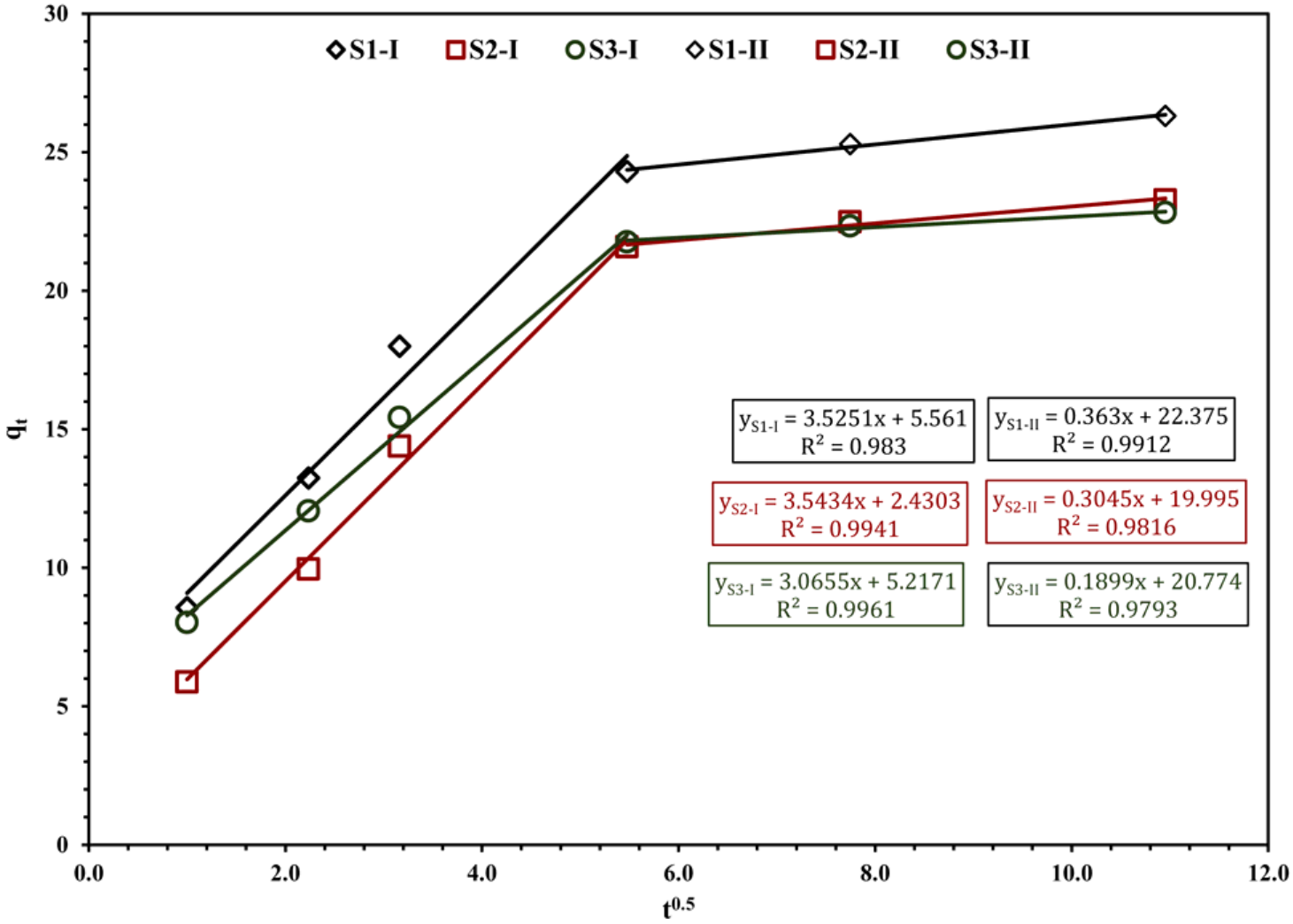

Figure 11

Weber and Morris illustration for organic matter sorption using WTS.

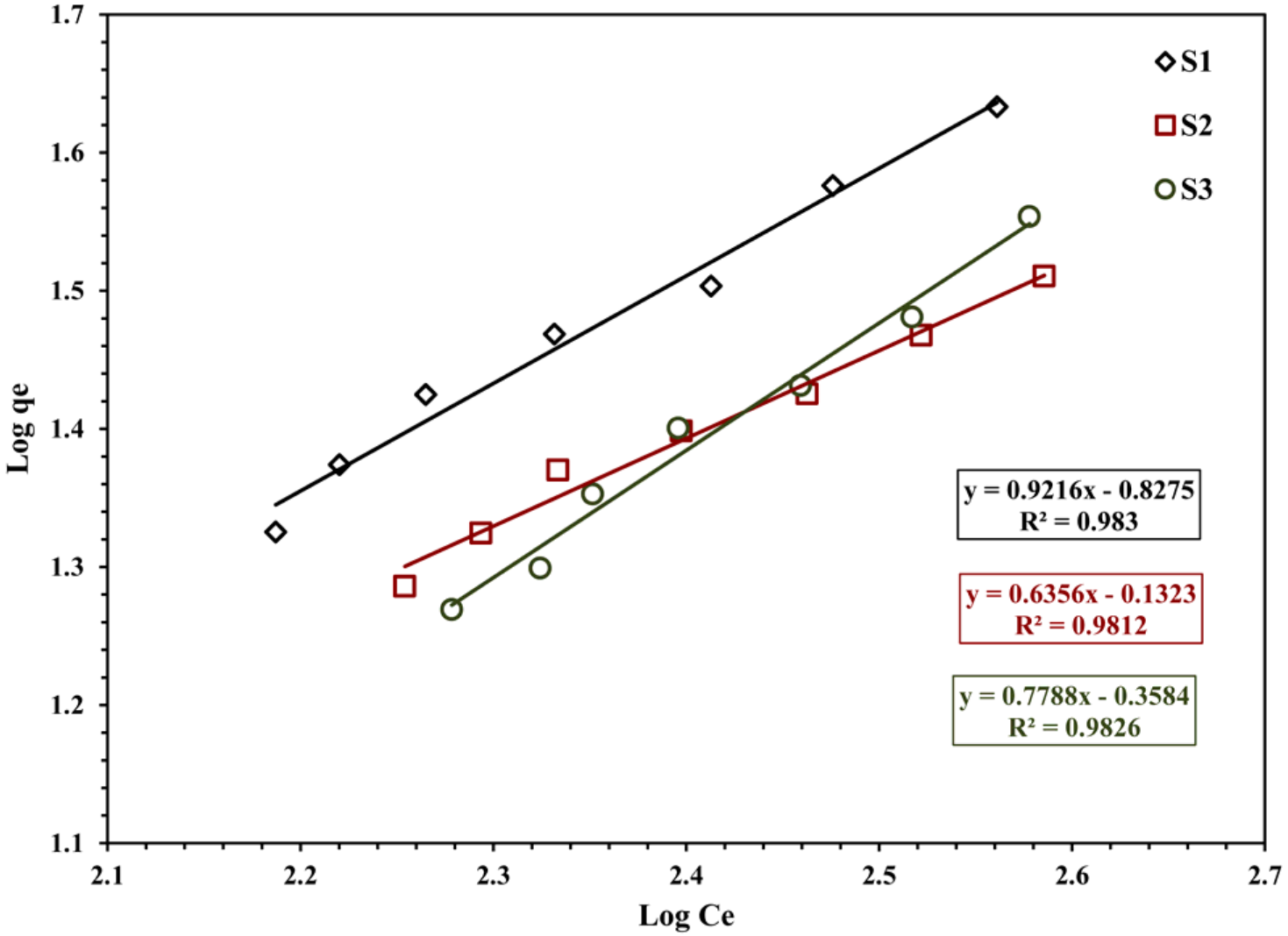

Figure 12

Freundlich model plot for organic matter sorption using different WTS samples.

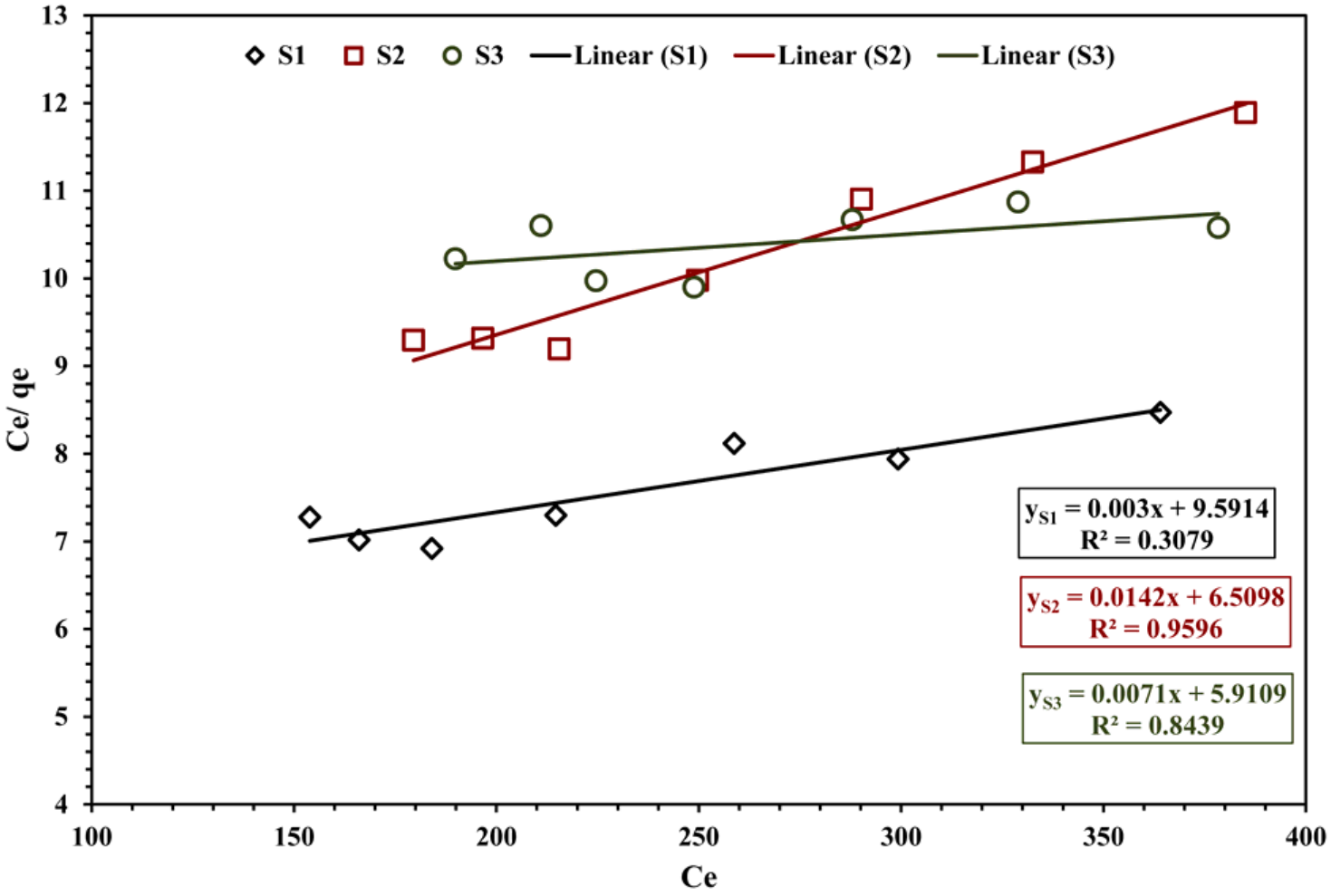

Figure 13

Langmuir model plot for organic matter sorption using different WTS samples.