Studies on kinetics, thermodynamics and sorption characteristics of an inorganic ion exchanger—Titanium phosphate synthetic from Abu-Tartur phosphoric acid towards Cu (II), Pb (II) and Zn (II)

A.T. Kandil[1], E.A. Abdel-Aal[2], M. H. Taha[3] and E.A. Abdel Rahman[4]

[1] Chemistry Department, Faculty of Science, Helwan University, Cairo, Egypt
[2] Central Metallurgical R & D Institute, P.O. Box 87 Helwan, Cairo, Egypt
[3] Nuclear Materials Authority, P.O. Box 530, El Maddi, Cairo, Egypt
[4] Misr Phosphate Company, New Valley, El-Kharga Oasis, Abu-Tartur, Egypt
emadchemali@yahoo.com

Abstract: In the current study, amorphous titanium phosphate (TiP) was produced from Abu-Tartur phosphoric acid. TiP has been characterized for elemental analysis (ICP-OES), spectral analysis (FT–IR), thermal analysis (TGA and DTA), X-ray diffraction studies and SEM-EDX. Chemical resistivity of the material has been assessed in various media–acids, bases and organic solvents. The Na^+ ion exchange capacity (IEC) has been determined. TiP was prepared as an adsorbent for heavy metals from waters. Uptake of Cu^{2+}, Pb^{2+} and Zn^{2+} onto TiP was assayed by batch tests; different parameters controlled the adsorption process are discussed. The kinetic models of adsorption were analyzed by the pseudo-first order, pseudo-second order, Elovich kinetic and Morris-Weber models. The results have been indicated that the Lagergren first order kinetic model is more appropriate than the others for titanium phosphate adsorption process for Cu, Pb, and Zn metal ions. Obtained adsorption thermodynamic parameters ($\Delta H°.\Delta S°$ and $\Delta G°$) expose that Cu, Pb, and Zn metal ions adsorption to be an endothermic, physical and spontaneous process.

1. Introduction

Industrial and mining wastewaters are important sources of pollution of heavy metals **(Quek *et al.,* 1998)**. A number of technologies have been developed over the years for the efficient removal of toxic/heavy metal from wastewater **(Deans and Dixon, 1992)**. The most important of these methods include filtration, chemical precipitation, ion exchange, adsorption, electrode position and membrane systems. All these approaches have their inherent advantages and limitations. Although filtration and chemical precipitation are low cost and effective in removing large quantities of metal ions quickly, neither is capable of removing at trace levels. Adsorption is also ineffective at very low concentrations. Ion exchange can be used to reduce metal concentrations to the region of parts per million.

Amongst the synthetic inorganic ion exchangers, tetravalent metal acid (TMA) salts **(Amphlett, 1964; Clearfield *et al.,* 1973; Clearfield, 1982; Varshney and Khan, 1991; Clearfield, 1995)** are gaining importance due to their excellent thermal stability and chemical resistivity. These materials possess structural hydroxyl groups, the H of the –OH being the exchangeable sites. They possess an appreciable ion exchange capacity as well as high selectivity for certain metal ions. TMA salts can be obtained in both amorphous and crystalline forms. Amorphous materials can be obtained in granular form, very suitable for column operations **(Kraus *et al.,* 1958; Alberti and Grassiani, 1960; Alberti *et al.,* 1967; Egorov and Makarova, 1971; Alberti *et al.,* 1980)**. TMA salts being synthesized by sol–gel routes, materials with varying water content, composition, ion exchange capacity and crystallinity can be obtained by varying parameters such as stoichiometry and concentration of the reagents used, temperature at which they are mixed, rate of addition, mode of mixing, pH, etc. Ion exchange materials with higher selectivities are continuously being investigated **(Möller, 2002)**. Amorphous titanium phosphate has been synthesized, characterized and its ion exchange behavior studied **(Kobayashi, 1979; Strelko, 1982; Kharchenko, 1990; Bortun *et al.,* 1997; Clearfield *et al.,* 1998; Sahu and Parida, 2002)**. The removal and recovery of toxic/heavy metals is an area of current interest **(Schmuhl, 2001)**. In the present endeavour, a new phase of amorphous titanium phosphate (TiP), an inorganic ion exchanger of the class of TMA salt, has been synthesized by sol–gel method. It has been characterized for elemental analysis (ICP-OES), spectral analysis (FT–IR),

thermal analysis (TGA and DTA), X-ray diffraction studies and SEM-EDX. Chemical resistivity of the material has been assessed in various media—acids, bases and organic solvents. The Na$^+$ ion exchange capacity (IEC) has been determined. Kinetic studies provide information relating to the mechanism and feasibility of ion exchange process occurring on the surface as well as the ability to predict correlation among experimental results. The sorption/ion exchange behavior of TiP towards Cu^{2+}, Pb^{2+} and Zn^{2+}has been studied. The kinetic models of adsorption were analyzed by the pseudo-first order, pseudo-second order, Elovich kinetic and Morris-Weber models. The results have been indicated that the Lagergren first order kinetic model is more appropriate than the others for titanium phosphate adsorption process for Cu, Pb, and Zn metal ions. Obtained adsorption thermodynamic parameters (ΔH°.ΔS° and ΔG°) expose that Cu, Pb, and Zn metal ions adsorption to be an endothermic, physical and spontaneous process.

Titanium phosphate has been used in metal adsorption because of its high cation exchange capacity and strong absorptive affinity with inorganic substances, low cost.

In this contribution and regards to environmental aspect, this paper aimed to investigate the toxic/heavy metal adsorption from aqueous solution using amorphous titanium phosphate materials by batch kinetics and equilibrium studies.

2. Experimental
Materials and Reagents:
Materials:

All chemicals used are analytical grad. Sulfuric acid ≥ 97.9 % was obtained from ADWIC, Egypt. Titanium dioxide and ammonium sulfate were supplied by (MERCK, Germany). Phosphoric acid (35.8 % H$_3$PO$_4$) produced laboratory from Abu-Tartur phosphate concentrate, by dihydrate process.

1. Preparations of titanyl sulfate:

Titanyl sulfate has been prepared by mixing 50 g of titanium oxide with 500 g of ammonium sulfate and 1.0 liter of sulfuric acid having a specific gravity of 1.825 (97.97%). The mixture is gradually heated to 200°C with continuous stirring **(Marie, 1968)**. A clear solution of titanyl sulfate in highly concentrated sulfuric acid is obtained.

2. Synthesis of titanium phosphate:

The reaction was carried out in a covered 250 ml beaker. phosphoric acid/ titanium oxide mass ratio, ml/ g, 5.0, phosphoric acid rate of addition of 5 min, temperature 65 °C, reaction time of 30 min, time of addition of titanyl sulfate to phosphoric acid 5 min and nucleation time of 30 min. A hot plat magnetic stirrer adjusted with temperature 65 °C and stirring speed

400 rpm. Filtration was performed using Buchner type filter of 8.5 cm diameter filter funnel. A vacuum pump was used for filtration. Produced titanium phosphate gel was kept in contact with mother liquor overnight for aging, and then washed with hot distilled water (60 °C) until pH 3.8-4.2 followed by filtration and drying on dryer for 5 hour at 60 °C. After drying, the titanium phosphate has been obtained as white hard granules.

3. Results and discussion
1. Characterization of titanium phosphate:

Titanium and phosphorus content in the obtained precipitate were analyzed by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES model Perkin-Elmer Optima 2000). X-ray powder diffraction (XRD) analysis for the prepared precipitate was carried out using a Bruker AXS diffractometer (D8-ADVANCE) with Cu Kα (λ=1.54056 Å) radiation, operating at 40 kV and 10 mA. The diffraction data were recorded for 2θ values between 20° and 80° and the scanning rate was 0.5° min^{-1}. Fourier Transform Infrared Spectrum (FT-IR) analysis was performed using JASCO 3600 spectrophotometer and the resolution was set to 4 cm^{-1} for all the samples. Thermal analysis (TGA/DTA) was carried out on a Shimadzu thermal analyzer at a heating rate of 10°C/min. SEM-EDX, a Scanning Electron Microscope and Energy dispersive X-ray spectroscopy was employed to evaluate the atomic composition of produced titanium phosphate. Chemical resistivity in various media (acids, bases and organic solvents) was studied by taking 500 mg of the prepared titanium phosphate in 50 ml of the particular medium and allowing standing for 24 h. The change in its color, nature and weight was observed.

1.1. XRD Study:

The crystalline structure of titanium phosphate synthesized from titanium oxide and phosphoric acid have been estimated using XRD patterns Figure (1). As shown in XRD pattern an amorphous titanium phosphate is produced because of the absence of any sharp peaks in the X-ray diffractograms **(Ludmány et al., 2004; Patel and Chudasama, 2007; Jia et al., 2008)**.

1.2. FTIR Study:

The FTIR spectra of titanium phosphate precipitate, Figure (2), exhibits a broad band in the region ~ 3400 cm^{-1} which is attributed to symmetric and asymmetric –OH stretching, while band at ~1632 cm^{-1}, a sharp medium band is attributed to aqueous (H–O–H) bending. A band in the region ~ 1026 cm^{-1} is attributed to the presence of P=O stretching. A medium intensity band at ~ 1427 cm^{-1} is attributed to the presence of δ (POH). These bands indicate the presence of structural hydroxyl groups/protonic sites in the material **(Maheria and Chudasama, 2006;**

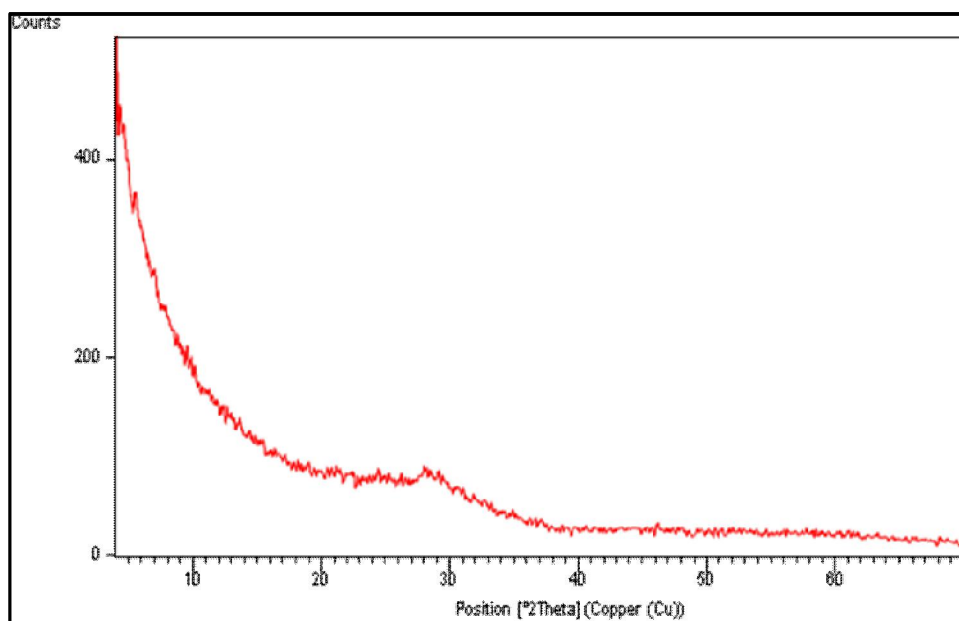**Patel   and   Chudasama,   2007;   Thakkar   and   Chudasama, 2009)**.

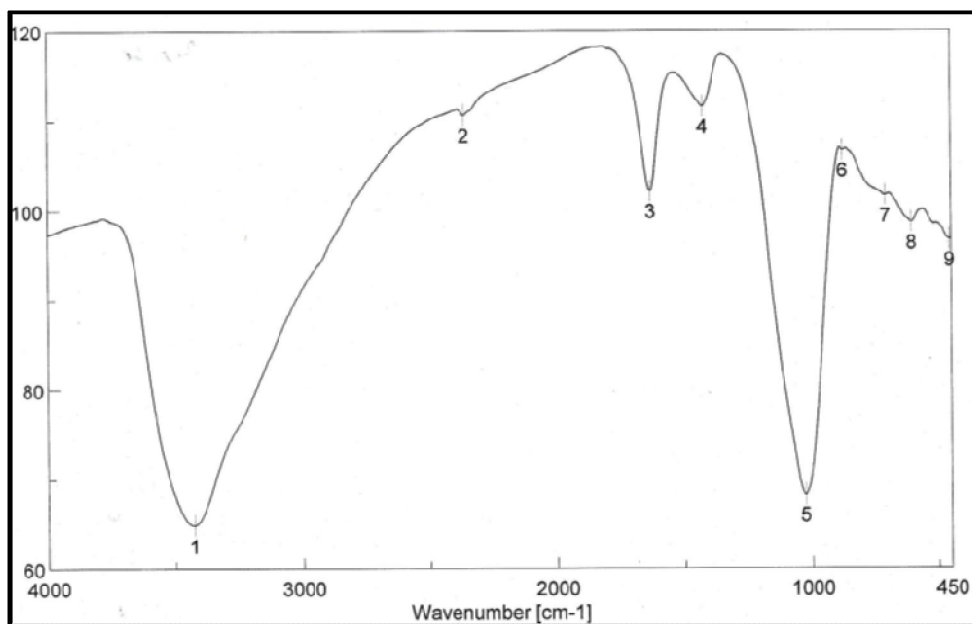**Figure (1): XRD of the produced titanium phosphate precipitate.**

Figure (2): FTIR of the produced titanium phosphate precipitate.

1.3. Thermal analysis:

TGA, Figure (3) indicates two weight-loss regions. The first weight-loss region (≈ 11.85% up to 270 °C) is attributed to loss of moisture/hydrated water. The second weight loss in the range 270–578 °C is attributed to condensation of structural hydroxyl groups. The material gets converted to the pyrophosphate at temperatures greater than 700°C and the oxide at very high temperatures. The DTA shows two endothermic peaks and one exothermic as shown in Figure (4). The minor endothermic process in 117°C is related to removing of surface water. The second endothermic process in 217°C, respectively, followed by an exothermic peak at 721°C. The third endothermic process occurs in the range 873–981°C. The DTA and TG results indicate a structure similar to amorphous TiP **(Suarez, 1983; Maslova *et al.,* 2012)**.
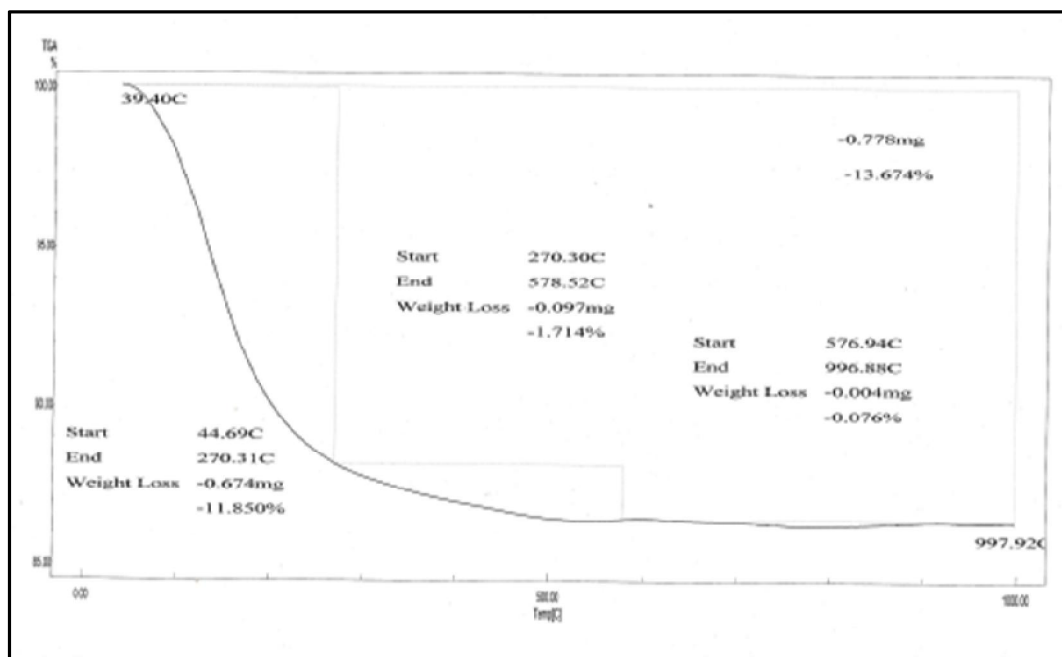
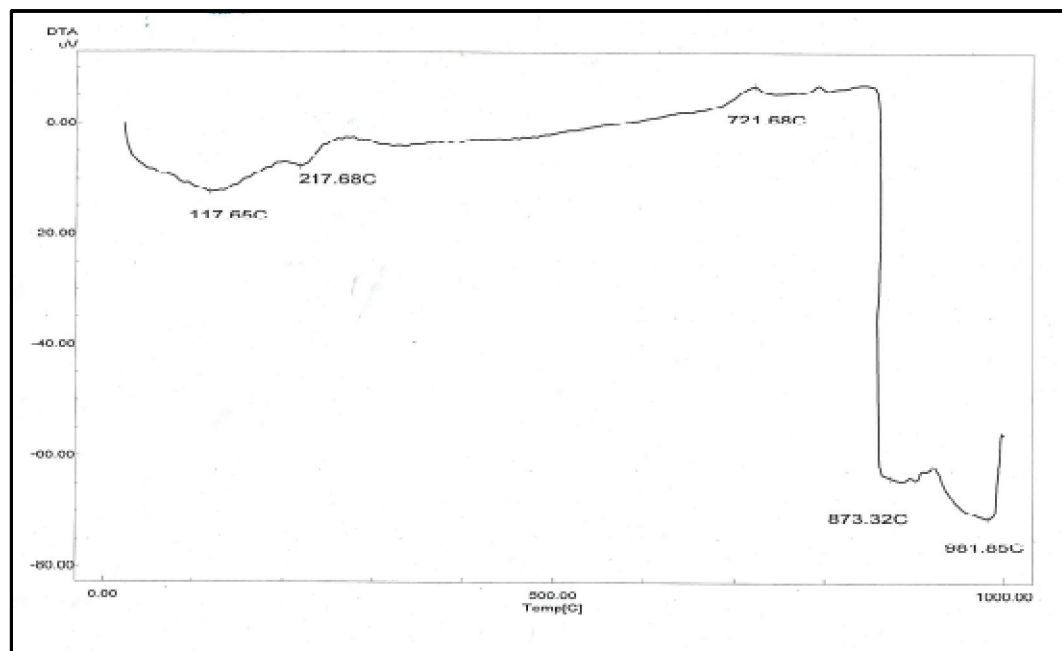**Figure (3): TGA the produced titanium phosphate precipitate.**

Figure (4): DTA the produced titanium phosphate precipitate

1.4. SEM-EDX analysis:

Elemental analysis of the prepared titanium phosphate (TP) precipitate has been performed by ICP-OES. The obtained data shows that the ratio of Ti: P in titanium phosphate precipitate is 1: 1with presence of small portion impurities of iron. SEM EDX analysis was used for further analysis (**Wang *et**

***al.,* 2007; Onoda and Yamaguchi, 2012; Onoda and Fujikado, 2014)**. As can be seen from the SEM micrographs in Figure (5), TP particles have no uniform with amorphous shape. EDX analysis graph determine the weight percent of element present in TP precipitate as shown in Figure (6).

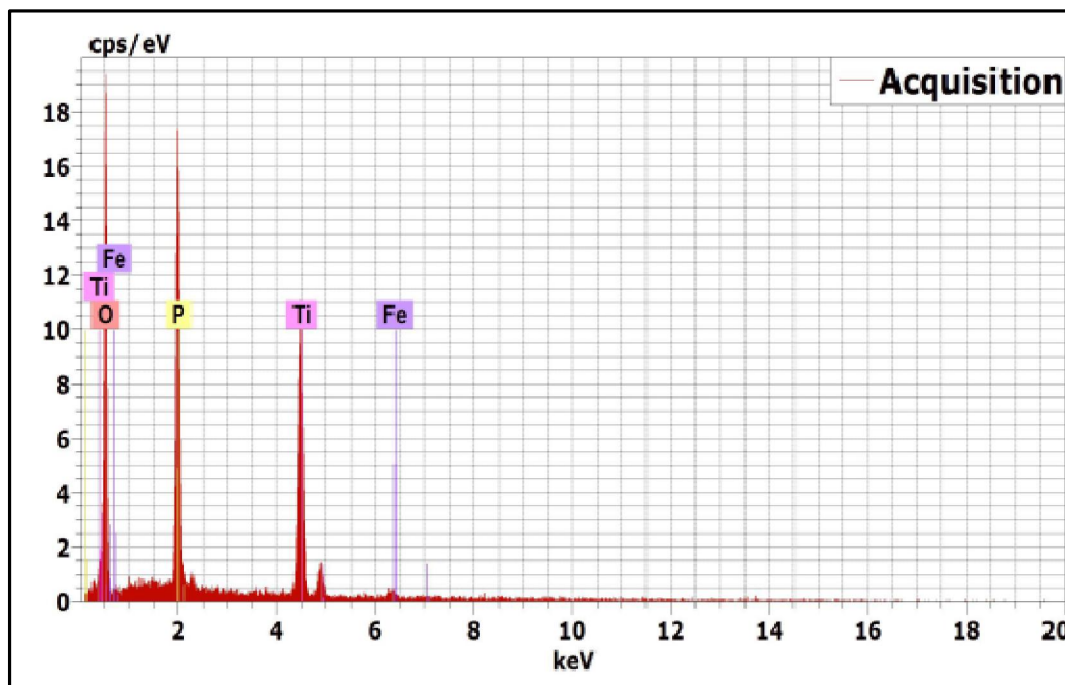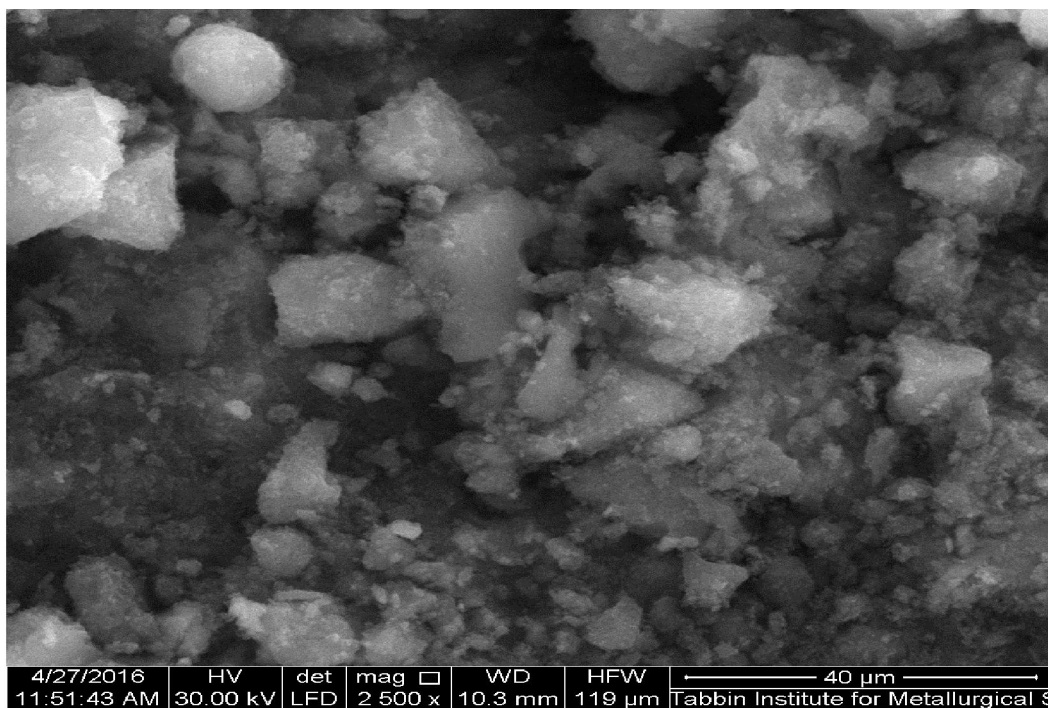**Figure (6): EDX of the produced titanium phosphate precipitate.**

From all previous characterizations and by using **Alberti Torracca formula (1968)**, the TiP formula is TiO (OH) (H_2PO_4).1.3H_2O **(Maheria and Chudasama, 2007)**. Table (1) shows a comparison between the theoretical weight percent and the experimental weight percent in EDX which confirm the chemical formula of produced titanium phosphate precipitate.

Table (1): Comparison between theoretical weight percent and EDX weight percent of titanium phosphate.

| Element	Theoretical Wt.%	Experimental Wt.%	Wt.% difference
Ti	23.79	24.73	0.94
P	15.39	15.66	0.27
O	58.03	58.69	0.66
Fe	0	0.92	0.92

1.5. Chemical resistivity:

Chemically resistivity/stability of prepared titanium phosphate in different solutions media; mineral acids, bases and organic solvent is useful and important while using the material for various applications in varied environments **(Naushad, 2009; Thakkar and Chudasama, 2009)**. Titanium phosphate is found to be stable in acidic medium with maximum limits being (15 N HNO_3, 10 N HCl and 15 N H_2SO_4) and also stable in organic solvent medium (benzene, acetone and ethanol) but not so stable in basic medium with maximum limits being (0.5 N KOH, 5 N NaOH).

1.6. Ion exchange capacity:

The ion-exchange capacity was measured by adapting the method used by **Helen et al. (2007)** 0.5 g of titanium phosphate sample was dispersed in 100 cm3 of 0.1 M NaCl, kept under magnetic stirring for 6 hours. The supernatant liquid was then titrated with 0.15 M NaOH and the ion exchange capacity (IEC) of Na^+ was calculated from the volume of consumed titrant required to reach pH 7 from the equation (1):

$$IEC = \frac{V.C}{W} \qquad (1)$$

Where IEC is the ion exchange capacity (meq/g), V the added NaOH volume when the solution pH was 7 (cm^3), C the molar concentration of NaOH (mol/L), and W the test sample mass (g). IEC can be determined from pH titration curve in Figure (7) (3.3 meq/gm) **(Clearfield, 1988)**;
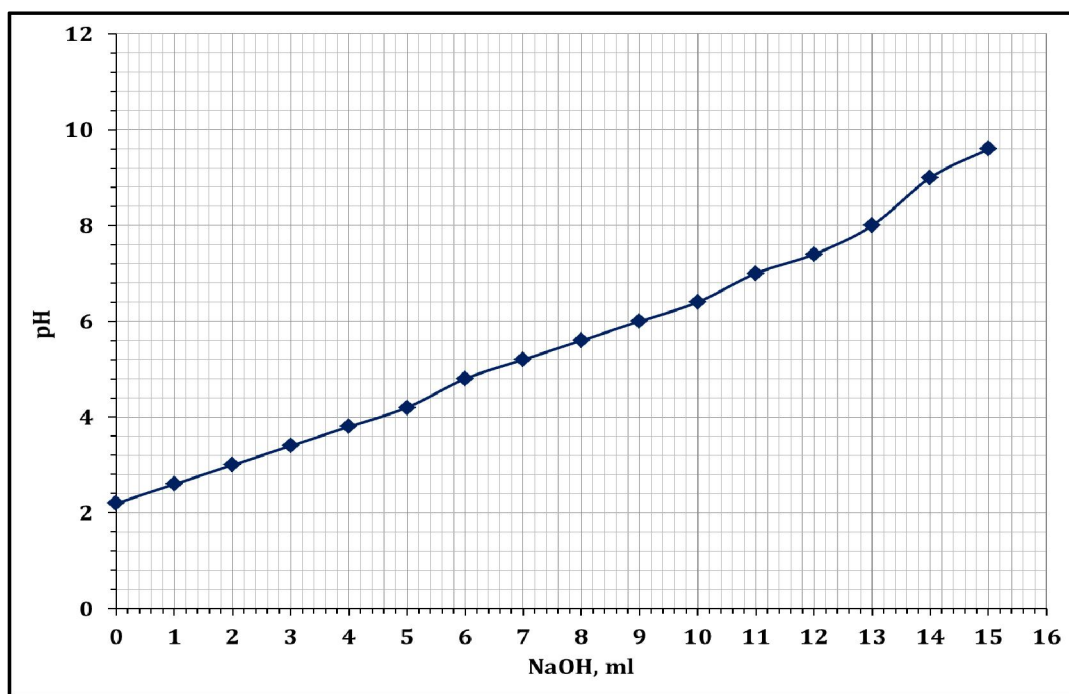
Figure (7): pH titration curve of 0.5 g TiP in 0.1 N NaCl (6 hr) with 0.15 N NaOH.

2. Batch investigation:

The following is a representation of the results obtained for the adsorption of Cu, Pb and Zn ions from aqueous solution using the synthesized titanium phosphate. The effects of reaction time, temperature, solution pH, ion concentration, adsorbent amount of addition, and stirring speed on the adsorption process have been investigated.

2.1. Effect of Reaction Time:

To study the effect of adsorption period on Cu, Pb and Zn ions adsorption from aqueous solutions using titanium phosphate, several experiments were carried at different contact times from 0.25 to 5 hrs at a reaction temperature of 25 °C, stirring speed of 400 rpm, adsorbent amount of addition of 0.5 g/ 100 ml, metal ions concentrations of 500 ppm, and solution pH of 5. The experimental results are given in Figure (8) as a relation between adsorption efficiency % and time.

From the Figure it is clear that, as the mixing time increases from 0.25 to 3.0 hrs, the adsorption percent of Cu, Pb and Zn increased from about 1.0 to 16.2 % for Cu, from about 4.4 to 32.3 % for Pb and from about 0.7 to 7.8 % for Zn. Further increase in the mixing time up to 5 hrs has no effect on the adsorption of Cu, Pb and Zn metal ions. This means that the adsorption equilibrium has reached after 3 hrs. Therefore, 3 hrs represents the preferred time to maximize the Cu, Pb and Zn metal ions adsorption using the synthesized titanium phosphate.
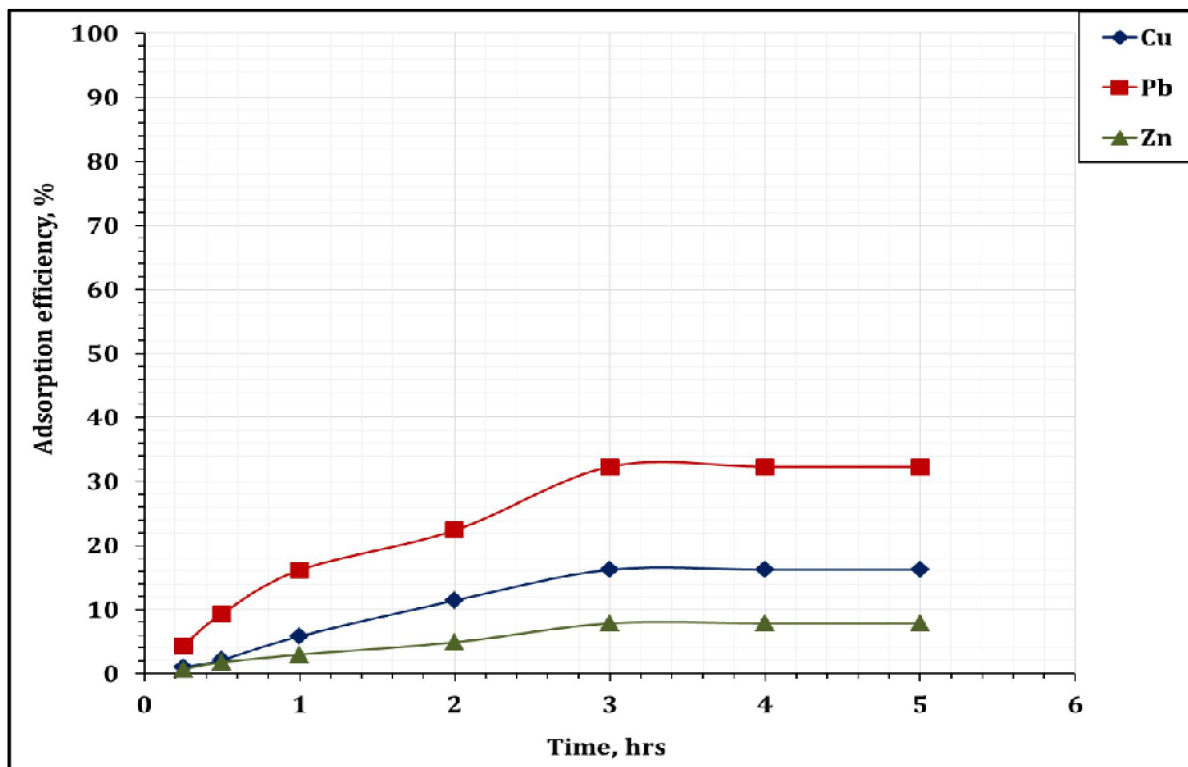

Figure (8): Effect of contact time on the adsorption of Cu (II), Pb (II) and Zn (II) by titanium phosphate.

2.2. Effect of Reaction Temperature:

The adsorption of Cu, Pb and Zn ions by titanium phosphate, at different temperature of 25, 40, 50, 60, 70 and 80 °C was investigated. The sorption experiments were carried out by mixing 0.5 g titanium phosphate with 100 ml of 500 ppm of individual solutions of Cu, Pb and Zn ions for time of 3 hrs at stirring speed of 400 rpm and solution pH of 5. The results are presented in Figure (9) as a relation between Cu, Pb and Zn adsorption % and temperature.

From the obtained data, it can be noticed that, by increase reaction temperature from 25 to 70 °C the Cu,

Pb and Zn adsorption % increased from 17.8 to 28.3 for Cu, from 32.3 to 60.9 for Pb and from 7.8 to 14.1 for Zn. This means that the Cu, Pb and Zn adsorption using titanium phosphate is an endothermic process. Further increase in the reaction temperature up to 80 °C has no effect on Pb adsorption %, while Cu and Zn adsorption % decreased. This may be due to the breaking down of the complex between titanium phosphate and Cu, and Zn however the titanium phosphate-Pb complex has thermal stability at 80 °C. Therefore, temperature 70 °C is the preferred reaction temperature for the Cu, Pb and Zn adsorption process.
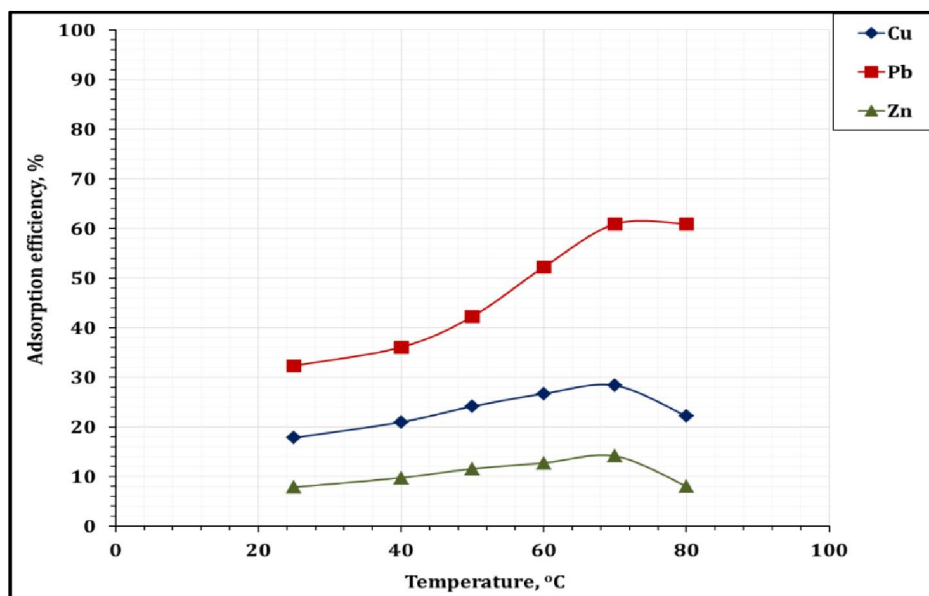
Figure (9): Effect of temperature on the adsorption of Cu (II), Pb (II) and Zn (II) by titanium phosphate.

2.3. Effect of Solution pH:

The effect of solution pH on Cu, Pb and Zn ions process were studied at different solution pH range, from pH 2 to 6 in case of Pb and from pH 2 to 5 in case of Cu and Zn. Other parameters were fixed at an adsorption time of 3 hrs, stirring speed of 400 rpm, temperature of 70 °C, initial ion concentration of 500 ppm, and adsorbent amount of addition of 0.5 g/ 100 ml aqueous solution. The experimental results are graphically presented in Figure (10) as a relation between Cu, Pb and Zn adsorption % and solution pH.

From the results it is clear that; (1) for Cu ions, the adsorption % increased from 22.9 to 26.7 by increase solution pH from 2 to 4, further increase in the solution pH to 5 has negative effect on the Cu adsorption process. (2) For Pb ions, by increase the solution pH from 2 to 6, the adsorption % increased from 28.6 to 70.9. (3) For Zn ions, the adsorption % increased from 13.3 to 17.6 by increase the solution pH from 2 to 3. Further increase in the solution pH has negative effect on the Zn adsorption process. Therefore, further adsorption experiments were conducted with solution pH of 4 for Cu ions, 6 for Pb ions, and of 3 for Zn ions.
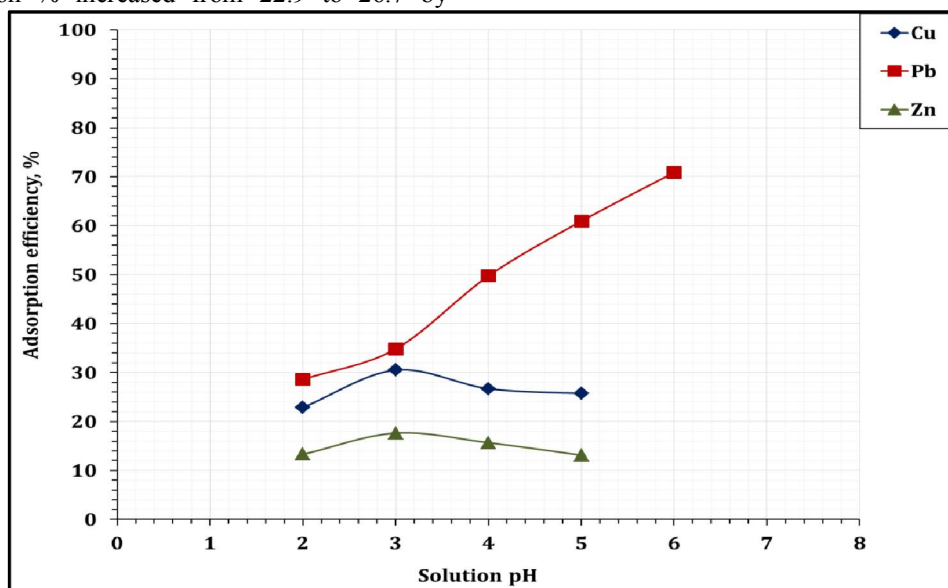

Figure (10): Effect of pH on the adsorption of Cu (II), Pb (II) and Zn (II) by titanium phosphate.

2.4. Effect of Initial Metal Ions Concentration:

To study the effect of initial ion concentration on the adsorption of Cu, Pb and Zn ions adsorption from aqueous solutions using titanium phosphate, several experiments were carried at different ion concentrations from 300 to 700 ppm at a reaction temperature of 70 °C, reaction time of 3 hrs, stirring speed of 400 rpm, adsorbent amount of addition of 0.5 g/ 100 ml. The experimental results are given in Figure (11) as a relation between adsorption efficiency % and initial ion concentration.

From the Figure it is clear that, as the initial ion concentrations increases from 300 to 500 ppm, the adsorption percent of Cu, Pb and Zn increased from about 24.9 to 30.7 % for Cu, from about 51.2 to 61.0 % for Pb and from about 13.1 to 18.0 % for Zn. Further increase in the initial concentration has slightly effect on the adsorption percent. Therefore, further adsorption experiments are conducted at Cu, Pb and Zn ions initial concentration of 500 ppm.
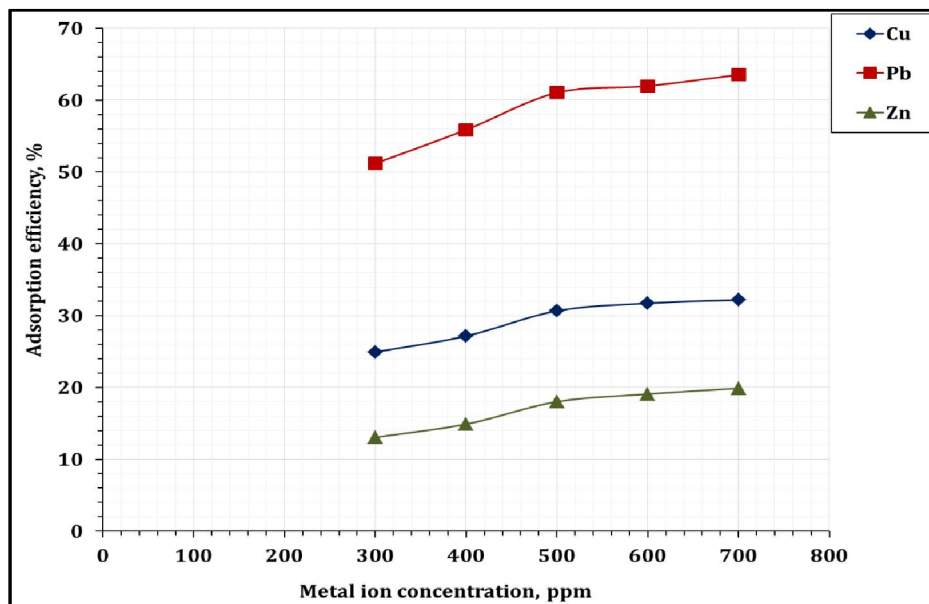

Figure (11): Adsorption of Cu (II), Pb (II), and Zn (II) at different initial concentrations.

2.5. Effect of Adsorbent Amount of Addition:

Optimum ratio of the quantity of adsorbent of titanium phosphate to Cu, Pb, and Zn aqueous solutions was determined in terms of the adsorbent amount of addition in the range of 0.4 to 1.0 g titanium phosphate/ 100 ml of Cu, Pb, and Zn individual aqueous solution, temperature of 70 °C, stirring speed of 400 rpm, and reaction time of 3 hrs. The results are presented graphically given in Figure (12) as a relation between Cu, Pb, and Zn adsorption % and adsorbent amount of addition.

The obtained results indicate that, as the titanium phosphate amount of addition increases from 0.4 g to 0.8 g/ 100 ml the adsorption percent of Cu and Pb ions increased from about 21.9 to 51.5 for Cu, from about 63.4 to 90.8 % for Pb. The titanium phosphate amount of addition increases from 0.4 g to 0.7 g/ 100 ml the adsorption percent of Zn ions increased from about 15.7 to 21.6 % for Zn. The increase in the adsorbent amount of addition has a slightly effect on Cu, Pb, and Zn adsorption %. 0.8 g titanium phosphate/ 100 ml aqueous solution is the choice ratio for Cu, Pb adsorption process and 0.7 g titanium phosphate/ 100 ml aqueous solution is the choice ratio for Zn adsorption process.

2.6. Effect of Mixing Stirring Speed:

Several sorption experiments were performed using titanium phosphate with different stirring speed ranging from 200 to 600 rpm and reaction time of 3 hrs, adsorbent amount of addition of 0.8 g/ 100 ml of individual aqueous solutions for Cu, Pb ions, 0.7 g/ 100 ml of individual aqueous solutions for Zn ions and temperature 70 °C to study the effect of mechanical stirring speed on the Cu, Pb, and Zn adsorption process.

The experimental results are given Figure (13) as a relation between Cu, Pb, and Zn adsorption % and stirring speed. As can be seen in Figure (13), by increase mixing stirring speed from 200 to 600 rpm the Cu, Pb, and Zn adsorption % increased slightly from 48.6 to 55.3 for Cu, from 87.0 to 93.2 for Pb and from 17.6 to 21.6 for Zn. Accordingly all experiments were carried out using a mixing speed of 400 rpm.

9
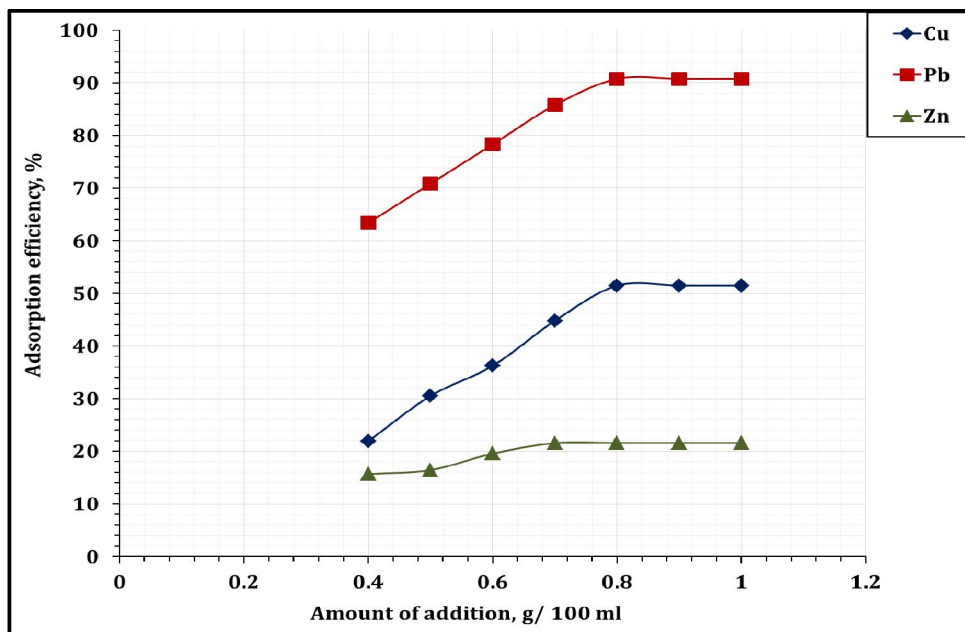
Figure (12): Adsorption of Cu (II), Pb (II), and Zn (II) at different amount of addition of titanium phosphate.
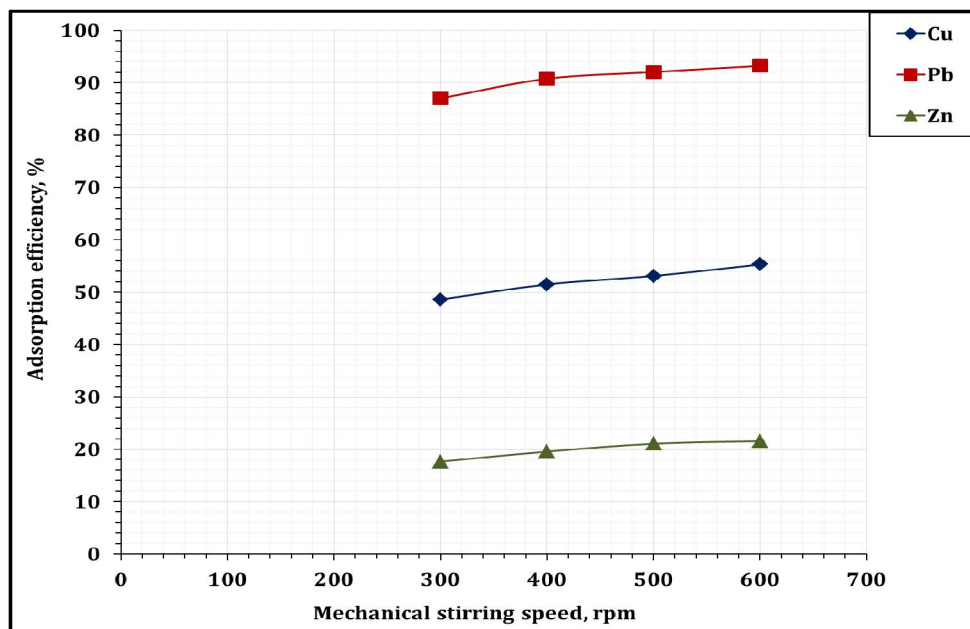
Figure (13): Adsorption of Cu (II), Pb (II), and Zn (II) by titanium phosphate at different stirring speed.

3. Adsorption Kinetic Modeling and Thermodynamics:

The mathematical treatment for the obtained results of Cu, Pb, and Zn ions adsorption from aqueous solution using synthesized titanium phosphate has been achieved for understanding and developing large scale adsorption process. In this concern, the thermodynamics and dynamics parameters of the Cu, Pb, and Zn ions adsorption process were calculating.

3.1. Adsorption kinetic modeling:

Modeling adsorption with isotherms allows for a better understanding of the factors that affect equilibrium and maximum adsorption capacity for a particular system. However, equilibrium isotherms do not provide information about the time response or kinetics of the system. An understanding of adsorption kinetics is important to system design parameters such as residence time, which dictate the physical size and flow rates for many unit operations. The kinetics of

physical and chemical reactions can be described by a series of models including: pseudo-first order model, pseudo-second order model, Elovich model and Morris-Weber model.

3.1.1. Pseudo-first-order model:

The kinetics of adsorption was analyzed by the Lagergren pseudo-first-order equation as depicted in equation (2):

$$\text{"}dq_t\text{"} / \text{"}dt\text{"} \text{"}= K_{p1} (q_e - q_t)\text{"} \quad \dotsc\dotsc (2)$$

Where: q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t (min), respectively. Kp1 (min^{-1}) is the pseudo-first-order rate constant for the kinetic model. Integrating equation (3) with the boundary conditions of q_t=0 at t=0 and q_t =q_t at t=t, yields **(Ho, 2004)**.

$$\log (q_e - q_t) = \log q_e - \frac{K_{p1}}{2.303} t \quad \dotsc\dotsc (3)$$

Based on experimental results, linear plot of log (q_e-q_t) versus t was tested the applicability of Lagergren first order equation to the adsorption of organic matter **(Lagergren, 1898)**. The rate constant was calculated from the slope.

3.1.2. Pseudo-second-order model:

The pseudo-second order equation **(Ho and McKay, 2000)** is depicted as follows;

$$\text{"}dq_t\text{"} / \text{"}dt\text{"} \text{"}= k_2 (q_e - q_t)^2\text{"} \quad \dotsc\dotsc (4)$$

Where k_2 is the rate constant of pseudo second-order adsorption (g mg^{-1} min^{-1}). For the boundary conditions t = 0 to t = t and q_t = 0 to q_t = q_t, the integrated form of equation (4) becomes:

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \quad \dotsc\dotsc (5)$$

The plot of (t/q_t) versus t of equation (5) should give a linear relationship from which q_e and k_2 were determined from the slope and intercept of the plot, respectively.

3.1.3. Elovich kinetic model:

The Elovich model equation is generally expressed as:

$$\frac{dq_t}{dt} = \alpha \, t^{-\beta q_t} \quad \dotsc\dotsc (6)$$

Where $\alpha\ell$ is the initial adsorption rate (mg min^{-1}) and β is related to the extent of surface coverage and the activated energy for chemisorption (g mg^{-1}).

Integrating this equation for the boundary conditions gives equation (7):

$$q_t = \frac{1}{\beta} \ln (\alpha\beta) + \frac{1}{\beta} \ln t \quad \dotsc\dotsc (7)$$

The Elovich equation has been shown to be useful in describing chemisorption on highly heterogeneous adsorbents. The initial adsorption rate α and the extent of coverage β were calculated from the slope and the intercept of the plot of q_t against lnt, respectively.

3.1.4. Intra-particle Diffusion-Controlled Adsorption (Morris-Weber model):

To investigate the internal diffusion mechanism during the adsorption of metal ions onto chitosan, the intra-particle diffusion equation has been used, considering that adsorption is usually controlled by an external film resistance and/or mass transfer is controlled by internal or intra-particle diffusion **(Gerente et al., 2007)**. For adsorption onto spherical particles with constant diffusion coefficient, **Crank (1970)** proposed the following equation (8):

$$q_t = k_i \, t^{0.5} \quad \dotsc\dotsc (8)$$

The coefficient k_i is determined from the initial linear slope of q_t versus (time) $^{0.5}$.

According to **Weber and Morris (1963)**, if the intra-particle diffusion is the rate-limiting step in the adsorption process, the graph of q_t vs. $t^{0.5}$ should yield a straight line passing through the origin. **McKay and Allen (1980)** suggested that three linear sections on the plot q_t vs. $t^{0.5}$ can been identified. That means that two or three steps can occur. The first portion represents external surface adsorption or an instantaneous adsorption stage.

The second portion is a gradual adsorption stage, where the intra-particle diffusion is the controlling factor. The third portion is a final equilibrium stage where the intra-particle diffusion starts to decelerate due to extremely low solute concentrations in the solution **(Wu et al., 2001)**.

Table (2): Kinetic models for evaluating experimental data.

Model	Plots
Lagergren Pseudo-first-order model	log $(q_e - q_t)$ versus t
Pseudo-second-order model	(t/q_t) versus t
Elovich kinetic model	q_t versus ln t
Morris-Weber model	q_t versus $t^{0.5}$

To identify the rate-controlling mechanisms during the adsorption of Cu, Pb, and Zn ions from aqueous solutions onto titanium phosphate, three steps were considered: **(I)** Mass transfer of the metal ions from the bulk aqueous solution to the adsorbent surface, **(II)** Adsorption of the Cu, Pb, and Zn ions onto the titanium phosphate, and **(III)** Internal diffusion of the metal ions onto titanium phosphate.

For this purpose, simplified models were applied to evaluate the experimental batch data for each metal ion as shown in Table (2). The goodness of the fit was estimated in terms of the coefficient of determination, R^2.

In this respect, the experimental results obtained in Figure (8) were used to calculate the difference model functions; q_t, (log ($q_e - q_t$)), and (t/q_t), as shown in Tables (3-5) for Cu, Pb, and Zn metal ions respectively according to the following equation (9):

$$q_e = (C_o - C_e) \times \frac{V}{m} \qquad \ldots\ldots (9)$$

Where C_o and C_e are the initial and equilibrium concentrations of the uranium (mg/L), respectively, V is the volume of the aqueous phase (L), and m is the weight of the clay used (g).

Table (3): The values of qt, (log (qe − qt)), and (t/qt) for Cu metal ion relative to the time values.

Time, min	$t^{1/2}$	C_e, ppm	q_t	log (q_e-q_t)	t/q_t
15	3.87	495.1	0.98	1.183	15.30
30	5.48	489.3	2.14	1.148	14.02
60	7.75	470.9	5.82	1.017	10.31
120	11.00	442.9	11.42	0.681	10.51
180	13.40	418.9	16.22	-	11.09
240	15.50	418.9	16.22	-	14.79
300	17.30	418.9	16.22	-	18.49

Table (4): The values of qt, (log (qe − qt)), and (t/qt) for Pb metal ion relative to the time values.

Time, min	$t^{1/2}$	C_e, ppm	q_t	log (q_e-q_t)	t/q_t
15	3.87	478.1	4.38	1.4462	3.424
30	5.48	453.3	9.34	1.3614	3.212
60	7.75	419.2	16.16	1.2084	3.712
120	11.00	388.1	22.38	0.9974	5.361
180	13.40	338.4	32.32	-	5.569
240	15.50	338.4	32.32	-	7.425
300	17.30	338.4	32.32	-	9.282

Table (5): The values of qt, (log (qe − qt)), and (t/qt) for Zn metal ion relative to the time values.

Time, min	$t^{1/2}$	C_e, ppm	q_t	log (q_e-q_t)	t/q_t
15	3.87	496.5	0.7	0.8537	21.429
30	5.48	491.1	1.78	0.7825	16.854
60	7.75	485.2	2.96	0.6884	20.270
120	11.00	475.5	4.9	0.4683	24.490
180	13.40	460.8	7.84	-	22.959
240	15.50	460.8	7.84	-	30.612
300	17.30	460.8	7.84	-	38.265

The plots of Lagergren Pseudo-first-order model, Pseudo-second-order model, Elovich kinetic model, and Morris-Weber model for Cu, Pb, and Zn metal ions adsorption from aqueous solutions using titanium phosphate have been illustrated in Figures (14-17). From the Figures a linear relationship was obtained and the Parameters of kinetic models with the linear correlation coefficients (R^2) of each plot are listed in Table (6).
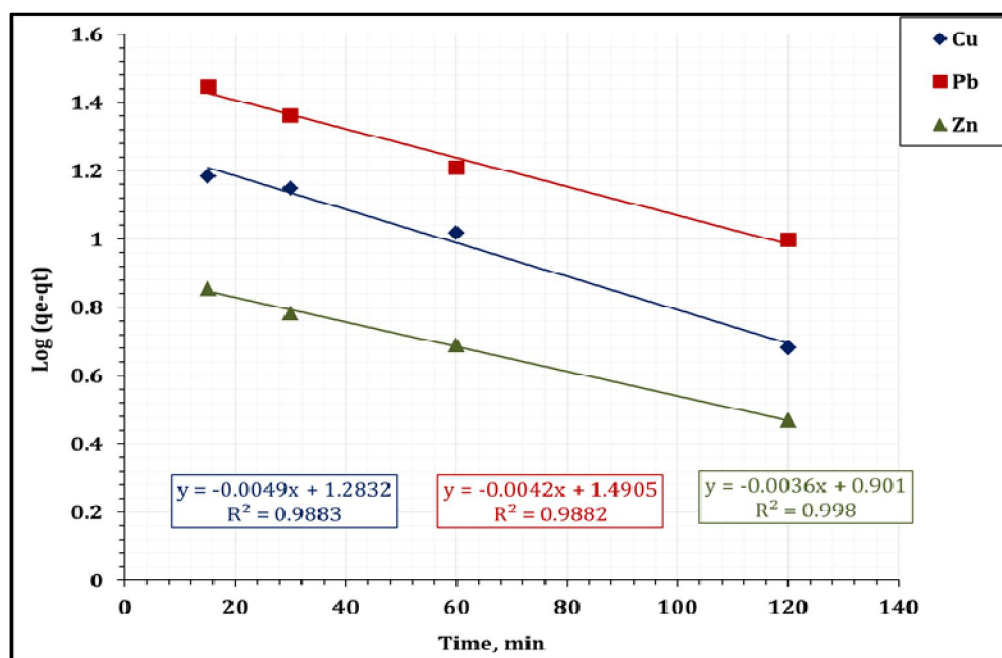
Figure (14): Langergren first-order model plot for Cu, Pb, and Zn metal ions adsorption from aqueous solutions using titanium phosphate.
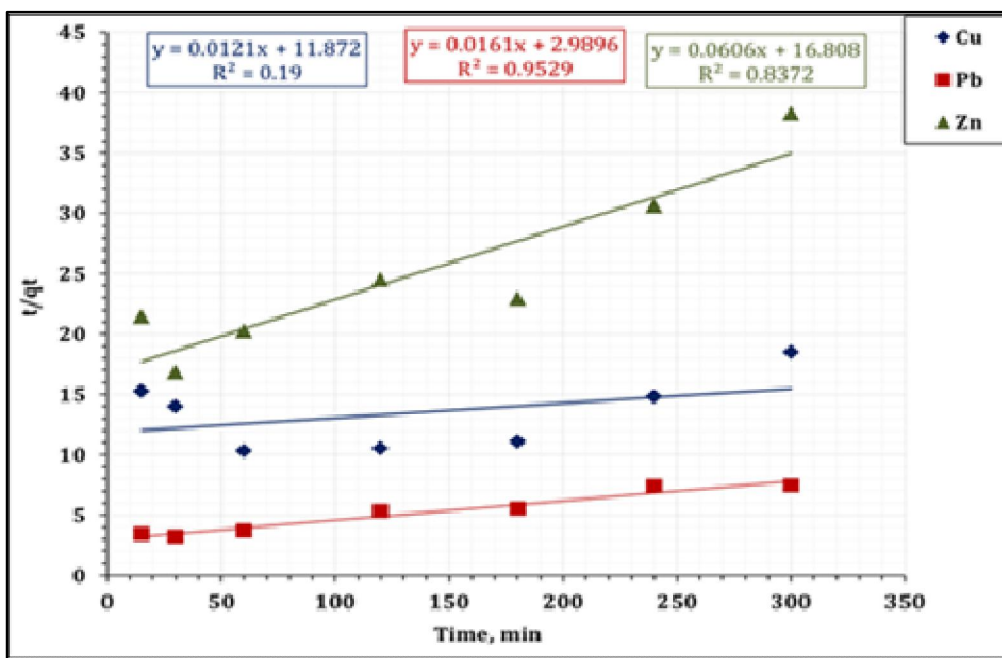

Figure (15): Pseudo second-order model plot for Cu, Pb, and Zn metal ions adsorption from aqueous solutions using titanium phosphate.
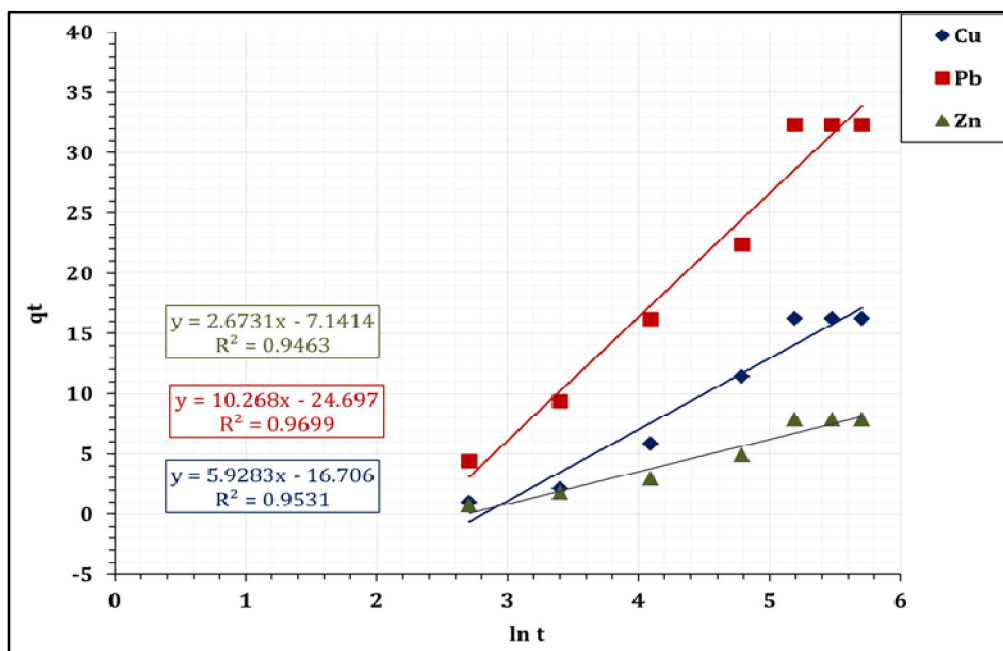
Figure (16): Elovich model plot for Cu, Pb, and Zn metal ions adsorption from aqueous solutions using titanium phosphate.
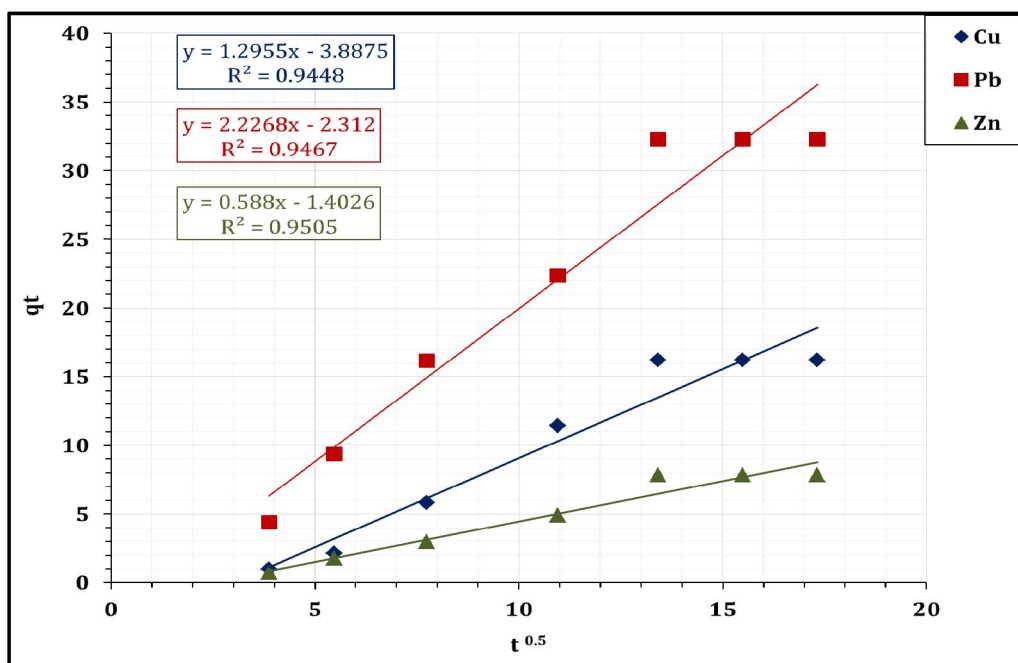
Figure (17): Morris-Weber model plot for Cu, Pb, and Zn metal ions adsorption from aqueous solutions using titanium phosphate.

From the results shown in Figures (14- 17) and Table (6), it is clear that the Lagergren first order model give straight-line plots for Cu, Pb, and Zn metal ions adsorption using titanium phosphate with an average correlation coefficient of 0.98, in addition the calculated values of q_e are close from the experimental q_e values. This means that the kinetic of the adsorption process for Cu, Pb, and Zn metal ions will follow this model **(Grbowska and Gryglewicz, 2007)**.

Table (6): The calculated parameters of the kinetic models with the linear correlation coefficients (R^2) of each plot.

		Cu	Pb	Zn
Lagergren pseudo first model	K_1 (min^{-1})	0.011	0.010	0.008
	$q_e$cal (mg/g)	19.20	30.94	7.96
	$q_e$exp (mg/g)	16.22	32.32	7.84
	R^2	0.98	0.98	0.99
Pseudo second model	K_1 (g. min^{-1}. mg^{-1})	0.00001	0.0001	0.0002
	$q_e$cal (mg/g)	82.64	62.11	16.50
	$q_e$exp (mg/g)	16.22	32.32	7.84
	R^2	0.19	0.95	0.83
Elovich kinetic model	α (mg. min^{-1})	-3.81E-09	-0.0001	-0.001
	β (mg/g)	-88.50	-103.09	-120.48
	R^2	0.98	0.98	0.99
Morris-Weber model	K_i (min^{-1})	1.30	2.23	0.59
	R^2	0.95	0.95	0.95

The pseudo second-order model gives straight-line plot for Pb, metal ion adsorption using titanium phosphate however, Cu, and Zn metal ions did not give good straight-line plots. Moreover, by comparing the calculating q_e values for the second order models with the experimental value of $q_e$it is found that the calculated q_e values are dramatically differ than the experimental q_e values for Cu, Pb, and Zn metal ions which confirm that the adsorption process is not follow the pseudo-second order model. Based on the results obtained in Table (6), it is clear that the affinity of titanium phosphate for Cu, Pb, and Zn metal ions adsorption is followed the order: Pb > Cu > Zn.

The Elovich model gives straight-line plot for Cu, Pb, and Zn metal ions adsorption using titanium phosphate with an average correlation coefficient of 0.98, which indicated that the adsorption process confirm to the Elovich model. However, the negative values for α and β in the Elovich model suggested that the sorption process is not follow Elovich model.

It has previously been pointed out that the intra-particle diffusion model can present multilinearity, and three stages can be distinguished **(Wu *et al.*, 2001)**. The plot corresponding to Cu, Pb, and Zn metal ions adsorption from aqueous solution using titanium phosphate Figures (14- 17) does not show the stage corresponding to the diffusion of the metal ions through the external film. This suggests that the stirring was strong enough to eliminate this resistance.

3.2. Adsorption Thermodynamics:

The proper assessment of the thermodynamic parameters is considered important to determine the effect of temperature on the adsorption capacity, and to provide information regarding the effect of adsorption process on the inherent energy and structure changes of the adsorbent **(Anirudhan and Radhakrishnan, 2009)**. The thermodynamic parameters of Cu, Pb, and Zn metal ions adsorption from aqueous solution using titanium phosphate were determined from the temperature dependent distribution coefficient using Van't Hoff equation (10) of **(Srinivasan *et al.*, 1997)**.

$$\log k_d = -\frac{\Delta H}{2.303 \, R} \times \frac{1}{T} + C \qquad \ldots\ldots (10)$$

Where ΔH is the enthalpy change (KJ/mol), R the universal gas constant (8.314 J/mol K), T is the absolute temperature (K) and $K_d$is the distribution coefficient of Cu, Pb, and Zn metal ions adsorption, between the aqueous bulk phase and the solid phase.

In this respect, the experimental results obtained in Figure (9) were used to calculate the distribution coefficient (K_d), as shown in Tables (7-9) according to the following equation (11):

$$k_d = \frac{C_o - C_e}{C_e} \times \frac{V}{m} \qquad \ldots\ldots (11)$$

Table (7): The values of Kd for Cu metal ion relative to the temperature values.

Temperature, $^\circ$C	1000/ T, ^{o}K	C_e, ppm	K_d	log K_d
25	3.35	495.1	0.035	1.551
40	3.19	489.3	0.041	1.622
50	3.09	470.9	0.048	1.683
60	3.00	442.9	0.053	1.727
70	2.91	418.9	0.056	1.753

Table (8): The values of Kd for Pb metal ion relative to the temperature values.

Temperature, °C	1000/ T, °K	C_e, ppm	K_d	log K_d
25	3.35	478.1	0.064	1.810
40	3.19	453.3	0.072	1.858
50	3.09	419.2	0.084	1.926
60	3.00	388.1	0.104	2.018
70	2.91	338.4	0.121	2.085

Table (9): The values of Kd for Zn metal ion relative to the temperature values.

Temperature, °C	1000/ T, °K	C_e, ppm	K_d	log K_d
25	3.35	496.5	0.015	1.195
40	3.19	491.1	0.019	1.290
50	3.09	485.2	0.023	1.363
60	3.00	475.5	0.025	1.406
70	2.91	460.8	0.028	1.450

According to van't Hoff equation, the relation between log K_d and 1/T for Cu, Pb, and Zn metal ions adsorption investigation will give straight lines from which the enthalpy change, ΔH, can be calculated as shown in Figure (18). From the Figure straight lines with an average linear correlation coefficient (R^2) of 0.99 were obtained. The adsorption enthalpy change, ΔH, for Cu, Pb, and Zn metal ions were calculated from the slope of the straight line and given in Table (10).
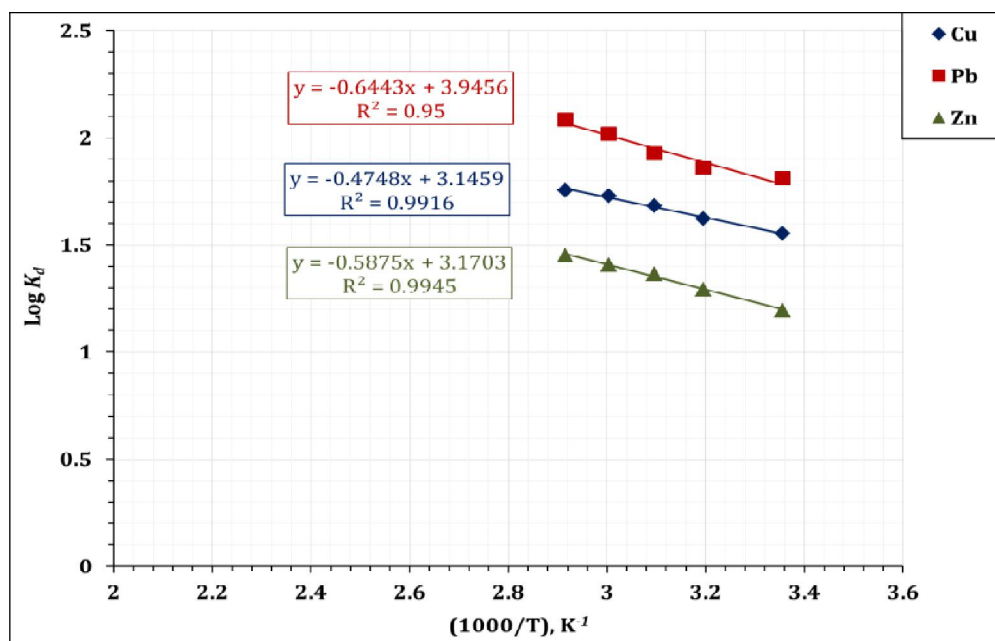

Figure (18): Variation of log Kd with 1/T for Cu, Pb, and Zn metal ions adsorption from aqueous solutions using titanium phosphate.

The Gibbs free energy change, Δ G was also calculated based on the logarithmic value of the distribution ratio Log K_d at the investigation temperature range 25 – 70 °C according to the following equation (12):

$-ΔG = 2.303 RT \log k_d$…… (12)

Also, the entropy change, ΔS was obtained from ΔG and ΔH with the following equation (13):

$ΔG = ΔH – T ΔS$…… (13)

The thermodynamic parameters of the adsorption of Cu, Pb, and Zn metal ions from aqueous solutions using titanium phosphate (25 – 70 ±1 °C) are given in Table (10).

Table (10): Thermodynamic parameters for Cu, Pb, and Zn metal ions adsorption from aqueous solutions using titanium phosphate.

	ΔG (kJ/ mol)						ΔH	ΔS
	25 °C	40 °C	50 °C	60 °C	70 °C	(kJ/ mol)	(kJ/ mol)	(J/ mol K)
Cu	-8.86 ± 0.2	-9.73 ± 0.1	-10.41 ± 0.3	-11.01 ± 0.2	-11.52 ± 0.2	3.52 ± 0.2	9.09 ± 0.3	60.22 ± 0.2
Pb	-10.33 ± 0.1	-11.14 ± 0.2	-11.92 ± 0.2	-12.87 ± 0.3	-13.70 ± 0.1	2.69 ± 0.3	12.33 ± 0.5	76.06 ± 0.1
Zn	-6.82 ± 0.4	-7.73 ± 0.3	-8.44 ± 0.2	-8.97 ± 0.4	-9.53 ± 0.4	2.69 ± 0.3	11.24 ± 0.2	60.63 ± 0.4

From the results obtained in Table (10) it is clear that, the enthalpy change (ΔH) for the adsorption process using titanium phosphate have positive sign which means that the adsorption process is endothermic process. The sign of the enthalpy change (ΔH) associated with the sorption process will consist of (1) enthalpy change for dehydration (ΔH_d) which can be expected to be positive because energy is required to break the ion–water and water–water bonding of the hydrated metal ions, and (2) enthalpy change for complexing (ΔH_c) which will make ΔH more negative due to the formation of metal complex **(Yang et al., 2010)**.

The positive ΔH value obtained for Cu, Pb, and Zn metal ions adsorption clears that the dehydration looks to be more significant than complexation in the adsorption system. The values of the enthalpy change (ΔH) for the adsorption process were less than 40 kJ/mol for Cu, Pb, and Zn which indicate that the adsorption process for Cu, Pb, and Zn metal ions was controlled by physical mechanism **(Yang et al., 2010)**.

Gibbs free energy change (ΔG) values for temperature range of 298–343 K were found to be negative which mean that the adsorption of Cu, Pb, and Zn metal ions from aqueous solution using titanium phosphate is feasible and spontaneous process. The higher the reaction temperature, the more negative the value of ΔG, indicating that the adsorption reaction is more favorable at higher temperatures.

This behavior could be as a result of that by increase the temperature, the mobility of metal ions in the solution increase and also the affinity of the adsorbate onto titanium phosphate increase (**Ding et al., 2012**). The absolute values of ΔG for Cu, Pb, and Zn ions adsorption onto titanium phosphate were smaller than 20 kJ mol^{-1}, which mean that the adsorption process is consistent with physisorption process **(Horsfall and Spiff, 2005)**.

The positive values of the standard entropy change ($\Delta S°$) for Cu, Pb, and Zn metal ions adsorption process indicate that the degrees of randomness increased at the solid-liquid interface with some structural changes at the adsorbent-adsorbate interface which confirming a physical adsorption process

(Horsfall and Spiff, 2005). The thermodynamic parameters showed that the Cu, Pb, and Zn metal ions adsorption from aqueous solution using titanium phosphate was feasible, spontaneous and endothermic process.

5. Conclusions

In this study, the adsorption of Cu, Pb, and Zn metal ionsfrom aqueous solutions, using titanium phosphate produced from Abu-Tartur phosphoric acid was investigated. Results indicate that Cu, Pb, and Zn metal ions adsorption removal on synthesized titanium phosphate was considerably affected by different factors such as: temperature, Cu, Pb, and Zn metal ions concentration, adsorption reaction time, solution pH, mixing stirring speed and weight of adsorbent. The adsorption process increased with increasing time, weight of adsorbent, temperature and mixing stirring speed. The experimental data were tested for different kinetic model expressions and the data were successfully modeled. The thermodynamics analysis for the Cu, Pb, and Zn metal ions adsorption results showed that the endothermic behavior of the process and the thermodynamics parameters (ΔH, ΔG and ΔS) were calculated.

References
1. Alberti G., Costantino U., and Luciani M. L., (1980): Crystalline insoluble acid salt of tetravalent metals. XXXII. Comparison of ion-exchange properties of crystalline a-zirconium phosphate and a-titanium phosphate, Gazz. Chim. It., 110, 61.
2. Alberti G., Giammari G., and Grassini-Strazza G., (1967): Chromatographic behaviour of inorganic ions on crystalline titanium phosphate and zirconium phosphate thin layers, J. Chromatogr., 28, 118–123.
3. Alberti G., and Grassiani G., (1960): Chromatography on paper impregnated with zirconium phosphate, J. Chromatogr.,4, 83–85.
4. Alberti G., Torracca E., (1968): Crystalline insoluble salts of polyvalent metals and polybasic acids-VI. Preparation and ion exchange

properties of crystalline titanium arsenate, J. Inorg. Nucl. Chem. 30: 3075-3080.

5. Amphlett C. B., (1964): Inorganic ion exchangers, Elsevier.

6. Anirudhan T.S., Radhakrishnan K., (2009): Kinetics, thermodynamics and surface heterogeneity assessment of uranium (VI) adsorption onto cation exchange resin derived from a lignocellulosic residue, Appl. Surf. Sci.; 255: 4983–4991.

7. Bortun A. I., Bortun L. N., Clearfield A., Khainakov S. A., Strelko V. V., Khryashevskii V. N., Kvashenko A. P., and Voitko I. I., (1997): Synthesis and characterization and ion exchange properties of spherically granulated titanium phosphate, Solv. Extr. Ion Exch., 15, 515–532.

8. Clearfield A., (1995): Inorganic ion exchangers: A technology ripe for development, Ind. Engng Chem. Res., 34,2865–2872.

9. Clearfield A., (1988): Role of ion exchange in solid-state chemistry, Chem Rev., 88, pp 125–148.

10. Clearfield A., (1982): Inorganic ion exchange materials, CRC Press, Boca Raton, Florida.

11. Clearfield A., Bortun A. I., Khainakov S. A., Bortun L. N., Strelko V. V., and Khryascherskii V. N., (1998): Spherically granulated titanium phosphate as exchanger for toxic heavy metals, Waste Mgmt, 18, 203–210.

12. Clearfield A., Nancollas G. H., and Blessing R. H., (1973): New inorganic ion exchangers, in Solvent extraction and ion exchange (J. H. Marinsky and Y. Marcus, eds), Dekker, Vol. 5.

13. Crank J., (1970): Mathematics of Diffusion, Clarendon Press, Oxford.

14. Deans J. R., and Dixon B. G., (1992): Uptake of Pb^{2+} and Cu^{2+} by novel biopolymers, Wat. Res., 26, 463–468.

15. Ding L., Deng H., Wu C., Han X., (2012): Affecting factors, equilibrium, kinetics and thermodynamics of bromide removal from aqueous solutions by MIEX resin, Chem. Eng. J. 181–182:360–370.

16. Egorov E. V., and Makarova S. B., (1971): Ion exchange in radiochemistry, Atomizdat, Moscow.

17. Gerente C., Lee VKC., Cloirec PL., McKay G., (2007): Application of Chitosan for the Removal of Metals from Wastewaters by Adsorption - Mechanisms and Models Review. Crit. Rev. Environ. Sci. Technol. 37:41-127.

18. Grabowska L., Gryglewicz G., (2007). Adsorption characteristics of Congo Red on coal-based mesoporous activated carbon. Dyes Pigm. 74: 34-40.

19. Helen M., Viswanathan B., Srinivasa S.M., (2007): Synthesis and characterization of composite membranes based on α-zirconium phosphate and silicotungstic acid, J. Membr. Sci. 292, 98-105.

20. Horsfall M., Spiff A., (2005): Effect of temperature on the sorption of Pb^{2+}, and Cd^{2+}, from aqueous solution by caladium bicolor (wild cocoyam) biomass, Election. J. Biotechnol., 8:162-169.

21. Ho YS., (2004): Citation review of Lagergen kinetic rate equation on adsorption reactions. Scientomet 59:171-177.

22. Ho Y.S., McKay G., (2000): The kinetics of sorption of divalent metal ions onto sphagnum moss peat. Water Research, 34(3):735-742.

23. Jia K., Pan B., Zhang Q., Zhang W., Jiang P., Hong C., Pan B., Zhang Q., (2008): Adsorption of Pb^{2+}, Zn^{2+}, and Cd^{2+} from waters by amorphous titanium phosphate, Journal of Colloid and Interface Science 318, 160–166.

24. Kharchenko R. S., Bortun A. I., Khainakov S. A., and Voitko I. I., (1990): Lead and iron cations sorption by inorganic exchangers. Sov. Progr. Chem., 56, 41.

25. Kobayashi E., (1979): Studies of inorganic ion exchangers III. Ion exchange properties of Ti $(HPO_4)_2$. $0–1/2$ H_2O to alkali metal and ammonium ions, Bull. Chem. Soc. Jap., 52, 1351–1358.

26. Kraus K. A., Phillips H. O., Carlson T. A., and Johnson J. S., (1958): Ion-exchange properties of hydrous oxides, Proc. U.N. Int. Conf. Peaceful Uses of Atomic Energy, Geneva, Paper no. 15/P/1832, United Nations, Vol.28, pp. 3–16.

27. Lagergren S., (1898): Adsorption gelosterstoffe, Kungliga Svenskavetenskapsakademiens. Handlingar 24:1-39.

28. Ludmány A., Kurek S., Stokłosa A., Wilczy´nski G., Wójtowicz A., Zajecki J., (2004): morphous titanium hydrogenphosphate—an inorganic sorbent and a catalyst, Applied Catalysis A: General 267, 149–156.

29. Maheria K., Chudasama U., (2006): Studies on kinetics, thermodynamics and sorption characteristics of an inorganic ion exchanger— Titanium phosphate towards Pb (II), Bi (III) and Th (IV), J. Indian Inst. Sci., 86, 515–525.

30. Maheria K., Chudasama U., (2007): Synthesis and characterization of a new phase of titanium phosphate and its application in separation of metal ions, Indian Journal of Chemical Technology, Vol. 14, pp 423–426.

31. Marie J., (1968): Preparation of Titanium Phosphate, U.S. Patent No. 3,418,075.

32. Maslova M.V., Rusanova D., Naydenov V., Antzutkin O.N., Gerasimova L.G., (2012): Extended study on the synthesis of amorphous titanium phosphates with tailored sorption properties, Journal of Non-Crystalline Solids 358, 2943–2950.

33. McKay G., and Allen S. J., (1980): Surface Mass Transfer Processes using Peat as an adsorbent for dyestuffs, Can. J. Chem. Eng. 58, pp. 521.

34. Möller T., (2002): Selective crystalline inorganic materials as ion exchangers in the treatment of nuclear waste solutions, Academic Dissertation, University of Helsinki, Finland.

35. Naushad Mu., (2009), Inorganic and Composite Ion Exchange Materials and their Applications, Ion Exchange Letters, 2, 1-14.

36. Onoda H., and Fujikado S., (2014): Influence of pH and Ultrasonic Treatment on Preparation of Titanium Phosphates and Their Powder Properties, Journal of Materials Science and Chemical Engineering, 2, 27-34.

37. Onoda H., and Yamaguchi T., (2012): Synthesis of Titanium Phosphates with Additives and Their Powder Properties for Cosmetics, J. Materials Sciences and Applications, 3, 18-23.

38. Patel H., Chudasama U., (2007): A comparative study of proton transport properties of metal (IV) phosphates, J Chem. Sci., 119, 35-40.

39. Quek S. Y., Wase D., and Forster C. F., (1998): The use of sago waste for the sorption of lead and copper, Wat. SA,24, 251–256.

40. Sahu B. B., and Parida K., (2002): Cation exchange and sorption properties of crystalline a-titanium phosphate, J. Colloid Interface Sci., 248, 221–230.

41. Schmuhl R., Krieg H. M., and Keizer K., (2001): Adsorption of Cu (II) and Cr (VI) ions by chitosan: kinetics and equilibrium studies, Wat. SA, 27, 1–8.

42. Srinivasan T., Rao P., Sood D., (1997). Solvent Extraction and Ion Exchange, 15, 15-31.

43. Strelko V. V., (1982): New inorganic ion exchangers and feasibilities of their use for their treatment of industrial wastewaters, Chemistry role in the environment protection, Naukova Dumka, Kiev, p. 179.

44. Suarez M., Garcia J.R., Rodriguez J., (1983): The preparation, characterisation and ion exchange properties of an amorphous titanium phosphate, Materials Chemistry and Physics, 8, 451-458.

45. Thakkar R., Chudasama U., (2009): Synthesis, characterization and proton transport property of crystalline –zirconium titanium phosphate, a tetravalent bimetallic acid salt, Journal of Scientific & Industrial Research, Vol.68, pp. 312-318.

46. Varshney K. G., and Khan A. M., (1991): Inorganic ion exchangers in chemical analysis (M. Qureshi and K. G.Varshney, eds) CRC Press, pp. 177–270.

47. Wang L., Yan Z., Qiao S., Max Lua G.Q., Huang Y., (2007): Structural and morphological transformations of mesostructured titanium phosphate through hydrothermal treatment, Journal of Colloid and Interface Science 316, 954–961.

48. Weber W.J., Morris J.C., (1963): Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. Am. Soc. Civ. Engrs. 89, 31–59.

49. Wu F.C., Tseng R.L., and Juang R.S., (2001): Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan. Water Res. 35, 613-618.

50. Yang S., Zhao D., Zhang H., Lu S., Chen L., Yu X., (2010): Impact of environmental conditions on the sorption behavior of Pb (II) in Na-bentonite suspensions, Journal of Hazardous Materials 183:632–640.

9/17/2017