

## Potentiality of white sand for the purification of wet process phosphoric acid from some metallic elements (U, Zn, Cd)

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### ABSTRACT

The potentiality of applying white sand for the purification of wet process phosphoric acid via adsorption of metallic impurities has batchwise been studied across U(VI), Zn(II) and Cd(II). Besides representing a low cost procedure for acid purification from hazardous metals, possible recovery of the adsorbed uranium would represent an important added value. The relevant adsorption factors are studied together with both the corresponding thermodynamic characteristics and equilibrium isotherms. From the latter, the Langmuir isotherm was found to be better in interpreting the obtained data. Thus, the theoretical capacities estimated for the studied metal cations U(VI), Zn(II) and Cd(II) upon Abu Zeneima white sand have been found to attain 0.87, 2.23 and 0.14 mg/g while the practical capacities at the studied optimum conditions have attained 0.44, 1.59 and 0.11 mg/g respectively. The thermodynamic parameters have shown that the exothermic nature of the study system due to the obtained negative enthalpy ( $\Delta H$ ) whereas the negative entropy ( $\Delta S$ ) reflects the affinity of the white sand towards the studied metal cations. © 2014 Trade Science Inc. - INDIA

### KEYWORDS

Purification;  
Phosphoric acid;  
White sand;  
Uranium;  
Zinc;  
Cadmium.

### INTRODUCTION

The phosphorite deposits in Egypt, represented by Duwi Formation are mined in three major localities; Red Sea Coast (Safaga-Qusier), Nile Valley (El Sibaiya) and Western Desert (Abu Tartur). The phosphorite ore as a raw material for phosphatic fertilizers and phosphoric acid, also considered as natural sources of uranium<sup>[1]</sup>. The concentration of uranium in phosphorite is ranging from less than 100 to 300 ppm<sup>[2]</sup>. The uranium in the phosphorites of Wadi Mishash east Luxor ranges from 50 to 270 ppm<sup>[3]</sup>, from 45 to 160 ppm at El Sibaiya and from 86 to 106 ppm at Safaga, Red Sea<sup>[4]</sup>. Phosphoric acid is generally produced in Egypt by the wet process method, where the phosphorite rocks are

treated mainly with sulfuric acid. Wet process phosphoric acid (WPPA) contains a number of organic and inorganic impurities that affect the grade of the acid. Some of these inorganic impurities are heavy ions such as uranium, zinc and cadmium which are considered as hazardous substances besides possible recovery of uranium as a secondary resource, while uranium causes environmental problems due to its radioactive properties, it is considered in the meantime as a strategic element with a high inherent value. On the other hand, Zn(II) and Cd(II) have been distinguished as a very dangerous substances because of their toxicity, persistence, bioaccumulation and carcinogenicity. The presence of these impurities is indeed the reason behind which 95% of the acid produced by the wet process is directly used

as fertilizers and not in other applications as foodstuff, pharmaceuticals and sugar industry<sup>[5]</sup>. The purified phosphoric acid can thus be used as raw materials for the production of detergents, food products, and alimentary supplies for cattle, toothpaste and fertilizers<sup>[6,7]</sup>.

Removal of such inorganic impurities from wet process phosphoric acid has actually been studied using many techniques, involving precipitation<sup>[8,9]</sup>, liquid–liquid extraction<sup>[10–16]</sup>, solid–liquid extraction<sup>[17]</sup>, sorption of heavy ions from phosphoric acid solution by impregnated charcoal with triphenyl phosphine sulphide extractant<sup>[18]</sup>, and membrane technologies such as electrodialysis (ED), reverse osmosis besides nanofiltration<sup>[19–22]</sup>. Applications of these techniques are however limited due to a number of disadvantages; viz, limited efficacy, high costs of organic solvents, difficulty in recovering all the solvent from both the raffinate and the purified acid as well as environmental pollution by some by-products. Promising techniques that have recently been applied include mainly, bentonite and activated carbon for the purification of wet process phosphoric acid from some impurities<sup>[23,24]</sup>.

Due to the wide range of application the white silica sand as an effective adsorbent of heavy metal cations, the objective of the present work has been directed for its application for the purification of WPPA from the highly toxic impurities. Special emphasis has been concerned with the three metal cations; namely, U(IV), Zn(II) and Cd(II).

Silica is indeed the most common substance on the earth where it represents a main constituent of most rocks as well as in plants such as bamboo, rice and barley. The general formula of silica is  $\text{SiO}_2$  or  $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  where most of its forms have the tetrahedral structure in which each atom occupies the centre of the tetrahedron while the oxygen atoms are on the apex in a regular form. The active surface which may participate in any chemical or physical interaction is limited to the external surface of the crystalline particles. The surface functional groups in silica would actually play a significant role in the adsorption process of metal ions. In the other words, silica can be regarded as a plane of oxygen atoms bound to the silica tetrahedral layer and hydroxyl groups that are associated with the edges of the silica structural units, in a manner to provide surface sites for the chemisorption of metal ions

(Donald, 1998 in Awan et al, 2003)<sup>[25]</sup>. Accordingly, the surface functional group can be represented by the following silanol group; viz,



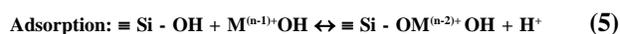
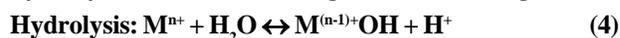
Where the surface hydroxyl groups dissociate in water to form deprotonated sites and which serve as Lewis bases towards metal cations ( $\text{M}^{n+}$ ); namely,



or else the adsorption reaction can generally be represented as follows.



Heavy metal cations  $\text{M}^{n+}$  may also hydrolyze in aqueous solutions and would then be adsorbed in the hydrolyzed forms according to the following reactions:



As a matter of fact, the metal surface bonding (adsorption) reaction would be favored by the properties of the metals that favor its hydrolysis i.e. its high charge, small radius and polarizability (Murray, 1994 in Awan et al, 2003)<sup>[25]</sup>.

## MATERIALS AND METHODS

### Materials

#### Abu Zaabal WPPA

A sample of the crude concentrated phosphoric acid has been kindly provided by Abu Zaabal Fertilizer and Chemicals Co., Cairo, Egypt. Analysis of the latter has been achieved using the wet chemical procedures of Shapiro and Brannock (1962)<sup>[26]</sup>. From this analysis, it was shown that its assay of  $\text{P}_2\text{O}_5$  attains up to 43.5%. Therefore it was found convenient to dilute it down to 29%  $\text{P}_2\text{O}_5$  to simulate the WPPA.

#### White silica sand

A natural white sand sample was collected from Abu Zeneima, south western Sinai, Egypt. It was ground and sieved to -200 mesh grain size (75  $\mu\text{m}$ ). Complete chemical analysis of the collected sand sample was achieved using the wet chemical procedures of Shapiro and Brannock (op.cited)<sup>[26]</sup>.

### Experimental procedures

## Full Paper

Prior to the experimental purification procedure of Abu Zaabal WPPA using Abu-Zeneima white sand, it was first repeatedly washed with hot distilled water followed by treatment of the washed sand with 1 M hydrochloric acid for 24 h. After filtration, the sand was twice washed with distilled water followed drying. On the other hand, the prepared wet process phosphoric acid (29%  $P_2O_5$ ) was mixed with a bentonite sample collected from Abu Tartur area in a concentration of 11.67 g/l for 30 min. in a manner to separate the suspended materials. To enhance settling of the latter, polyacrylamide to the extent of only 0.5 mg/l was added as a flocculating agent whereas the relatively pure green acid was obtained<sup>[15]</sup>.

Several series of batch adsorption experiments of the three study metal ions (U VI, Zn II and Cd II) from Abu Zaabal diluted phosphoric acid were then performed using the treated Abu Zeneima white sand. The purpose was to optimize the different parameters such as adsorbate concentration or dose, contact time as well as the temperature. All these experiments were achieved in duplicate tests to establish the accuracy of the procedure. To realized these objectives, a known volume of the working crude phosphoric acid (10 ml) was mechanically shaker at a rate 150 rpm with known weights of the adsorbate in a 100 ml conical flask. Except otherwise sited, all the experiments were carried out at room temperature for 24 h. Filtration of the slurry was then performed and the working metal ions concentration in the filtrate was determined. Concerning the effect of the initial concentration of the study three metal ions upon their adsorption a synthetic 5.1 M phosphoric acid sample (29.2%  $P_2O_5$ ) was prepared from phosphoric acid (85%), (ADWIC, El-Nasr Pharm.). In the latter, different concentrations of the three study metal values were dissolved from their corresponding reagents of Winlab, England; namely  $UO_2(CH_3COO)_2 \cdot 2H_2O$ ,  $ZnSO_4 \cdot 7H_2O$ ,  $3CdSO_4 \cdot 8H_2O$ .

### Analytical procedures

Analysis of the major oxides of Abu Zaabal concentrated crude phosphoric acid and the working natural white sand was attained using Shapiro and Brannock procedures<sup>[26]</sup>. In the latter,  $SiO_2$ ,  $Al_2O_3$  and  $TiO_2$  have been spectrophotometrically analyzed using Unicam

UV2-100 UV/Vis Spectrometer according to standard methods of analysis while Na and K oxides have determined by the flame photometric technique. The  $Fe_2O_3$ , MgO and CaO have however been titrimetrically determined. In the meantime, the concentration of the trace elements in the working phosphoric acid has been determined through atomic absorption for Zn(II) and Cd(II) while the inductively coupled plasma optical emission spectrometry (ICP-OES) has been used for U(VI) and the other trace elements. On the other hand, for control analysis of the study metal values; viz, zinc(II) and cadmium(II) in all the stream acidic was performed using atomic absorption whereas, uranium(VI) in these solutions was spectrophotometrically measured<sup>[27]</sup>.

## RESULTS AND DISCUSSION

### Materials characteristics

The analytical results of Abu Zaabal concentrated crude phosphoric acid are shown in TABLE 1. From these results, the  $P_2O_5$  assays 43.5% and the  $Fe_2O_3$  content attains 2.3% while F assays 0.9% and the other constituents are less than 1% except  $SO_4^{2-}$  which assays 1.5%. The study metal values were found to attain 51, 170 and 11 mg/l for U(VI), Zn(II) and Cd(II) respectively. However, this provided concentrated acid was first diluted to simulate the WPPA down to 29%

TABLE 1 : Analysis of interested components of Egyptian wet process phosphoric acid

Constuents	Conc. %	Constuents	Conc. ppm (mg/l)
$P_2O_5$	43.5	Zn	170
$Fe_2O_3$	2.3	Mn	623
CaO	0.4	Th	0.9
F	0.9	U	51
$SiO_2$	0.4	Cd	11
$Na_2O$	0.2	As	9
$K_2O$	0.07	Pb	27
MgO	0.4	Cu	20
$Al_2O_3$	0.6	Cr	129
$SO_4^{2-}$	1.5	Co	32
		Ba	0.7
		Ni	38
		Sr	50
		Y	41

P<sub>2</sub>O<sub>5</sub> upon which the adsorption experiments or any purification procedure would be carried out before its concentration through evaporation. Accordingly, the assay of the study metal values in the dilute acid has been decreased to 34, 93 and 7 mg/l for U(VI), Zn(II) and Cd(II) respectively.

On the other hand, the collected white sand sample has also been completely analyzed after its proper water and acid leaching. The obtained results are shown in TABLE 2 while indicates a purity of up to 99.11% of the treated sand sample.

TABLE 2 : Chemical analysis of natural white sand sample

Constuents	Conc. %	Constuents	Conc. %
SiO <sub>2</sub>	99.11	MgO	0.0
Al <sub>2</sub> O <sub>3</sub>	0.11	Na <sub>2</sub> O	0.14
TiO <sub>2</sub>	0.02	K <sub>2</sub> O	0.01
Fe <sub>2</sub> O <sub>3</sub>	0.19	H <sub>2</sub> O	0.05
CaO	0.01	U	0.0

## Sorption parameters of the studied metal ions

### Effect of adsorbent dose

The effect of the natural white sand dose on the removal efficiency of U(VI), Zn(II) and Cd(II) ions from the working phosphoric acid was studied in the range from 10 to 100 g/l while the other parameters were fixed at room temperature and 24 h as contact time. From the obtained results in Figure 1 it is clearly evident that the adsorption of the interesting metal ions increases by increasing the adsorbent dose until attain-

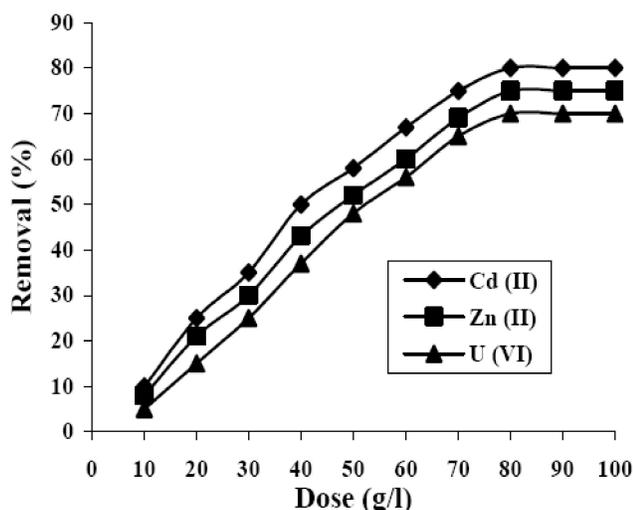


Figure 1 : Effect of the natural white sand dose on the removal % of U(VI), Zn(II) and Cd(II) ions from the crude diluted phosphoric acid

ing an adsorbent concentration of 80 g/l. This is due to a greater availability of the surface area and in turn the corresponding exchange site. Any further increase of the adsorbent did not cause any significant change in the adsorption efficiency. This may be interpreted as due to the formation of clusters of the adsorbent particles in a manner to result in decreasing the available surface area. At this concentration, the maximum removal % of U(VI), Zn(II) and Cd(II) were found to be 70, 75 and 80% respectively. It has also to be indicated herein that the realized variable adsorption efficiency can be due to the fact that, the preference of an adsorbent for a specific metal ion may be explained on the basis of electronegativity of the metal ions and also their ionic radius<sup>[28]</sup>.

### Effect of contact time

The effect of the contact time on the removal efficiencies of U(VI), Zn(II) and Cd(II) from the working acid by Abu Zeneima white sand was carried out between 2 and 28 h while the other parameters were kept constant at room temperature and using 80 g/l dose concentration. The obtained results in Figure 2 indicate that the removal efficiencies of U(VI), Zn(II) and Cd(II) ions have gradually increased by increasing the contact time till reaching their maximum efficiencies at 24 hour. This relatively long contact time might be interpreted as due to the relatively high acidic nature of the working WPPA.

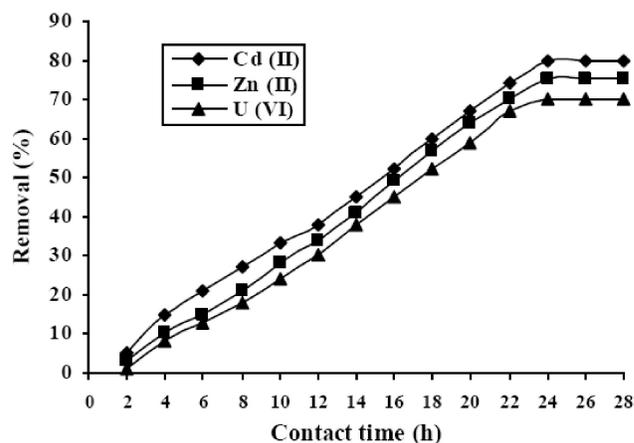


Figure 2 : Effect of the contact time on the removal efficiencies of U(VI), Zn(II) and Cd(II) ions from the crude diluted phosphoric acid by Abu Zeneima white sand

### Effect of temperature

The effect of temperature on the purification pro-

## Full Paper

cess of the crude phosphoric acid from the working metal ions using natural white sand was carried out in the range from 298–338 °K. The operating conditions used involved an adsorbent concentration dose of 80 g/l for 24 h contact time. From the results showed in Figures 3 & 4 it is clear that the removal efficiency and the distribution coefficient ( $K_d$ ) have decreased with the increasing temperature. This indicates that the process is exothermic in a manner that the removal of each metal ion is favored at low temperatures. This may be attributed to the relative increase in the escaping tendency of the metal ions from the solid phase to the bulk phase by increasing the temperature and or increased weakness of adsorptive forces between the active sites of the adsorbent and the adsorbate species as well as between the adjacent molecules of adsorbed phase<sup>[29]</sup>.

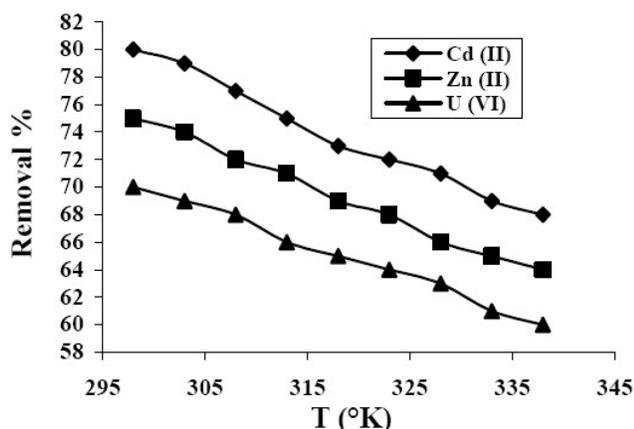


Figure 3 : Effect of temperature on the removal efficiencies of U(VI), Zn(II) and Cd(II) ions from the crude diluted phosphoric acid using Abu Zeneima white sand

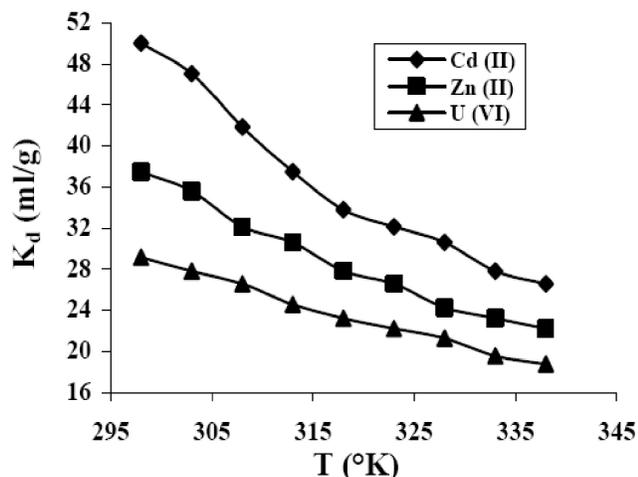


Figure 4 : Effect of temperature on the distribution coefficient ( $K_d$ ) of U(VI), Zn(II) and Cd(II) ions from the crude diluted phosphoric acid using Abu Zeneima white sand

### Effect of initial metal ion concentration

The effect of the initial metal ions concentration U(VI), Zn(II) and Cd(II) on their removal was however studied using the prepared synthetic 5.1 M phosphoric acid (29.2%  $P_2O_5$ ) in which different concentration of the studied three metal ions have been dissolved. In these experiments the other parameters were kept constant at room temperature for 24 h and using 80 g/l of Abu Zeneima white sand. In these experiments, metal ions concentrations were ranging from 10-51, 30-170 and 2-11 mg/l for U(VI), Zn(II) and Cd(II) respectively. The obtained data shown in TABLE 3 have illustrated that, both the removal % and the distribution coefficients have been decreased with increasing the initial concentrations of U(VI), Zn(II) and Cd(II). Thus, at the lower initial metal concentrations, sufficient adsorption sites are available for the sorption of metals ions whereas at higher metal ions concentrations the available adsorption sites have not increased. Hence the removal efficiency of the metal ions was decreased with increasing the metal ions concentrations.

### Thermodynamic parameters of the study adsorption procedure

The thermodynamic parameters including the change in the standard free energy  $\Delta G$  ( $\text{kJmol}^{-1}$ ), enthalpy  $\Delta H$  ( $\text{kJmol}^{-1}$ ) and entropy  $\Delta S$  ( $\text{Jmol}^{-1}\text{k}^{-1}$ ) for the study sorption of U(VI), Zn(II) and Cd(II) from the Abu Zaabal phosphoric acid by Abu Zeneima white sand were calculated using the following Vant hoff's equations<sup>[30]</sup>:

$$\Delta G = -RTL \ln K_d \quad (6)$$

$$\Delta G = \Delta H - T \Delta S \quad (7)$$

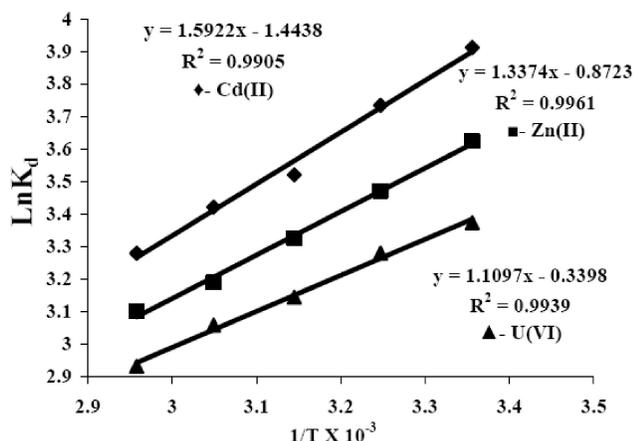
$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

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

Accordingly, the values of enthalpy  $\Delta H$  and entropy  $\Delta S$  were calculated from the slopes ( $-\Delta H/R$ ) and intercepts ( $\Delta S/R$ ) of the  $\ln K_d$  versus  $1/T$  plot (Figure 5). The obtained values of  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  for the sorption of the metal ions U(VI), Zn(II) and Cd(II) are reported in TABLE 4. It has to be mentioned in this regard that the obtained negative value of the enthalpy change ( $\Delta H$ ) for the process further confirms its exothermic nature while the negative entropy ( $\Delta S$ ) reflects the affinity of

**TABLE 3 : Effect of initial concentrations of U(VI), Zn(II) and Cd(II) on their removal % and distribution coefficient ( $K_d$ ) from synthetic 5.1 M phosphoric acid using Abu Zeneima white sand**

U(VI)			Zn(II)			Cd(II)		
$C_0$ mg/l	Removal %	$K_d$	$C_0$ mg/l	Removal %	$K_d$	$C_0$ mg/l	Removal %	$K_d$
10	80.0	50.0	30	88.6	97.15	2	91.0	126.38
20	77.8	43.81	60	85.8	75.53	4	88.8	99.11
30	75.6	38.73	90	83.3	62.35	6	85.6	74.30
40	72.5	32.95	120	80.0	50.0	8	82.3	58.12
51	70	29.16	150	78.0	44.32	11	80.0	50.0
-	-	-	170	75.0	37.5	-	-	-



**Figure 5 : Plot of  $\text{Ln}K_d$  versus  $1/T$  of the studied adsorption systems**

the adsorbent material towards each metal ion. The negative free energy values ( $\Delta G$ ) indicate the feasibility of the process and its spontaneous nature.

### Adsorption isotherms

The adsorption isotherm is one of the most important tools to understand the mechanism of an adsorption system where it relates the concentration of a solute on the surface of the adsorbent to its concentration in the fluid with which it is in contact. From the available isotherm models both Langmuir and Freundlich isotherms were selected to be applied in the present work.

### Langmuir isotherm

The Langmuir equation is probably the best known and most widely applied adsorption isotherm. Langmuir adsorption isotherm models indeed the monolayer coverage of the sorption surface where the energy of adsorption is constant with no transmigration of adsorbate in the plane of the surface<sup>[31]</sup>. This model supposes that adsorption takes place at a specific adsorption surface and that the attraction between the molecules de-

**TABLE 4 : Thermodynamic parameters for U(VI), Zn(II) and Cd(II) adsorption from Abu Zaabal crude phosphoric acid by Abu Zeneima white sand**

	T(°K)	U(VI)	Zn(II)	Cd(II)
$\Delta G$ (kJmol <sup>-1</sup> )	298	-10.07	-13.28	-16.82
	308	-10.10	-13.35	-16.94
	318	-10.13	-13.42	-17.06
	328	-10.16	-13.50	-17.18
	338	-10.19	-13.57	-17.30
$\Delta H$ (kJmol <sup>-1</sup> )	-	-9.23	-11.12	-13.24
$\Delta S$ (Jmol <sup>-1</sup> k <sup>-1</sup> )	-	-2.82	-7.25	-12.00

creases as getting further from the adsorption surface. The Langmuir isotherms of the working system have been obtained by contacting the adsorbent at a fixed dose 80 g/l with the adsorbate solution at different concentrations after an equilibration time of 24 h. The Langmuir isotherm is represented by the following equation:

$$\frac{1}{q_e} = \frac{1}{q^0} + \left( \frac{1}{bq^0} \right) \left( \frac{1}{C_e} \right) \quad (9)$$

where  $q_e$  is the amount of metal ions adsorbed per unit weight of the working Abu Zeneima white sand (mg/g),  $C_e$  is the equilibrium metal ions concentration in the solution (mg/l),  $q^0$  is the maximum metal ions uptake per unit mass of adsorbent (mg/g) and which is related to adsorption capacity while  $b$  is the Langmuir constant (l/mol). The latter is exponentially proportional to the heat of adsorption and is related to the adsorption intensity. Thus, a plot of  $1/q_e$  vs  $1/C_e$  should be linear if Langmuir adsorption is operative a matter which would permit calculation of Langmuir constants. Accordingly, it can be found from the obtained data in Figure 6 that the equilibrium adsorption isotherms of U(VI), Zn(II) and Cd(II) from Abu Zaabal wet process phosphoric acid using Abu

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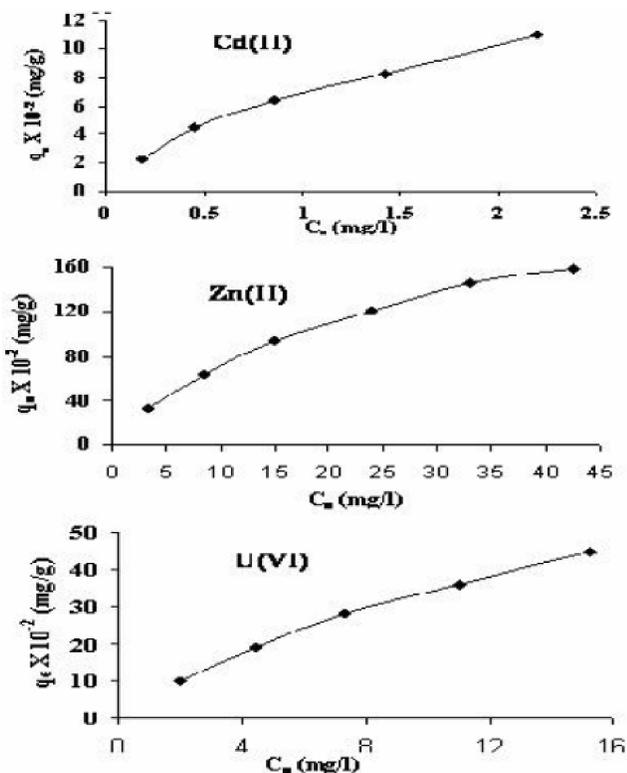


Figure 6 : Equilibrium adsorption isotherms for U(VI), Zn(II) and Cd(II) removal from Abu Zaabal crude phosphoric acid by Abu Zeneima white sand at room temperature

Zeneima white sand as an adsorbent have increased with increasing both the  $C_e$  and  $q_e$  values. The considerably increase of 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 U(VI), Zn(II) and Cd(II) ions partially covering the surface sites. Therefore, to optimize the design of a sorption system to remove U(VI), Zn(II) and Cd(II) from Abu Zaabal wet process phosphoric acid, it is important to set the most appropriate correlation of the equilibrium curve. The obtained linear relation indicates that the adsorption of the studied metal ions obeys langmuir isotherm (Figure 7). The Langmuir parameters have been calculated from the  $1/q_e$  vs.  $1/C_e$  plot, where  $q^0 = \text{intercept}^{-1}$  and  $b = \text{slope}^{-1} \times \text{intercept}$  (Figure 7 and TABLE 5).

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

$$R_L = \frac{1}{1 + bC_0} \quad (10)$$

where  $b$  is the Langmuir constant and  $C_0$  is the initial

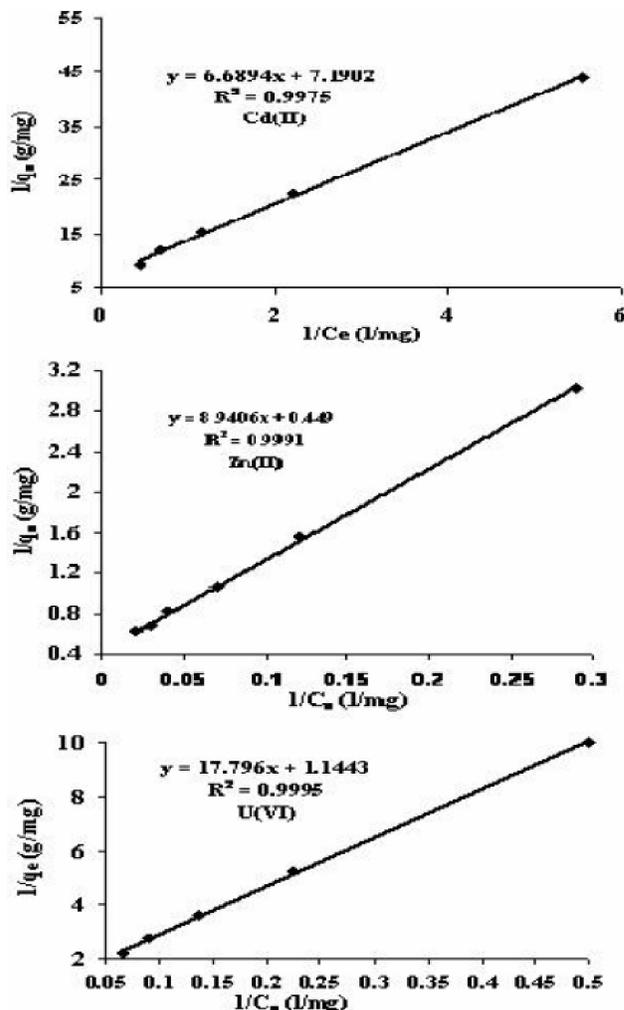


Figure 7 : The linearized langmuir plot for U(VI), Zn(II) and Cd(II) adsorption from Abu Zaabal crude phosphoric acid by Abu Zeneima white sand at room temperature

concentration of the adsorbate in solution<sup>[32]</sup>. The obtained value of  $R_L$  was found to be less than one indicating favorable adsorption.

### Freundlich isotherm

In the present work the Freundlich model has also been applied to estimate the adsorption intensity of the sorbate on the sorbent surface<sup>[33]</sup>. In all cases, the Freundlich isotherm would predict the saturation level of the sorbent by the sorbate in a manner that the surface coverage is mathematically predicted, indicating multilayer sorption of the surface. The Freundlich equation is represented as follows:

$$q_e = K_f C_e^{1/n} \quad (11)$$

$$\text{Log} q_e = \text{Log} K_f + \frac{1}{n} \text{Log} C_e \quad (12)$$

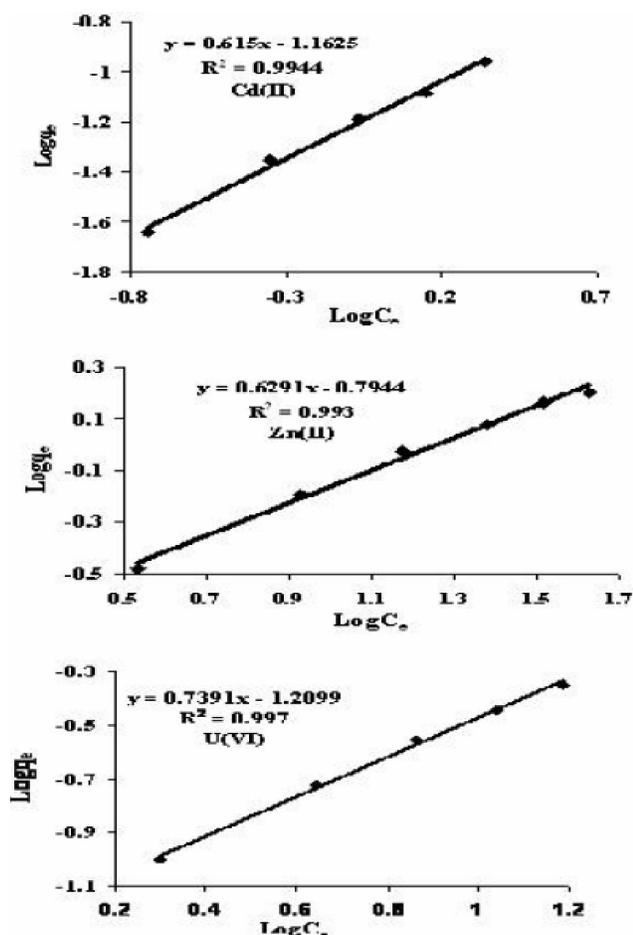


Figure 8 : Freundlich adsorption isotherm for U(VI), Zn(II) and Cd(II) adsorption from Abu Zaabal crude phosphoric acid by Abu Zeneima white sand at room temperature

TABLE 5 : Langmuir and Freundlich adsorption constants for U(VI), Zn(II) and Cd(II) ions from Abu Zaabal crude phosphoric acid by Abu Zeneima white sand at room temperature

Langmuir constants								
U(VI)			Zn(II)			Cd(II)		
$q^0$ (mg/g)	$b$ (l/g)	$R^2$	$q^0$ (mg/g)	$b$ (l/g)	$R^2$	$q^0$ (mg/g)	$b$ (l/g)	$R^2$
0.87	0.064	0.999	2.227	0.05	0.999	0.139	1.075	0.997
Freundlich constants								
U(VI)			Zn(II)			Cd(II)		
$n$	$K_f$ (mg/g)	$R^2$	$n$	$K_f$ (mg/g)	$R^2$	$n$	$K_f$ (mg/g)	$R^2$
1.353	0.061	0.997	1.59	0.161	0.993	1.623	0.069	0.994

## CONCLUSION

This study has been interested in the purification of Abu Zaabal WPPA using Abu Zeneima white sand from some of its metal impurities; namely uranium(VI), zinc(II) and cadmium(II) as being undesirable in the acid due to their hazardous effects besides possible recovery of the

uranium values. From the obtained results, it has been concluded that the optimum conditions of adsorption of the studied metal cations involve 80 g/l of the working white sand for an equilibration time of 24 h at room temperature where the realized adsorption efficiencies of U(VI) Zn(II) and Cd(II) have attained 70, 75 and 80% respectively. However, it was found that the distribution coefficient of the study metal cations decrease

where  $q_e$  (mg/g) is the equilibrium concentration of the studied metal ions in the solid phase,  $C_e$  (mg/l) is the equilibrium concentration of the metal ions in the liquid phase,  $K_f$  (mg/g) is the adsorption capacity and  $n$  is the intensity of adsorption.

The adsorption data obtained of the studied three metal ions on Abu Zeneima white sand from Abu Zaabal crude phosphoric acid have thus been fitted to the Freundlich model by plotting  $\text{Log } q_e$  versus  $\text{Log } C_e$  (Figure 8). The obtained linear plot enables  $K_f$  and  $n$  to be determined and where their values are represented in TABLE 5. From the latter, it can be concluded that Langmuir isotherm describes the study system much better than that of Freundlich. These conclusions have mainly been based by comparing the achieved practical capacity of the studied metal cations with the theoretical capacity calculated from Langmuir equation shown in TABLE 5. Thus U(VI), Zn(II) and Cd(II) practical capacities of Abu Zeneima white sand have attained 70, 75 and 80 % at the studied operating conditions i.e. 0.44, 1.59 and 0.11 mg/g respectively. Comparing these results with the theoretical capacities calculated for these metal cations from Langmuir equation, it has been found to attain 0.87, 2.23 and 0.14 mg/g respectively. In the other words, the achieved capacities have attained 50.5, 71 and 78.5% of the theoretical values for U(VI), Zn(II) and Cd(II) respectively.

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as the temperature was increased. The negative values of the enthalpy change ( $\Delta H$ ) of the process confirmed the exothermic nature of the study system while the negative entropy ( $\Delta S$ ) values indicate the applicability of the study adsorption process which was proved to be spontaneous in nature due to the obtained negative values of  $\Delta G$ . The Langmuir and Freundlich adsorption isotherms have been applied on the experimental procedures however the former has better explained the study system. Using the natural white sand as an adsorbent of metal impurities from WPPA can indeed be considered as a promising economic technology for the purification procedure of the acid given its proven efficiency.

### REFERENCES

- [1] I.H.Zidan; Geological, mineralogical and geochemical studies of Abu Tartur phosphate, Western Desert, Egypt., Ph.D.Thesis, Fac.Sci., Al Azhar Univ., (2002).
- [2] M.Slansky; Geology of sedimentary phosphates, North Oxford Academic Publishers, London, (1986).
- [3] A.B.Salman; Structure and radioactivity of some phosphate deposits, East Luxor area, Eastern Desert. Ph.D.Thesis, Fac.Sci., Ain Shams Univ., (1974).
- [4] I.H.Zidan; Environmental Impact of the Radioactive and some Heavy Metals in the Egyptian Phosphorite Ores and Fertilizers Product, J.Al Mansoura Environm.Sci., **41(2)**, 153-164 (2012).
- [5] J.C.Kotz, K.F.Purcell; Uses of Phosphate Containing Rock Chemistry and Chemical Reactivity, 2nd Edition, McGraw-Hill, Inc., Tokyo, Japan, (1991).
- [6] L.A.Guirguis, H.K.Fouad, R.M.EL-Rakaiby; Purification of commercial phosphoric acid to the food grade quality by liquid/liquid solvent extraction, Mansoura J.Chem., **35(1)**, 51-72 (2008).
- [7] A.A.El-Asmy, H.M.Serag, M.A.Mahdy, M.I.Amin; Purification of phosphoric acid by minimizing iron, copper, cadmium and fluoride, Sep.Purif.Technol., **61**, 287-292 (2008).
- [8] E.E.Z.Qafas, K.El-Kacemi, M.C.Edelahi; Simultaneous removal of Cd(II) and As(III) from phosphoric acid solutions by co-precipitation of CdS and As<sub>2</sub>S<sub>3</sub> with Na<sub>2</sub>S, Sci.Lett., **3**, 3 (2001).
- [9] Ennaassia, K.El Kacemi, A.Kossir, G.Cote; Study of the removal of Cd(II) from phosphoric acid solutions by precipitation of CdS with Na<sub>2</sub>S, Hydrometallurgy, **64**, 101-109 (2002).
- [10] N.S.Awwad, S.A.El-Reefy, H.F.Aly; Comparative studies on the kinetics of uranium (VI) and uranium (IV) extraction by TBP and Cyanex-921 from nitric acid solution, in: Sixth Arab Conference on Peaceful Uses of Atomic Energy, Cairo, Egypt, **14**, 379 (2002).
- [11] A.Mellah, D.Benachour; The solvent extraction of zinc, cadmium and chromium from phosphoric acid solutions by tri-*n* butyl phosphate in kerosene diluent, Sep.Pur.Technol., **56**, 220-224 (2007).
- [12] N.S.Awwad, S.A.El-Reefy, H.F.Aly; Kinetics studies on the extraction and stripping of uranium(VI) from pretreated phosphoric acid by HDEHP + Cyanex921 using single drop technique, in: Proceedings of the Eighth International Conference of Nuclear Science and Application, **1**, 42 (2004).
- [13] A.Mellah, D.Bauer; The extraction of titanium, chromium and cadmium from phosphoric acid solutions by p (1,1,3,3- tetramethyl butyl) phenyl phosphoric acid in kerosene diluent, Hydrometallurgy, **37**, 117-121 (1995).
- [14] A.Mellah, D.Benachour; The solvent extraction of zinc and cadmium from phosphoric acid solution by di-2-ethyl hexyl phosphoric acid in kerosene diluent, Chem. Eng.Proces., **45**, 684-690 (2006).
- [15] M.I.Amin, M.M.Ali, H.M.Kamal, A.M.Youssef, M.A.Akl; Recovery of high grade phosphoric acid from wet process acid by solvent extraction with aliphatic alcohols, Hydrometallurgy, **105**, 115-119 (2010).
- [16] R.Singh, S.L.V.Kshmi, S.L.Mishra, C.K.Gupta; Studies on uranium extraction from phosphoric acid using di-nonyl phenyl phosphoric acid-based synergistic mixtures, Hydrometallurgy, **59**, 69-76 (2001).
- [17] M.H.Soliman, H.S.Gado, M.N.Kouraim; Chemical studies on the removal of iron from crude phosphoric acid using an organosilicon compound, E.J.Chem., **6(S1)**, S329-S341 (2009).
- [18] E.A.El-Sofany, W.F.Zaher, H.F.Aly; Sorption potential of impregnated charcoal for removal of heavy metals from phosphoric acid, J.Hazard.Mater., **165**, 623-629 (2009).
- [19] A.A.M.Daifullah, N.S.Awwad, S.A.El-Reefy; Purification of wet phosphoric acid from ferric ions using modifying rice husk, Chem.Eng.Process., **43**, 193-201 (2004).
- [20] A.M.Urriaga, A.Aloso, I.Qrtiz, J.A.Daoud, S.A.El-Reefy, S.Perez de Qrtiz, T.Gallego; Comparison of liquid membrane processes for the removal of cad-

- mium from wet phosphoric acid, *J.Membr.Sci.*, **164(1-2)**, 229-240 (2000).
- [21] M.B.C.Elleuch, M.B.Amor, G.Pourcelly; Phosphoric acid purification by a membrane process: electro deionization on ion-exchange textiles, *Sep.Purif.Technol.*, **51**, 285-290 (2006).
- [22] M.P.Gonzalez, R.Navarro, I.Saucedo, M.Avila, J.Revilla, C.Bouchard; Purification of phosphoric acid solutions by reverse osmosis and nanofiltration, *Desalination*, **147**, 315-320 (2002).
- [23] S.Zermane, A.H.Meniai; Experimental study of competitive adsorption of heavy metals and organic matter for the phosphoric acid purification, *Energy Procedia*, **18**, 888-895 (2012).
- [24] D.Doulija, C.Leodopoulos, K.Gimouhopoulos, F.Rigas; Adsorption of humic acid on acid-activated Greek bentonite, *J.Colloid Interface Sci.*, **340**, 131-141 (2009).
- [25] M.A.Awan, Ishtiaq A.Qazi, I.Khali; Removal of heavy metals through adsorption using sand, *J.Environ.Sci.*, **15(3)**, 413-416 (2003).
- [26] L.Shapiro, W.W.Brannock; Rapid Analysis of silicate, carbonate and phosphate rocks. *U.S. Geol.Surv.Bull.A*, **1144**, 56 (1962).
- [27] Z.Marczenko, M.Balcerzak; Separation, Preconcentration and Spectrophotometry in Inorganic Analysis. Elsevier Science B.V., Amsterdam the Netherlands, (2000).
- [28] C.Quintelas, Z.Rocha, B.Silva, B.Fonseca, H.Figueiredo, T.Tavares; Removal of Cd(II), Cr(VI), Fe(III) and Ni(II) from aqueous solutions by an E. coli biofilm supported on kaolin, *Chem.Eng.J.*, **149**, 319-324 (2009).
- [29] A.K.Meena, G.K.Mishra, P.K.Rai, C.Rajagopal, P.N.Nagar; Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent, *J.Hazard.Mater.*, **B122**, 161-170 (2005).
- [30] G.Bereket, A.Z.Aroguz, M.Z.Ozel; Removal of Pb(II), Cd(II), Cu(II), and Zn(II) from aqueous solutions by adsorption on bentonite, *J.Colloid Interface Sci.*, **187**, 338-343 (1997).
- [31] G.Wang, J.Liu, X.Wang, Z.Xie, N.Deng; Adsorption of uranium (VI) from aqueous solution onto cross-linked chitosan, *J.Hazard.Mater.*, **168**, 1053-1058 (2009).
- [32] A.Bhatnagar, A.K.Jain; A comparative adsorption study with different industrial wastes as adsorbents for the removal of cationic dyes from water, *J.Colloid Interface Sci.*, **28(1)**, 49-55 (2005).
- [33] A.Mellah, S.Chegrouche; The removal of zinc from aqueous solution by natural bentonite, *Water Res.*, **31**, 621-629 (1997).