



Treatment of Crude Phosphoric Acid from Some Undesirable Impurities

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Abstract

Organic matter contained in wet process phosphoric acid (WPPA) usually interacts with organic solvents and forms stable foams, as well as third layer those prevent phase settling and other separation problems. Hence, removal of these organics seems to be an important step for the production of decontaminated phosphoric acid and successful recovery of undesirable elements. Removal of organic matter from crude phosphoric acid was carried out by adsorption using Kaolin and Ball clay minerals. The different factors affecting the adsorption process were investigated. Under the optimum conditions the results show that, the adsorption process is applicable for the high strength and diluted phosphoric acid. Ball clay was more effective than Kaolin clay in the removal of organic matter as the adsorption efficiency was 53.6 & 39% respectively. The kinetic models were applied to the adsorption rate data and the results indicate that, the process was found to obey pseudo second order rate model. The recovery of 84.7%U and 87.8% REE from the WPPA was obtained using di-nonyl phenyl phosphoric acid (DNPPA) alone in kerosene under desirable conditions, and the stripping of 93.7 and 88.2% of U and REE respectively was achieved by carbonate solution.

Keywords: Organic matter, adsorption, uranium, crude phosphoric acid, di-nonyl phenyl phosphoric acid (DNPPA)

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1. Introduction

Phosphoric acid is an important alternate source of uranium: the world's reserves of phosphate rock are estimated to be about 18 000 million tones with an average uranium content of 50 to 200 and there are approximately 400 wet process phosphoric acid plants in operation from which some 13000 metric tones of U₃O₈ could be recovered each year. Phosphoric acid was used as raw materials for the production of detergents, food products, and alimentary supplies for cattle, toothpastes and fertilizers.

Commercially, phosphoric acid is manufactured using different techniques; the most commonly used is wet process (WPPA), which involved reaction of phosphate rock with strong acid (mainly sulfuric acid) and accompanied by a number of undesirable ionic impurities, like fluoride, iron, copper, and organic matters (OM), etc. [1].

Organic matters (OM) those present in phosphoric acid such as fulvic acid, and humic acid are chemically reactive and have a wide range of functionalities which vary according to the origin of the minerals. Humic acid contains both hydrophobic and hydrophilic components as well as many chemical functional groups such as carboxylic, phenolic, carbonyl, and hydroxyl groups. The presence of these impurities affects the quantity and the quality of the product. For this reason, about 95 % of the acid produced by

WPPA is directly used as fertilizers and excluded from use in non-fertilizer applications [2].

Numerous studies have shown the presence of a strong interaction between humic substances and clay minerals even though both are negatively charged under normal pH conditions [3]. The phenolic and carboxylic groups (-OH & -COOH) are believed to be the most active adsorption sites on humic acid. Many research techniques have been investigated for the removal of organic matters (OM) from WPPA, such as adsorption on activated carbon [4-5]; crystallization [6] and extraction with chelating or impregnated resins [7]. Although these methods have been widely employed, they have several drawbacks such as high operating and waste treatment costs, high consumption of reagents, and large volume of sludge formation [8]. However, due to their high cost and sometimes low availability, the use of these methods is not as feasible as it should be [9-10], therefore, cost-effective alternative technologies or adsorbents for the treatment of metal and OM containing WPPA are needed.

An improved process for extraction of U(VI) from phosphoric acid especially strong phosphoric acid using a selective synergistic extractants mixed of an organo-phosphorous acid and a neutral extraction agent was performed. The process basically involves the steps of

extraction comprising contacting of phosphoric acid with a selective synergistic extractant system of di-nonyl phenyl phosphoric acid (DNPPA) and a neutral agent selected from di-butyl butyl phosphonate (DBBP) and tri-n-octyl phosphine oxide (TOPO); and recovering the uranium values from the loaded organic phase using a suitable stripper. The above process would provide for an improved process for recovery of uranium both from weak and strong phosphoric acids using a stable and relatively cheap extractant system. The process is directed to improved recovery of U(VI) from phosphoric acid by way of a simple, industrially applicable and cost-effective process [11].

Zhang et al, studied the recovery of rare earth elements during the wet processing of phosphoric acid, the method of emulsion liquid membrane (ELM) with di(2-ethylhexyl) phosphoric acid (D2EHPA) as carrier give a high selectivity for REE. The effects of different parameters such as type and concentration of carrier and surfactant, hydrochloric acid concentration, organic to internal phase volume ratio, membrane to external phase volume ratio on extraction of RE³⁺ were investigated. The method could increase the extraction rate of REE in the real sample to 93% [12].

The present work aims to i the investigation of organic matter adsorption from crude phosphoric acid using Kaolin

and Ball clay minerals by batch kinetics and equilibrium studies to improve the quality of uranium and REE recovery from the phosphoric acid. The extraction of uranium and REE was investigated by DNPPA in kerosene and the stripping process was carried out by Na₂CO₃.

2. Experimental

2.1. Materials and reagents

Commercial Ball and Kaolin clay minerals were obtained from Al Amier Ceramic Co. Cairo, Egypt. The provided clay samples were crushed, ground in a mortar and sieved to grain size of 200 mesh. The clay samples were purified by water gravitational sedimentation. The washed solid clay samples were dried in electric furnace at 110 °C until complete dryness. The dried samples were pulverized, homogenized and stored under vacuum condition in desiccators for further analysis.

The characterizations of clay samples have been shown using XRF, XRD, and FT-IR in Table 1, as well as Fig. 1-2 respectively. According to these analysis, it is clear that, Ball clay mineral is Kaolinite [Al₂Si₂O₅ (OH)₄], and low Quartz [SiO₂], while Kaolin clay mineral is mainly Kaolinite [Al₂Si₂O₅ (OH)₄], and high Quartz [SiO₂].

Table (1): Chemical composition (%) of the two type of clay

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	L.O.I	Total
Ball Clay %										
53.8	26.5	4.79	0.19	0.30	0.32	0.46	2.26	0.19	10.9	99.76
Kalin Clay %										
59.5	24.8	3.39	1.89	0.51	0.76	0.34	2.61	0.19	5.74	99.84

The concentration of organic matter (OM) in phosphoric acid was determined by spectrophotometer at a wavelength of 418 nm [13-14]. Commercial phosphoric acid under study was produced from Abu-Zaabal Company for Fertilizer and Chemical Materials (AZFC), its chemical composition is

given in Table 2. Table 2, shows that the acid contains 45% P₂O₅, 0.44%, 5.8% SO₄⁻, 1.2% F, and 2.4% Fe with trace amount of uranium, REE, and OM of 60, 310, & 590 ppm respectively.

Table (2): Chemical analysis of crude phosphoric acid produced from AZFC

Components	P ₂ O ₅	Ca	SO ₄ ⁻	SiO ₂	F	Fe	U	REE	OM
Conc.	45 %	0.44%	5.8 %	0.96%	1.2 %	2.4 %	60 ppm	310 ppm	590 ppm

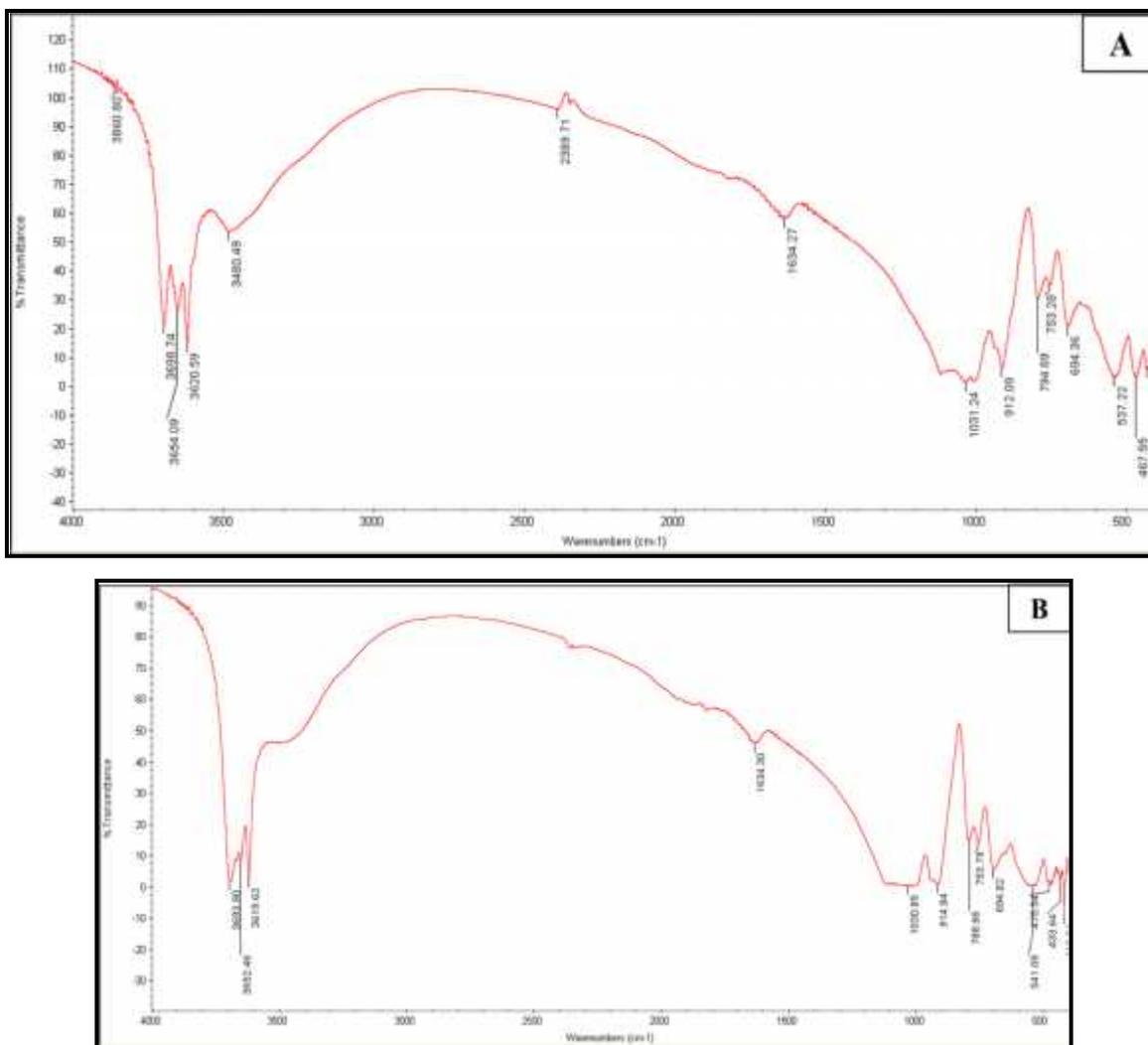


Fig (2): IR for (A) Ball clay mineral, & (B) Kaolin clay mineral samples

2.3. Experimental procedures

Batch adsorption experiments were performed by shaking 1g of Ball or Kaolin clay samples with 50 ml of the crude phosphoric acid in a thermostatic shaker bath at (25°C). All the experiments were carried out in triplicate and the mean values were presented. The organic matter adsorption efficiency was calculated by the difference between the equilibrium concentration and the initial concentration. The amount of organic matter retained in the solid phase q_e (mg/g) was calculated using the following relation:

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

where C_o and C_e are the initial and equilibrium concentrations of the organic matter (mg/L), respectively, V is the volume of the aqueous phase (L), and m is the weight of clay used (g). The percent of removal efficiency (A) % of

ions from the aqueous phase is calculated from the following relation:

$$\text{Organic matter adsorption (A) \%} = \frac{C_o - C_e}{C_o} \times 100$$

3. Results and discussion

3.1. Adsorption investigation

Organic matter adsorption from crude phosphoric acid has been investigated by using Ball and Kaolin clay minerals [15-16]. The effect of contact time, amount of clay addition, temperature, mechanical stirring speed, and phosphoric acid concentration on the organic matter adsorption efficiency has been studied as following:

3.1.1. Effect of contact time

The kinetic of organic matter removal (590 ppm) from 45% P_2O_5 phosphoric acid by Ball and Kaolin clays was studied as a function of contact time during intervals ranged from 20 to 100 min. with speed equals 400 rpm at 25°C. The

result of adsorption kinetic of organic matter is shown in Fig.3

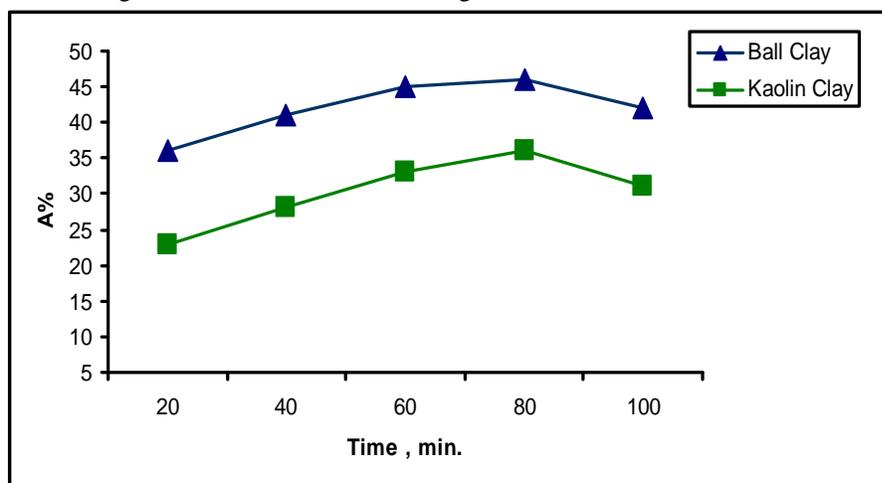


Fig (3): Effect of contact time on the A% of OM in 45% P₂O₅ phosphoric acid using both Ball & Kaolin clay

From Fig.3, it was found that the adsorption of organic matter by Ball and Kaolin clays are increased with time until reach a steady state of 60 min., after that there is no significant change in the removal efficiency percent after that time. This means that the equilibrium of organic matter adsorption is reached at 60 min. for acid sample.

3.1.2. Amount of clay addition

The effect of clay amount added to 50 ml of (45% P₂O₅) phosphoric acid on the A% was studied in the range of 0.5g to 3g under room temperature for 60 min. as a contact time, while the other parameters were fixed on. The relation between organic matter adsorption efficiency (A) % and amount of clay addition was plotted in Fig.4.

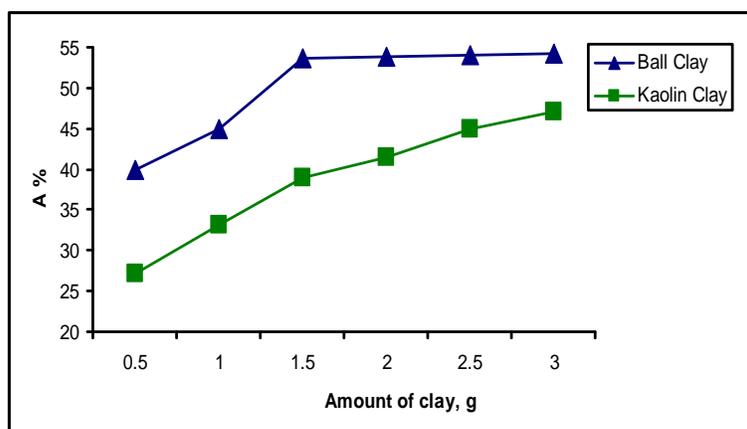


Fig (4): Effect of clay amount addition to (45% P₂O₅) phosphoric acid on A%

As shown in Fig.4, the increase in the amount of clays from 0.5g to 1.5g/50 ml, result in the increase of the A% from 40 to 53.6% as well as from 27.2 to 39% for Ball & Kaolin clays respectively. Further increase in the amount of clays addition up to 3g/50 ml, has almost no effect on the organic matter adsorption efficiency. Therefore, the amount 1.5g/50 ml was fixed during all the other experiments.

3.1.3. Effect of Temperature

The effect of temperature ranging from 25-55°C on the A% for Ball and Kaolin clays was investigated under fixed conditions. The relation between the A% and temperature

are represented in Fig.5. From the results, it is clear that, by raising the temperature from 25 to 55°C, the A% was increased slightly from 53.6 to 55.2 % for Ball clay & from 39 to 43.7 % for Kaolin clay. Economically, the other adsorption experiments were performed at room temperature, which was chosen as an optimum temperature.

3.1.4. Effect of phosphoric acid concentration

Several experiments were performed to study the effect of phosphoric acid concentration (ranged from 30 to 50% P₂O₅ under fixed conditions) on the organic matter adsorption efficiency (A) %. The experimental results are given in Fig.6

as a relation between organic matter adsorption efficiency (A) % and phosphoric acid concentration.

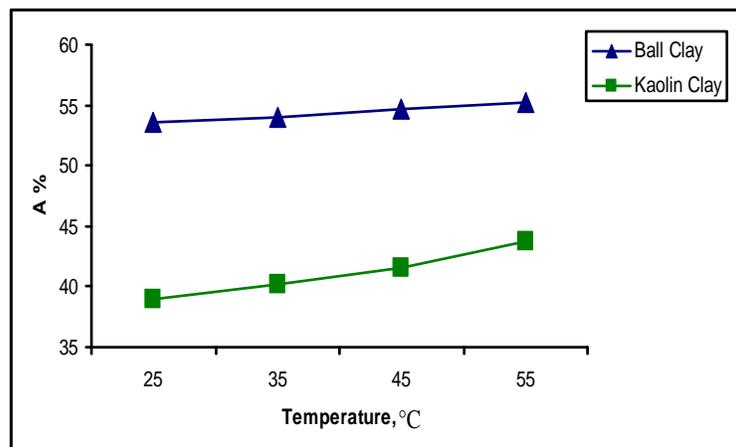


Fig (5): Effect of temperature on the A% for both types of clay

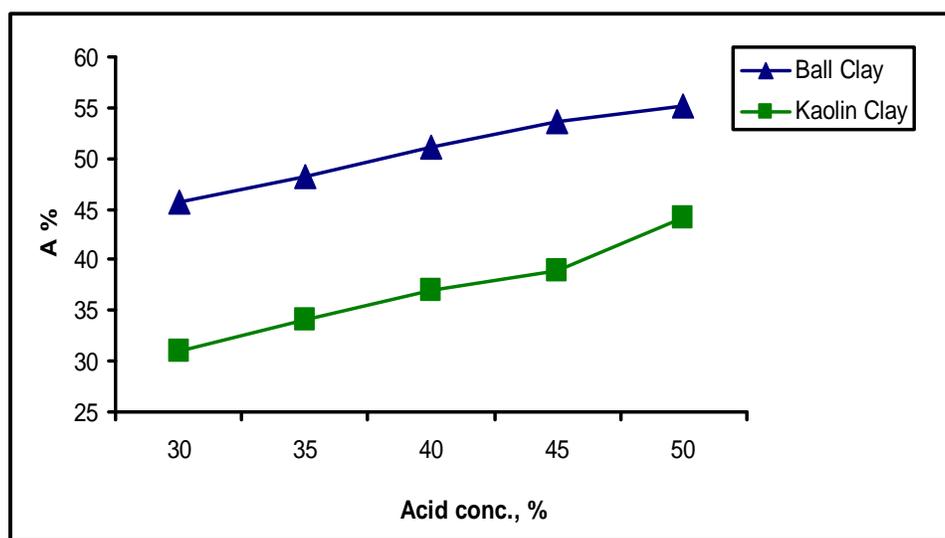


Fig (6): Effect of phosphoric acid concentration on A% using Kaolin and Ball

The result indicates that, as phosphoric acid concentration increased from 30 to 50% P₂O₅, the A% increased from 45.7 to 55.1 % with Kaolin clay and from 31 to 44.2 % for of Ball clay. This means that, this process is applicable for the high strength phosphoric acid and the dilute one.

3.2. Sorption kinetic modeling

The characteristic of the sorbent surface is a critical factor that affects the sorption rate parameters and that diffusion resistance plays an important role in the over all transport of the ions. Pseudo-first order & pseudo-second order rate equations were applied to experimental data for evaluating the adsorption of organic matter ions by Ball and Kaolin clays at 25°C.

(i) Lagergreen pseudo first-order expression is written as [17]:

$$\text{Log } [q_e - q_t] = \text{Log } q_e - (K_1/2.303) t$$

Where q_e is the concentration of the ion sorbed at equilibrium (mg/g), q_t is the concentration of the ion sorbed at time t and K_1 is the overall rate constant.

It was observed that the sorption of all ions followed the Lagergreen equation. From the slopes of the plots, in Fig.7 the values of the first-order rate constants (K_1) and the theoretical sorption capacities (q_e) were evaluated. The calculated values of K_1 and q_e with the linear correlation coefficients (R^2) of each plot are listed in. Straight

lines obtained from the pseudo first-order kinetic plots suggest the applicability of this model to fit the experimental data over the initial stage of the sorption process. But it is also required that the theoretically calculated equilibrium sorption capacities, q_e should be in accordance with the experimental sorption capacity values. As shown in Table 3, although the linear correlation coefficients of the plots are so good, the q_e (calculated) values are not in agreement with q_e (experimental) for all studied sorption process. So, it could suggest that the sorption of the organic matter onto both clays is not a first-order rate reaction.

(ii) The pseudo second-order rate model is expressed as [18]:

$$\frac{t}{qt} = \frac{1}{K_2q_e^2} + \frac{1}{q_e}t$$

Where, K_2 is the rate constant for pseudo second-order equation.

The kinetic plots of t/q_t versus t for organic matter sorption onto Ball and Kaolin clays are represented in Fig.8. The relations are linear and the values of the correlation coefficients (R^2) suggest strong relationships between the parameters and also explain that the process of sorption of ions follows the pseudo second-order kinetic model. The products $K_2q_e^2$ is the initial sorption rate represented as $h = K_2q_e^2$.

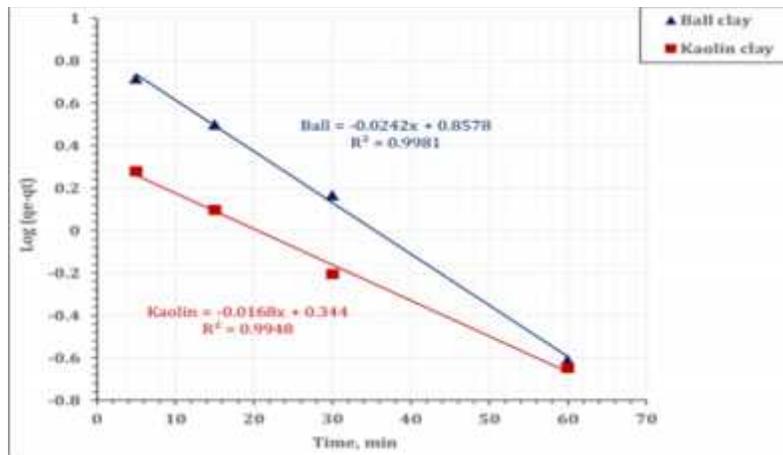


Fig (7): Lagergren plots for adsorption of OM from phosphoric acid

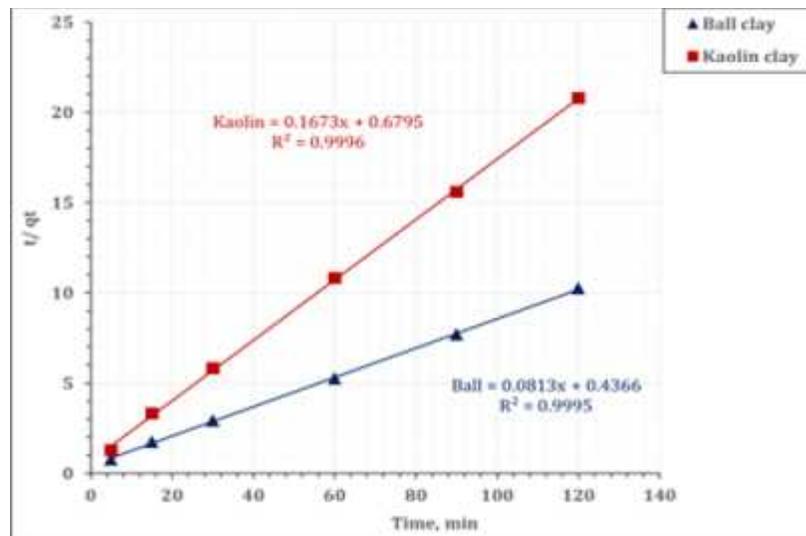


Fig (8): Pseudo second-order plots for adsorption of OM from phosphoric acid using Kaolin and Ball clays

The kinetic parameters of this model are calculated from the slope and intercept of the linear plots and are given in Table 3. The correlation coefficients (R^2) have some extremely high values and its calculated equilibrium sorption capacity (q_e) is consistent with the experimental data. So, it is possible to suggest that the sorption of organic

matter (OM) onto Ball and Kaolin clays followed the pseudo second-order kinetic model and that the overall rate constant of each sorption process appears to be controlled by the chemical sorption process [19-20].

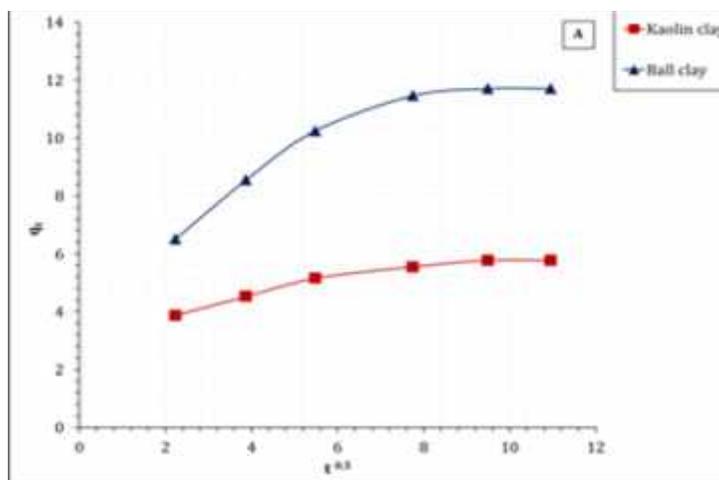
Table (3): The calculated parameters of the pseudo first-order and pseudo second-order kinetic models for OM adsorption from crude phosphoric acid (45% P_2O_5) by Kaolin and Ball clays

	Lagergren pseudo first-order				pseudo second-order			
	K_1 (min^{-1})	$q_{e_{cal}}$ (mg/g)	$q_{e_{exp}}$ (mg/g)	R^2	K_2 (min^{-1})	$q_{e_{cal}}$ (mg/g)	$q_{e_{exp}}$ (mg/g)	R^2
Ball clay	0.05	7.2	11.7	0.99	0.01	12.3	11.7	0.99
Kaolin clay	0.03	2.2	5.77	0.99	0.04	5.9	5.77	0.99

From the Figs. 7-8 and Table 3, it is clear that both of Lagergren first-order model and the pseudo second-order rate model give straight-line plot with correlation coefficient of 0.95 and 0.99 respectively for Kaolin clay, and straight-lines with correlation coefficient of 0.99 for Ball clay. This means that both of the two models could express the kinetics of the adsorption process. By comparing the calculating q_e values for the first and the second order models in case of Kaolin clay (2.2 and 5.9 respectively) with the experimental value of q_e (5.77).

The calculated q_e value of the pseudo second-order model is closer to the experimental q_e value than the calculated q_e value of the Lagergren first order model. The same for Ball clay, where the calculated q_e value of the pseudo second-order model is closer to the experimental q_e value than the calculated q_e value of the Lagergren first order model.

This means that the pseudo second order model is appropriate to predict the adsorption kinetics of organic matter from phosphoric acid (45% P_2O_5) using both Kaolin and Ball clays.



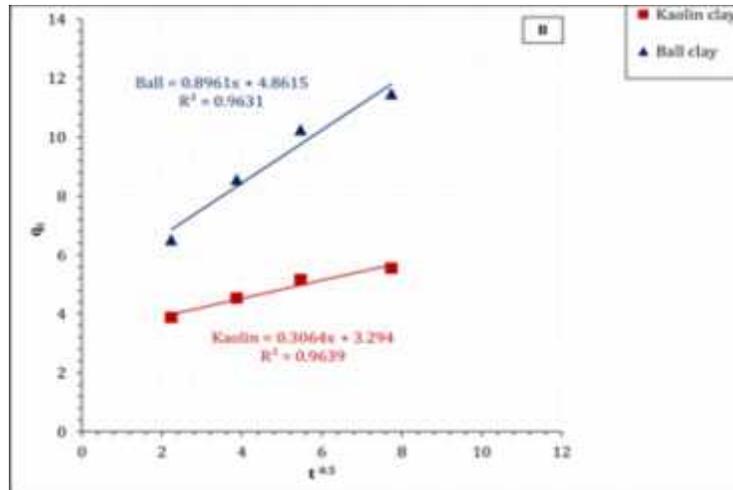


Fig (9): Morris-Weber plots for kinetic modeling of OM adsorption from phosphoric acid (45% P₂O₅) using Kaolin and Ball clays (A), and their linear plots (B)

The kinetic of sorption of organic matter from commercial phosphoric acid (45% P₂O₅) using Kaolin and Ball clays was also evaluated by applying the Morris-Weber equation [16]:

$$q_t = K_{ip} \sqrt{t}$$

Where q_t is the concentration of organic matter ion (mg/g) sorbed at time t (min) and K_{ip} is the rate constant of intra-particle transport (mg/g. min^{0.5}).

According to Morris-Weber model, a plot q_t versus $t^{1/2}$ should be a straight line with a slope K_{ip} when the intra-particle diffusion is the rate determining step (RDS) of the process. When the line does not go through origin the intra-particle diffusion could be accompanied by slow film diffusion. According to Fig. 9A it is clear that, for time up to 60 min the organic matter adsorption onto Kaolin and Ball clays follow Morris-Weber model. There is a deviation for higher shaking time more than 60 min. Fig. 9B show a straight line in the initial stage with correlation coefficient of

0.97 and 0.99 for Kaolin and Ball clays respectively which means that the intra-particle diffusion is the rate determining step (RDS). From the slope of the straight line, the value of K_{ip} was estimated and found to be equal 0.30 and 0.89 mg/g. min^{0.5} for Kaolin and Ball clays respectively.

3.3. Extraction Investigations

The extraction investigation for U & REE (in phosphoric acid that treated by Ball clay) was performed using di-nonyl phenyl phosphoric acid (DNPPA) in kerosene [11]. The extraction efficiency (E) % was plotted versus experimental parameters such as: shaking time, concentration of solvent, and phase ratio as following:

3.3.1. Effect of shaking time

By shaking 10 ml of phosphoric acid with the same volume and phase ratio of (0.05M) DNPPA in kerosene under room temperature for time ranging from 5-20 min., the results were shown in Fig.10:

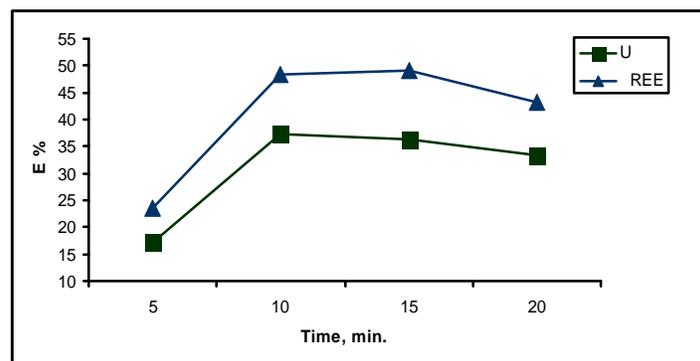


Fig (10): Effect of time on the E% of U & REE in the treated phosphoric acid

It is clear that, the increase in shaking time to 10 min. increases the removal efficiency (E%) of U & REE. There

is a remarkable decrease in E% from 10 to 20 min. So, 10 min. is enough to reach the maximum E% of U and REE

which equals 37.4 & 48.3% respectively.

3.3.2. Effect of solvent concentration

The effect of concentration of DNPPA in kerosene is considered as an important factor for the removal of U & REE from the phosphoric acid. This effect was investigated

using series of DNPPA solutions in different concentrations ranged from 0.05 to 0.5 M. The extraction process was carried out using the standard conditions at room temperature and equal volume of phosphoric acid and DNPPA solution for 10 min. The data was shown in Fig.11.

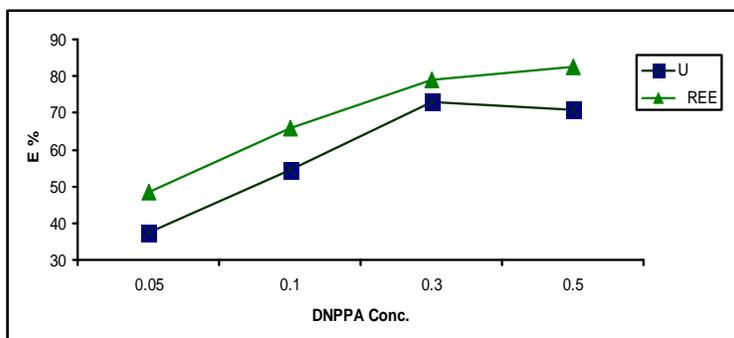


Fig (11): Effect of solvent conc. on the E% of U & REE in treated phosphoric acid

The results indicate that, after the concentration 0.3 M, the E% for U decreases gradually due to increase the viscosity of DNPPA. The E% reaches the maximum values of 72.8 for U at the concentration 0.3, while the E% reaches 82.7% for REE at concentration of DNPPA equals 0.5M. Economically, the concentration of 0.3 M (DNPPA) was chosen as an optimum value for extraction of 72.8% U & 79.1% REE in the treated phosphoric acid.

3.3.3. Effect of organic/aqueous phase

The ratio of the DNPPA volume that added to certain volume of phosphoric acid was studied. The extraction processes were performed at room temperature with 0.3 M of DNPPA in kerosene for 10 min., while the organic:

aqueous phase ratio was ranged from 0.5:1 to 5:1. The results were diagrammatically represented in Fig.12.

The data show that the triple organic: aqueous phase ratio is the suitable ratio for the acceptable extraction efficiency of U and REE in phosphoric acid then there is an appreciable decrease in the E %. At 3:1 phase ratio the maximum extraction efficiency (E) % for U & REE reaches 84.7 and 87.8% respectively, Fig.12. This behavior indicates that, with increasing the concentration and volume of organic extractant (DNPPA) the ability to extract U and REE tends to decrease due to the effect of viscosity and maximum capacity [21].

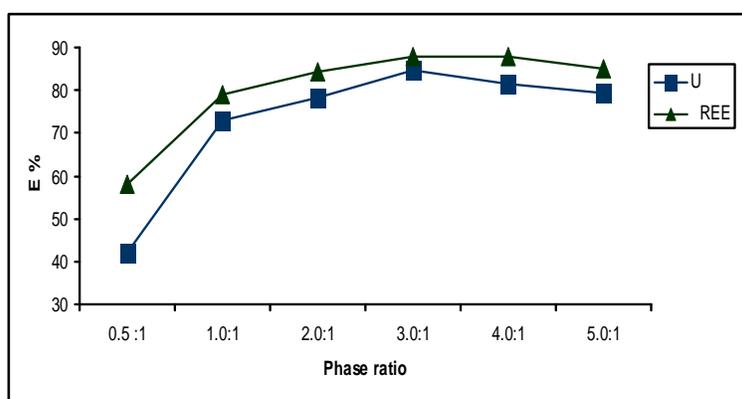


Fig (12): Effect of phase ratio in the E% of U from treated phosphoric acid

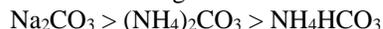
It can be concluded that the best extraction conditions of U & REE from phosphoric acid, treated by Ball clay, were carried out using 0.3M DNPPA in kerosene under room temperature for 10 min. using 3:1 liquid phase ratio.

3.4. Stripping studies

Stripping process of U & REE from the treated

phosphoric acid was performed using sodium carbonate. The stripping investigations were carried out to choose the best conditions that can successfully strip most of uranium from the organic extractants DNPPA. Khorfan et al. studied the stripping of uranium from organic extractants in kerosene using different acids and alkalis and the results showed that

stripping by alkaline solutions was always higher than any acidic solutions [22]. Stripping by alkaline solutions decreased in the following order:



The effect of contact time, and aqueous: organic phase ratio was studied as in the following:

3.4.1. Effect of contact time

The effect of contact time on the stripping of U & REE from DNPPA in kerosene has been investigated using (0.5M) Na_2CO_3 with equal aqueous: organic phase ratio at

room temperature, while the contact time was ranged from 3 to 12 min. The results were represented in Fig.13 as a relation between time & stripping percent (S) %.

The results indicate that stripping efficiency has a progress increase from a time of 3 to 9 min. and then remains constant at 12 min. This indicates that the process is rapid, i.e. is not a diffusion controlled process. The optimum time is 9 min. in which the stripping (S) percent equals 61.4 & 73.1% for U and REE respectively.

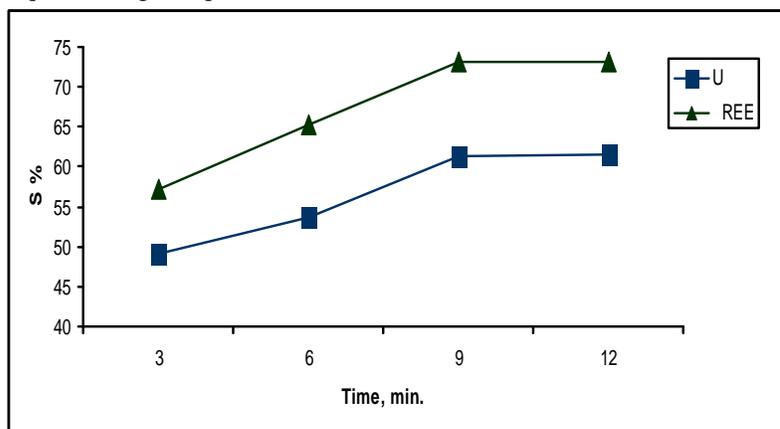


Fig (13): Effect of contact time on the stripping of U and REE from DNPPA

3.4.2. Effect of aqueous: organic ratio

The stripping process was performed by (0.5M) Na_2CO_3 at room temperature for 9 min. to show the effect of aqueous: organic phase ratio on the recovery of U and REE from DNPPA in kerosene. The aqueous: organic phase ratio was varied from 1:1 to 4:1, and the results were represented in Fig.14.

The results indicate that upon increasing aqueous: organic ratio, the stripping efficiency (S) % of U and REE

increased to exhibit a maximum at 3:1 ratio which equals 93.7 & 88.2% respectively. Further increase in aqueous: organic ratio was associated with a very slight change of the uranium stripping percent. Accordingly, aqueous: organic ratio of 3:1 is recommended for uranium stripping with sodium carbonate solution.

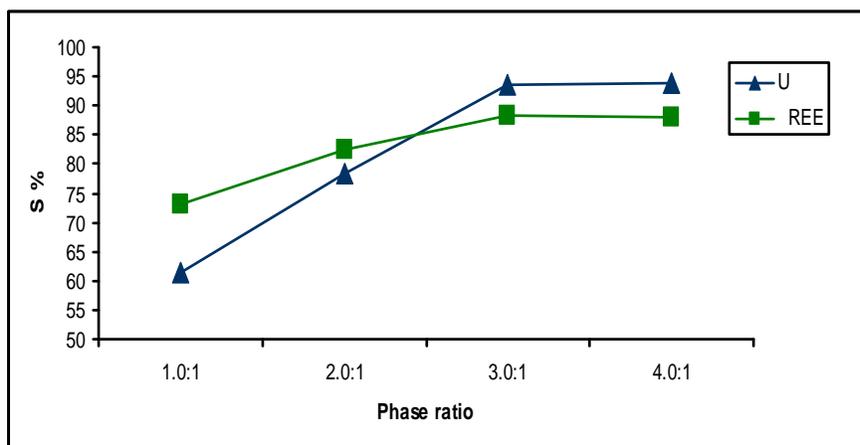


Fig (14): Effect of aqueous: organic ratio on the stripping of U from DNPPA

4. Conclusion

Ball and Kaolin clay minerals have been used for organic matter adsorption from crude phosphoric acid. The obtained results clarify that, the adsorption process using Ball and Kaolin clays were fast where both of them get equilibrium after 60 min. The adsorption process is applicable for the high strength phosphoric acid and diluted one. Under the optimum conditions, the organic matter adsorption efficiency was 53.6 and 39.0 % for Ball and Kaolin clays respectively, which means that Ball clay is more effective than Kaolin clay for the removal of organic matter from

phosphoric acid. The experimental data were tested for different kinetic model expressions and the data were successfully modeled using the pseudo second order for both of Ball and Kaolin clays. The extraction of 84.7% U & 87.8% REE were carried out using DNPPA alone in kerosene, while the stripping of about 93.7 and 88.2% was achieved for uranium and total rare earth elements respectively. The clarification of crude phosphoric acid using Ball clay has a good effect on the recovery processes of uranium and REE by DNPPA alone in kerosene.

Acknowledgments

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References

- [1] A. V. Slack, "Phosphoric Acid", Marcel Dekker, New York, 1 (1968) 515p.
- [2] M. Fuentes, M. Olaetxea, R. Baigorri, A. M. Yamarreno, P. Etienne, P. Laine, A. Ourrz, J.C. Zvin, J. M. Garcia-Mina, "Main binding sites involved in Fe(III) and Cu(II) complexation in humic-based structures", J. Geochem. Explor., 129 (2013) 14-17.
- [3] M. Schnitzer, H. Kodama, "Montmorillonite: Effect of pH on its adsorption of soil humic compounds", Science, 153 (1966) 274-277.
- [4] L. Monser, M. Ben Amor, M. Hsibi, "Purification of wet process phosphoric acid using modified activated carbon, J. Chem. Eng. Process, 3 (1999) 267-271.
- [5] S. Maghsoodloo, B. Noroozi, A. Haghi, G. Sorial, "Consequence of chitosan treating on the adsorption of humic acid by granular activated carbon", J. Hazard Mater, 191(2011) 380-387.
- [6] A. Hannachi, D. Habaili, C. Chtara, A. Ratel, "Purification of wet process phosphoric acid by solvent extraction with TBP and MIBK mixtures", Sep. Purif. Technol., 55 (2007) 212–216.
- [7] M. Gonzalez, R. Navarro, I. Saucedo, "Purification of phosphoric acid solutions by reverse osmosis and nano filtration", J. Desalination, 147 (2002) 315-320.
- [8] N. Bishnoi, M. Bajaj, N. Sharma, A. Gupta, "Adsorption of Cr (VI) on activated rice husk carbon and activated alumina", Bioresour. Technol., 91 (2004) 305-307,
- [9] E. Olyaei, H. Banejad, A. Afkhami, A. Rahmani, J. Khodaveisi, "Development of a cost-effective technique to remove the arsenic contamination from aqueous solutions by calcium peroxide nano-particles", Sep. Purif. Technol., 95 (2012) 10-15.
- [10] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, "Removal of heavy metals from industrial waste waters by adsorption onto activated carbon prepared from an agricultural solid waste", Bioresour. Technol., 76(2001) 63-65.
- [11] A. Abdel Maged, M. Amin, "Uranium (VI) extraction from concentrated Egyptian wet process phosphoric acid using a synergistic organophosphorous solvent mixture, Int J Ind Chem., 7 (2016) 21–28.
- [12] L. Zhang, Q. Chen, C. Kang, "Rare earth extraction from wet process phosphoric acid by emulsion liquid membrane", Journal of Rare Earths, 34 (7), (2016) 717-723.
- [13] A. Boualia, T. Mellah, T. Aissaoui, K. Menacer, and A. Silem, "Adsorption of organic matter contained in industrial H₃PO₄ onto bentonite: batch-contact time and kinetic study", J. Applied Clay Science, 7(6) (1993) 431-445.
- [14] S. Najar, A. ben Fraj, A. Zammouri, M. ouederni, and A. Ratel, "Removal of OM from IPA by AC prepared from olives stones," J. Materials Science & Technology, 10 (2002)73-81.
- [15] B. Ili, A. Mitrovi, L. Mili, "Thermal treatment of kaolin clay to obtain meta-kaolin", J. Hemijska Industrija, 64 (4) (2010) 351-356.
- [16] M. Abdel Raouf, A. El-Kamash, "Kinetics and thermodynamics of the sorption of organic matter and thorium ions from nitric acid solutions onto a TBP-impregnated sorbent", J. Radioanalytical and Nuclear Chemistry, 267 (2) (2006) 389-395.
- [17] R. Donat, "The removal of organic matter (VI) from aqueous solutions onto Kaolinsepiolite. J. Chem., Thermodynamics, 41 (2009) 829-835.
- [18] W. Guanghui, W. Xuegang, V. Xinjun., L. Jinsheng., D. Nansheng, "Adsorption of organic matter (VI) from aqueous solution on calcined and acid-activated kaolin", J. Applied Clay Science, 47 (2010) 448-451.
- [19] C. Min-Yun, J. Ruey-Shin, "Adsorption of tannic acid, humic acid, and dyes from water using the composite of chitosan and activated clay", J. Colloid Inter. Sci., 18 (2004) 278-286.

- [20] H. Zaitan, D. Bianchi, O. Achak, T. Chafik, “Adsorption of copper and nickel on Na-bentonite”, *J. Hazard Mater.*, 42 (2008) 852-859.
- [21] N. Chohey, “Handbook of Chemical Engineering Calculations”, 3rd Edition, McGraw-Hill, (2004).
- [22] S. Khorfan, J. Stas, M. Kassem, “Stripping of uranium from DEHPA/kerosene solvents by different aqueous media”, *J. of Radio-analytical & Nuclear Chemistry*, 238 (1998) 145-149.