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Purification of wet process phosphoric acid by decreasing iron and uranium using white silica sand

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ABSTRACT

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1. Introduction

The necessity of very pure phosphoric acid has increased in recent years. It is used as raw materials for the production of detergents, food products, and alimentary supplies for cattle, toothpaste and fertilizers [1–3]. Phosphoric acid is manufactured using different processes, the most commonly used are: thermal and wetprocess [4]. In thermal process, phosphoric acid is firstly produced by reduction of phosphate rock, followed by oxidation and hydration. The wet-process involves reaction of phosphate rock with an acid (mainly sulfuric acid) to produce crude phosphoric acid, which contains a variety of impurities that vary according to the original of minerals. Wet process phosphoric acid contains a number of organic and inorganic impurities that affect on the grade of the acid. Some of these inorganic impurities are Fe(III) and U(VI). The presence of these impurities effects the quantity and the quality of the product. For this reason, about 95% of the acid produced by the wet-process is directly used as fertilizers and excluded from the use in non-fertilizer applications [5]. Purification of phosphoric acid is the goal in the production of some industrial and food grade phosphate derivatives. Miscellaneous applications for food, beverage, toothpaste and cleaning markets require high purity [6].

Many research techniques have been investigated for purifying phosphoric acid, the techniques proposed were; liquid–liquid

Natural white silica sand as an adsorbent has been developed to reduce the concentration of iron and uranium ions as inorganic impurities in crude Egyptian phosphoric acid. Several parameters such as adsorbate concentration, adsorbent dose, volume to weight ratio and temperature, were investigated. Equilibrium isotherm studies were used to evaluate the maximum sorption capacity of adsorbent. Thermodynamic parameters showed the exothermic nature of the process and the negative entropy reflects the affinity of the adsorbent material towards each metal ion.

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extraction, solid–liquid extraction, crystallization, concentration of additives adsorption on activated carbon, and membrane technologies such as electrodialysis (ED), reverse osmosis and nanofiltration. The uses of these techniques were limited due to a number of disadvantages such as: limited efficacy, high costs of organic solvents, difficulty in recovering all the solvent from both the raffinate and the purified acid and environmental pollution by some by-products [7–12].

Sand can be formed in nature by natural weathering of sandstone and quartzite or mechanically by crushing a sandstone/quartzite. Otherwise, by a process of flotation whereby the various constituents in a pegmatite or kaolin mixture are separated. The occurrence of silica sand is widespread and extensive. Silica is an adsorbent widely used in the purification and separation due to its adsorption properties, high surface area and porosity [13]. A surface functional group in silicates plays a significant role in adsorption process. It is a plan of oxygen atoms bound to silica tetrahedral layer and hydroxyl groups that are associated with the edge of the silicate structure units. These functional groups provide surface sites for the chemisorptions of transition and heavy metals. The surface hydroxyl groups dissociate in water and serve as Lewis bases towards metal cations Mⁿ⁺. The metal surface bonding (adsorption) reaction is favored by the metals properties that its hydrolysis. Such properties include high charge, small radius and polarizability [14].

Relatively little research has been carried out using natural white silica sand to reduce the concentrations of Fe(III) and U(VI) in crude Egyptian phosphoric acid. The present study concerns the elimination of the Fe(III) and U(VI) ions present in phosphoric acid

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Table 1

Chemical analysis of wet phosphoric acid before and after treatment with natural white silica sand (60 g/L).

lons constituent	Conc. (ppm) Before treatment	Conc. (ppm) After treatment	Removal%
As(III)	11.42	11.00	3.68 ± 0.04
Ba (II)	0.70	0.60	14.28 ± 0.03
Cd(III)	8.40	3.00	64.28 ± 0.04
Cr(III)	15.40	9.00	41.55 ± 0.05
Cu(II)	17.02	12.00	29.50 ± 0.03
Fe(III)	$25 imes 10^3$	4×10^3	84.00 ± 2.05
Ni(II)	36.29	22.00	39.37 ± 0.06
Pb(II)	31.10	15.10	51.44 ± 0.08
Zn(II)	41.00	25.00	39.02 ± 1.20
U(VI)	20.00	16.00	20.00 ± 0.05
Organic matter	0.51		

The error margin for all the driven entities were between 0.03-2%.

obtained from Abu-Tartur Cairo, Egypt by adsorption onto natural white silica sand as an adsorbent.

2. Materials and methods

2.1. Phosphoric acid

All experimental runs were done using crude phosphoric acid of 5 M ($P_2O_5 = 52\%$, pH 0.6) as obtained from Abu-Tarture, Cairo, Egypt. Any trials to modify pH will be unsuccessful (just as buffering action) and this study deals with the purification of acid during its manufacture (i.e. under these pH conditions). The crude acid was firstly purified from suspended matter by sand filter column (with internal diameter of 2.5 cm; length 10 cm, filled with sand of particle size 64 mesh) to obtain green acid. In the initial experimental runs, and to ensure that all Fe²⁺ ions are oxidized to Fe³⁺ ions, an oxidizing agent (H₂O₂, 30%) was added in various volumes. It was obvious that 20 mL is sufficient for oxidation of all Fe²⁺ ions in 1 L green acid and thus iron is treated as Fe³⁺ ions during this study. The obtained chemical analyses of starting material for this work (wet process phosphoric acid) were shown in Table 1.

2.2. Natural white silica sand

Natural white silica sand was supplied from Sinai desert, Egypt. It was ground and then screened into particle size of 200 μ m using standard Tyler screen series. Specific surface area was 145 m² g⁻¹. In order to remove impurities, chemical treatment was performed. Natural white silica sand was washed with 0.1 M HCl, After 24 h; the solid phases were separated from solution then washed twice with distilled water and air-dried. Afterwards, the materials were stored under vacuum for several days at room temperature.

The composition of sand is highly variable, depending on the local rock sources and conditions. Natural white silica sand was subjected to chemical analysis before starting the experiments. Chemical analysis showed that the presence of large amount of silica as shown in Table 2.

Natural white silica sand was observed using scanning electron microscope (SEM) for morphological studies. Scan electron microscope studies reveal that the quartz grains are angular to sub rounded marked by peeling of surface as a result on intense

Table 2	
Chemical analysis of natural white silica.	

Element	Concentration (%)	Element	Concentration (%)
SiO ₂ Al ₂ O ₃ H ₂ O	99.51 0.12 0.05	Na ₂ O TiO ₂	0.16 0.06

chemical weathering, angular grain with smoothed edges and sides, weathered, and blockage with smoothed surface.

3. Reagents

All chemicals were of analytical reagent grade. Doubly distilled water was used in all preparations.

3.1. Apparatus

The concentration of the elemental composition of the phosphoric acid was detected by atomic-absorption spectrophotometer using an air – acetylene flame and inductively coupled plasma mass spectrometry (ICP-Ms) Plasma Optical Emission-Mass Spectrometer (POEMS III); Thermo Jarrell - Ash, USA). Multi-element certified standard solution; Merck, Germany was used as stock solution for instrument calibration. The intensity of the emission peak was used to develop the each element calibration curves. The mixtures were mixed by a thermostat mechanical shaker (Isothermal Gefellschaft Fur 978).

3.2. Adsorption studies

Batch mode adsorption studies for individual metal compounds such as Fe(III) and U(VI) were carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dose and volume to weight ratio at 25 °C. In these experiments, new stopper glass bottles were used for each analysis. Bottles were treated with different chemical acid (chromic acid) or commercially available detergents followed by washing with doubly distilled water before being used in the batch adsorption. In all cases known volume of the crude phosphoric acid (5 mL) was contacted with known weights of the adsorbate in a stopper glass bottles. The conditions of each experiment were adjusted and the bottles were shaken at 150 rpm in a mechanical shaker. The experimental set-up was equilibrated 24 h. At the end of time, the mixture was filtered and the supernatant was analyzed for metal concentration using POEMS III. The amounts of the metal ions adsorbed were obtained by difference. The concentration of metal before and after adsorption was obtained using the calibration curves. Interferences caused by presence of acid in the samples can be minimized by the optimization of plasma operating condition. To avoid the adsorption of adsorbate on the container walls, the containers were pretreated with the respective adsorbate for 24 h.

3.3. Data analysis

The percentage of removal was calculated using the equations:

$$Remoal\% = 100 \frac{(C_o - C_e)}{C_o} \tag{1}$$

where, C_o and C_e are the concentrations of each metal ion in initial and final solutions respectively.

The distribution coefficients K_d were calculated using the equations:

$$K_d = \frac{\text{amount of metal ion on adsorbent}}{\text{amount of metal ion in solution}} \quad \frac{V}{m} \text{ mL/g}$$
(2)

where V is the volume of the solution (mL) and m is the weight of adsorbent (g).



Fig. 1. Effect of natural white silica sand doses on the removal % of Fe(III) and U(VI) ions from wet phosphoric acid at $25 \degree C$, [Fe(III)] = 25×10^3 and [U(VI)] = 20 ppm.

4. Results and discussion

4.1. Effect of adsorbent doses

Different weights of natural white silica sand were used at 25 °C. The natural white silica sand doses used covers the range from 20 to 200 g/L while the other parameters were kept constant. Wetprocess phosphoric acid with concentration 25×10^3 and 20 ppm of Fe(III) and U(VI) respectively were used to optimize the required amount of adsorbent under prescribed conditions for maximum uptake. Fig. 1 shows the adsorption Fe(III) increases by increasing adsorbent doses due to greater availability of the surface area at higher concentration of the adsorbent. The significant increase in uptake was observed when the dose was increased from 20-60 g/L. Any further addition of the adsorbent beyond this did not cause any significant change in the adsorption may be due to the formation of clusters of adsorbent particles resulting in decreased surface area. This result is found matching with studies using natural zeolite and guartz [15,16]. The maximum removal % of Fe(III) was found to be, 84% with adsorbent doses 60 g/L. Fig. 1 revealed that the U(VI) removal % increases by increasing natural white silica sand concentration. This is expected because increasing sorbent particles in the solution causes more uranyl ions interact to these particles. The maximum removal % of U(VI) was found to be, 75% with adsorbent doses 200 g/L. The preference of an adsorbent for a metal may be explained on the basis of electronegativity of the metal ions and ionic radius. Better adsorption was obtained for iron can be justified with the higher electronegativity and smaller ionic radius [17].

The sorption of metal ions can take place by the cation exchange reaction through the substitution of protons from silanol groups on the surface by the metal ions from the solution, as follows

 $m(SiOH) \leftrightarrow m(SiO^{-}) + mH^{+}$

 $M^{n+} + m(SiO^{-}) \leftrightarrow M(OSi)_m^{(n-m)+}$

The overall reaction can thus be represented as:

$$M^{n+} + m(SiOH) \leftrightarrow M(OSi)_m^{(n-m)+} + mH^+$$

where M^{n+} = metal ion with n^+ charge, SiOH = silanol group on SiO₂ surface, mH⁺ = number of protons released. Although the ionexchange reaction is able to explain the sorption process, metal sorption on the white silica sand may also take place through complex formation on the cell surface after interaction between the metal and active groups present on white silica sand surface [18].



Fig. 2. Effect of initial Fe(III) and U(VI) concentrations on the distribution coefficient, K_d and removal % at 25 °C.

5. Effect of initial metal ions concentration

Experiments were conducted to study the effect of varying initial metal ions concentration on the removal of Fe(III) and U(VI) from wet phosphoric acid by natural white silica sand as an adsorbent while the other parameters were kept constant. The experiments were done using 60 g/L adsorbent with different metal ion concentrations ranging from $3-25 \times 10^3$ and 5-20 ppm for Fe(III) and U(VI) respectively at 25 °C. Fig. 2 illustrates that at the same adsorbent doses, there is a decrease in removal % and distribution coefficient with higher initial concentrations. Due to lower initial metal concentrations, sufficient adsorption sites were available for the sorption of metals ions. However, at higher concentrations the numbers of metal ions were relatively higher as compared to availability of adsorption sites. Hence, removal of metal ions decreases with increase concentrations. The difference in removal of different metal ions at the same initial metal ions concentration and adsorbent doses may be attributed to the difference in their chemical affinities and ion exchange capacity with respect to the chemical functional groups on the surface of the adsorbent. In other words, the distribution coefficient, K_d values increase as dilution of metal ions in solution proceeds. These results indicate that energetically less favorable sites became involved with increasing metal ions concentration and attributable to competition which cause blocking to available adsorption sites on adsorbent [19].

6. Adsorption isotherms

6.1. Langmuir isotherm

Adsorption data for wide ranges of adsorbate concentrations are most conveniently described by adsorption isotherms. The Langmuir isotherm model [20] is based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface that the energy of adsorption is constant and that there is no transmigration of adsorbate in the plane of the surface. Langmuir isotherms were obtained by shaking the adsorbent of fixed doses and the adosrbate solu-



Fig. 3. Equilibrium adsorption isotherm for U(VI) removal from wet phosphoric acid by natural white silica sand at 25 $^\circ\text{C}.$

tion of different concentrations. The samples were equilibrated for 24 h, in order to reach equilibrium. The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The following equation can be used to model the adsorption isotherm:

$$\frac{1}{q_e} = \left(\frac{1}{q^\circ}\right) + \left(\frac{1}{bq^\circ}\right) \left(\frac{1}{C_e}\right) \tag{3}$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium time (mg/g), q° is the maximum metal ions uptake per unit mass of adsorbent (mg/g), which is related to adsorption capacity and *b* is Langmuir constant (L/mol) which is exponentially proportional to the heat of adsorption and related to the adsorption intensity. Thus, a plot of $1/q_e$ vs. $1/C_e$ should be linear if Langmuir adsorption were operative, permitting calculation of Langmuir constants

Fig. 3 shows the equilibrium adsorption isotherm of Fe(III) and U(VI) in wet phosphoric acid using natural white silica sand as an adsorbent. The isotherm rises sharply in the initial stages for low C_e and q_e values. This indicates that there are plenty of radial accessible sites. Eventually a plateau is reached, indicating that the adsorbent is saturated at this level. The decreases in the curvature of the isotherm are tending to a monolayer adsorption. Considerably increasing the C_e values for a small increase in q_e , is possibly due to less active sites being available at the end of the adsorption process and/or the difficulty of the edge molecules in penetrating the adsorbent, Fe(III) and U(VI) ions partially covering the surface sites. In order to optimize the design of a sorption system to remove Fe(III) and U(VI) from commercial wet process phosphoric acid, it is important to establish the most appropriate correlation for the equilibrium curve. The linearzed Langmuir plot according to Eq. (3) is shown in Fig. 4. The Langmuir parameters were calculated and recorded in Table 3.

The favorable nature of adsorption can be expressed in terms of a dimensionless separation factor of equilibrium parameter, which

Table 3

Langmuir and Freundlich constants for Fe(III) and U(VI) ions by natural white silica sand in wet phosphoric acid at 25 $^\circ$ C.

Langmuir constants					
Fe(III)			U(VI)		
$q^0 (mg/g)$	<i>b</i> (L/g)10 ⁴	R^2	$q^0 (mg/g)$	<i>b</i> (L/g)	R^2
344.828	7.639	0.991	0.141	0.216	0.996
Freundlich constants					
Fe(III)			U(VI)		
1/n	Log K _f	R^2	1/n	Log K _f	R^2
0.586	0.395	0.951	0.688	1.607	0.986



Fig. 4. The linearzed Langmuir plot for Fe(III) and U(VI) removal from wet phosphoric acid by natural white silica sand at 25 °C.

is defined by using Eq. (5)

$$R_L = \frac{1}{(1 + bC_0)}$$
(4)

where *b* is the Langmuir constant and C_o is the initial concentration of the adsorbate in solution [21]. R_L was less than one indicating favorable adsorption.

The Langmuir constant values (q^0) can be used to estimate the specific surface area, S, of sorbent [22] using the following equation

$$S = \frac{q^0 N A}{M} \tag{5}$$

where *S* is the specific surface area, m^2/g of adsorbent; q^0 is monolayer sorption capacity, gram metal per gram adsorbent; *N* is Avogadro number, 6.02×10^{23} ; *A* is the cross-sectional area of metal ions, *M* is molecular weight of metal. The cross-sectional areas of Fe(III) and U(VI), have been determined to be 0.949 Å² and 2.487 Å² respectively. The maximum specific surface area of natural white silica sand towards Fe(III) and U(VI) binding are $35.157 \text{ m}^2/g$ and $8.859 \times 10^{-3} \text{ m}^2/g$ respectively. The increased adsorbent surface area tends to increase the adsorbent removal efficiency [23]. The result indicate that natural white silica sand preferentially sorbed Fe(III), followed by U(VI).

7. Freundlich isotherm

The Freundlich model was chosen to estimate the adsorption intensity of the sorbate on the sorbent surface. The Freundlich equation is presented as [24]

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{6}$$

Where K_f (mg/g) and n are Freundlich constants incorporating all factors affecting the adsorption process such as of adsorption capacity and intensity of adsorption. These constants are determined from the intercept and slope of linear plot of log q_e versus log C_e , respectively. The constants are listed in Table 3. Although the correlation coefficients are greater than 95%, they do not corre-



Fig. 5. Effect of temperature on the distribution coefficient and removal% for Fe(III) and U(VI) removal from wet phosphoric acid by natural white silica sand.

late the data as well the Langmuir isotherm, which has consistently higher correlation coefficients.

7.1. Effect of temperature

The effect of temperature on the purification of wet phosphoric acid from Fe(III) and U(VI) using natural white silica sand were studied from 298–343 K. The operating conditions used were, initial Fe(III) and U(VI) concentration in wet phosphoric acid are 25×10^3 and 20 ppm respectively, amount of adsorbent are 60 and 200 g/L for Fe(III) and U(VI) respectively. Fig. 5 illustrated that the distribution coefficient and removal % decreases as the temperature increased, indicating that the process were exothermic in nature. Further, the removal of each metal ion is favored at low temperatures. This result was found matching with studies the removal of U(VI) from aqueous solutions onto activated carbon [25]. The decreasing in adsorption as temperature increases may be due to the relative increase in the escaping tendency of the metal ions from the solid phase to the bulk phase; or due to the weakness of adsorptive forces between the active sites of the adsorbents and the adsorbate species and between the adjacent molecules of adsorbed phase [26].

7.2. Thermodynamics studies

The thermodynamic equilibrium constant *K* for the adsorption was determined by using the equation $K = q_e/C_e$, where q_e is the amount of metal ions adsorbed on the adsorbent of the solution at equilibrium (mol/L) and C_e is the equilibrium concentration of metal ions in the solution (mol/L). The change in standard free energy (G° in kJ mol⁻¹, enthalpy (H° in kJ mol⁻¹ and entropy (S° in kJ mol⁻¹ of adsorption were calculated using the following equations [27–29].

$$\Delta G^o = -RT \ln K \tag{7}$$

where R is the universal gas constant (8.314 J/mol K) and T is temperature (K).

$$\ln K = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$
(8)

Table 4

Thermodynamic parameters for Fe(III) and U(VI) removal from wet phosphoric acid by natural white silica sand.

	<i>T</i> (K)	Fe(III)	U(VI)
	298	11.079	6.709
	308	11.356	6.477
$-\Delta G^{2}$	318	10.847	6.044
(KJ IIIOI)	328	10.937	6.077
	338	10.787	6.018
	343	10.716	5.865
$-\Delta \mathrm{H}^{\circ}$ (kJ mol ⁻¹)	-	14.273	11.850
$-\Delta S (J \operatorname{mol}^{-1} K^{-1})$	_	10.306	17.547

According to Eq. (8), (H° and (S° parameters can be calculated from the slope and intercept of the plot of ln K versus 1/*T*. The values of (G° , (H° and (S° were reported in Table 4. In fact, the negative value of enthalpy change (H° for the processes further confirms the exothermic nature of the process, the negative entropy reflects the affinity of the adsorbent material toward each metal ion, and the negative free energy values indicate the feasibility of the process and its spontaneous nature.

7.3. Effect of interfering ions

The elimination procedures for trace metals can be strongly affected by other constituents of samples. Realistically, in the application of adsorption for the removal of metal ions from phosphoric acid, there will be a mixture of several solutes. The solutes may mutually enhance adsorption, may act independently, or may interfere with one another. The competitive adsorption is influenced by the interaction of each solute with the surface and with the solvent. The porosity and heterogeneity of the adsorbent are also factors in adsorption. If the solutes are adsorbed at different sites on the adsorbent surface, the total adsorption could be higher than for the individual solutes. If they compete for the same sites, there may be a lowering of the total amount adsorbed.

In order to compare effects of various cations on Fe(III) and U(VI) adsorption, batch experiments were conducted for single metal ions in aqueous solution. The operating conditions used were, initial Fe(III) and U(VI) concentration in aqueous solution are 25×10^3 and 20 ppm respectively, amount of adsorbent are 60 and 200 g/L for Fe(III) and U(VI) respectively. As shown in Fig. 6, values of Fe(III) and U(VI) adsorption obtained from the experiment results intended for the Phosphoric acid were less than those for the single component solution. This result indicated that U(VI) and Fe(III) ions competed with other metal ions for the same sites on the natural white silica sand.



Fig. 6. Removal % of Fe(III) and U(VI) from aqueous solution and wet phosphoric acid at 25 $^\circ\text{C}.$

Simultaneous determination of metal ions in phosphoric acid before and after treatment with natural white silica sand (60 g/L) was examined. The results showed that the residual concentration of metal ions decreases as shown in Table 1.

8. Conclusion

According to the results obtained in the study of the removal of Fe(III) and U(VI) from wet phosphoric acid by natural white silica sand, we can conclude that, the natural white silica sand has been used for reducing the concentration of Fe(III) and U(VI) from wet phosphoric acid. The maximum removal of Fe(III) (84%) was observed at initial concentration of 25×10^3 ppm and an amount of adsorbent equal to 60 g/L. The maximum removal of U(VI) (75%) was observed at initial concentration of 20 ppm and an amount of adsorbent equal to 200 g/L. The distribution coefficient decreases as the temperature increased. The experimental results analyzed by the Langmuir and Freundlich adsorption isotherms. The dimensionless separation factor R_L has shown that natural white silica sand can be used for removal of Fe(III) and U(VI) from wet phosphoric acid. The negative values of enthalpy change (H° for the processes confirm the exothermic nature. The negative entropy values were an indication of the probability of favorable nature of adsorption and the process was spontaneous. Therefore, the developed natural white silica sand adsorbent adsorbent considered a better replacement technology for removal of Fe(III) ions due to its low-cost and good efficiency in this application.

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