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Sorption of Organic Matter From Phosphoric Acid using Activated Charcoal Carbon as Efficient Adsorbent

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***ABSTRACT*: A study was conducted to determine the effectiveness of modified active carbon species in sorbing organic matter from commercial phosphoric acid. Various factors such as shaking time, adsorbent dose (g/ml), temperature, mechanical stirring speed, and phosphoric acid concentration were examined to determine their effect on the adsorption process of raw carbon (R-C) and activated carbon (A-C). The results showed that the sorption process was effective for both high-strength and diluted phosphoric acid, but it was more preferable in the case of the latter. The adsorption capacity was found to be 22 and 28 mg/g for R-C and A-C, respectively**.

Keywords Organic Matter, sorption, phosphoric acid, R-C, A-C, and Capacity

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I. INTRODUCTION

Phosphorus is a vital element of all active systems. It is the second most abundant element in the human body, surpassed only by calcium [1]. Phosphate rock is a naturally occurring source of phosphorus. Phosphate rock occurs mainly in the form of hydroxy- and fluoroapatite, $Ca_{10}(PO_4)_6(OH)_2$ and $Ca_{10}(PO_4)_6F_2$, respectively [2]. Approximately 90% of the worldwide produced phosphate rock is consumed for agricultural or food purposes, therefore It is very important to ensure global food supply and security [3].

Organic matters (OM) present in phosphoric acid such as fulvic acid, and humic acid are chemically reactive and have a wide range of functionalities that 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 [4]. 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 [5]. 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 [6-9]. 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 [10].

In this contribution and with regards to environmental aspect, this paper deal aims to investigate the organic matter adsorption from commercial phosphoric acid by raw Raw Carbon (R-C) and Activated Carbon (A-C) materials by equilibrium studies.

2. EXPERIMENTAL

2.1. Materials and Reagents

In this research work carbon-based structures were introduced as efficient adsorbents for the extraction of organic matter from a commercial phosphoric acid obtained from Al Amier Ceramic Co. Cairo. H_2SO_4 were chemical reagent grade and were supplied from ADWIC, Egypt. The phosphoric acid working sample was supplied from Abu Zaabal Company for Fertilizer and Chemical Materials (AZFC), and has been utilized through this investigation without a purification process. The

chemical analysis of the crude phosphoric acid sample is given in **Table (1)** as analyzed in the central laboratory of the Nuclear Materials Authority.

Table (1): Chemical analysis of crude phosphoric acid.

Component	Concentration
Fe	2.40 %
Ca	0.44 %
F	1.18 %
SiO_2	0.95 %
P_2O_5	≈ 44.0 %
$SO4^{--}$	5.78 %
O.M.	600 ppm

2.2. Preparation of Activated Charcoal Carbon
Charcoal Carbon activation by Sulfuric acid is adding 50 g of Carbon to 500 mL of sulfuric acid solution (2M) and refluxing at 110°C under atmospheric pressure for 4 hours. The activated solid was washed with distilled water until free from sulfate and dried at 80 °C.

2.3. Characterization of adsorbents
2.3.1. FT-IR spectra: R-C, and A-C structures were carried out and recorded on ATI Mattson Genesis series (KBr disc method) apparatus, Model 960 M009 series.

2.3.2. Scanning Electron Microscope (SEM): SEM model Philips XL 30 ESEM (25-30keV accelerating voltage, 1-2mm beam diameter and 60-120 s counting time). Minimum detectable weight concentration ranges from 0.1 to 1 wt % with realized precision lower than 1%.

2.3.3. XRD: XRD pattern of structure namely; the activated carbon is exhibited in Figures 2

2.4. Sorption methodology
Sorption batch experiments were conducted in 10 mL polyethylene tubes at a temperature of 298 K under ambient conditions. Briefly, 1.0 g of R-C and A-C samples were mixed with 50.0mL of crude di-hydrate phosphoric acid, 44% P2O5, sample using a thermostatic shaker. All experiments were carried out in duplicate and the data were the averages of detection with the relative errors of 4%. Organic matter (OM) concentration in phosphoric acid was determined spectrophotometrically at 418nm [9]. The sorption percentage and sorption amount were calculated from the following equations:

$$\text{sorption } \% = \frac{(C_o - C_e)}{C_o} X100 \qquad (1)$$

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

where Co and Ce are the initial and equilibrium concentrations (mg/L), respectively, V is the volume of the aqueous phase (L), and m is the weight of sorbent used (g).

The dimensionless distribution coefficient (kd) was calculated according to the following Equation [10]:

$$K_d\left(\frac{mL}{g}\right) = \frac{C_o - C_e}{C_e} \times \frac{V}{m} \qquad (3)$$

3. RESULTS AND DISCUSSION

3.1. Characterization of raw materials
FTIR spectra of raw Charcoal Carbon (R-C) and Activated Charcoal Carbon (A-C) are presented (Fig. 1). (R-C), (A-C) depends on its functional groups reactivity. IR spectra of R-C (1 a before) and A-C (1 b after) complexed with metal ions were contact it in. As can be seen in Fig. 1: by compare the FTIR bands between (R-C), (A-C) before sorption, the data showed that there is an additional band for A-C than R-C. appear after chemical activated Carbon due to the increased substitution of metal by O.M.

SEM images of the macrostructure Charcoal Carbon (R-C) and Activated Charcoal Carbon (A-C) before adsorption (Fig. 1-a,b), showed the rudimentary on the R-C and A-C surface which formed due to the volatility and constituents decomposition during chemical treatment.

The **XRD** pattern of structure namely; the activated carbon is exhibited in Figures 2. The XRD spectra illustrate the presence of broad peak located between 2θ of 20.4 and 30 which is the main indicative peak for the activated carbon structure. The broad peaks are generally reflecting the amorphous nature of the presented structures.

Nevertheless, the degree of broadness as well as the relative intensity of each peak is slightly different. Although the XRD signals exhibit amorphous nature of the produced activated carbon, it had presented high surface area.
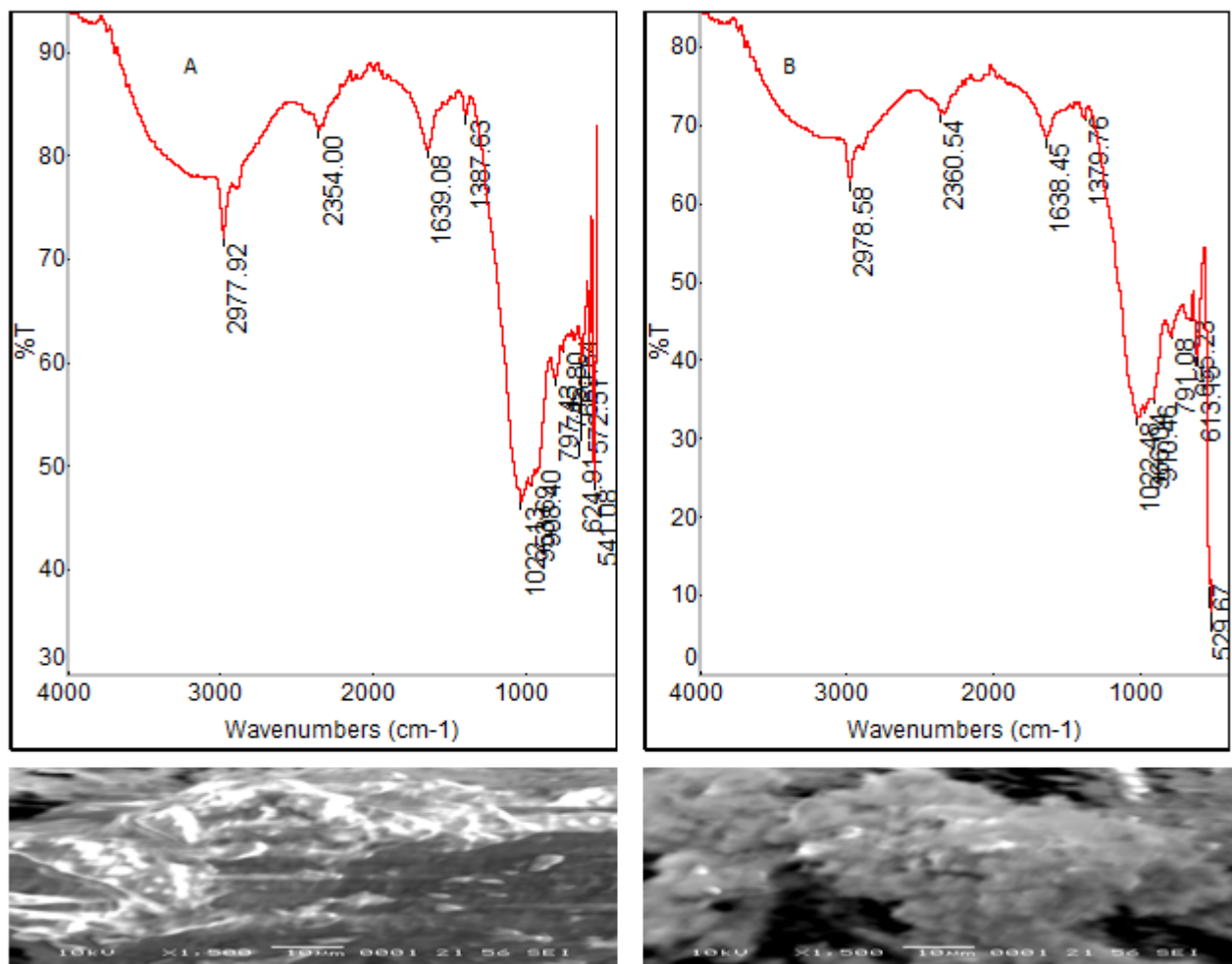

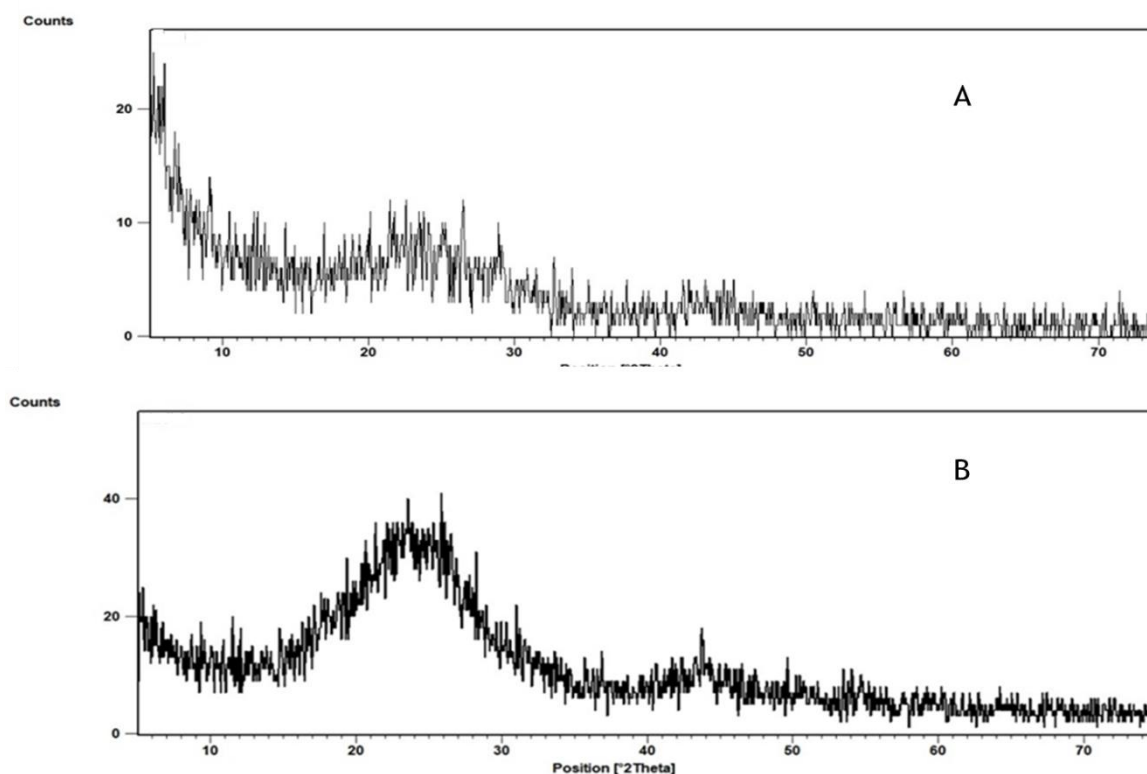**Fig. 1.** FT-IR-SEM images of R-C(A), A-C(B) before adsorption.

Figure 2: XRD pattern of plain carbon (A, B) before and after activation.

3.2. Sorption investigation

In this section, the effect of numerous parameters on the sorption behavior of the (R-C) and (A-C) has been investigated, by batch technique, to figure out the optimum sorption conditions that could achieve effective removal of organic matter (OM) from phosphoric acid. These parameters include mixing time (5- 300min), sorption temperature (20- 60oC), phosphoric acid concentration (15- 44 % P2O5), mechanical stirring speed (100- 1000rpm), and sorbent amount of addition (0.1-6g/ 50ml).

3.2.1. Effect of shaking time

The effect of contact time on organic matter adsorption from crude phosphoric acid, 44% P2O5, onto R-C, A-C sorbents was carried out at different time intervals ranged from 5 to 300 min. The other factors were sorbent dose; 1g/ 50 ml, reaction temperature of 25±1oC, and mechanical stirring speed of 400rpm. The experimental results are given in Figure 3 as a relation between O.M. adsorption efficiency % and time. From the Figure it is clear that, the rate of O.M. uptake increased rapidly for both sorbents at initial time of 180 min. The maximum OM sorption efficiency reached 40 and 60% respectively for R-C and A-C. This behavior could be due to the availability of adsorbent active groups. Further increase in contact time brings no significant increase in OM removal percentage. Therefore, other sorption experiments were conducted at 180 min.
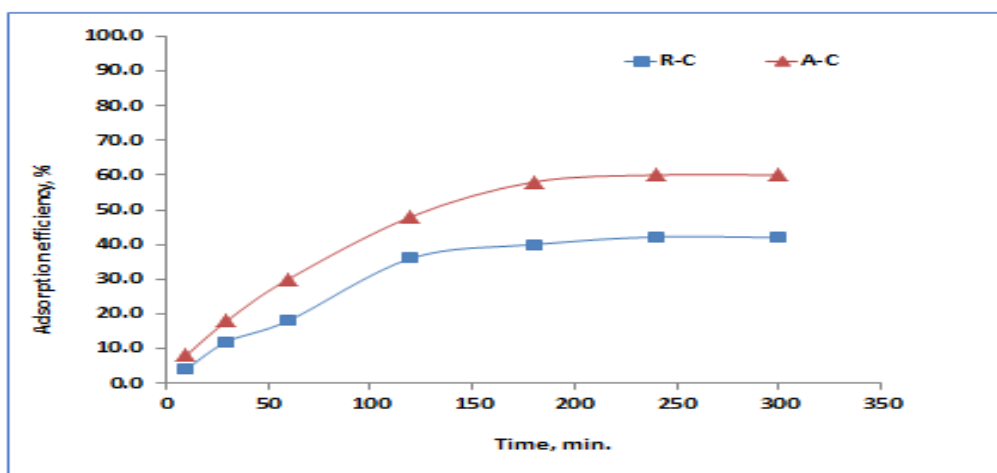
Figure 3: Effect of time on OM sorption efficiency, % (1 g sorbent/ 50ml of commercial phosphoric acid; temperature 25 ± 1∘C, 400 rpm).

3.2.2. Effect of the Temperature

To study the effect of temperature on OM sorption from commercial phosphoric acid, 44% P2O5, onto R-C, A-C, a set of experiments have been investigated in the range 20– 60 ±1OC at amount of addition 1g/ 50ml, mechanical stirring speed of 400 rpm and shaking time of 180 min. Figure 4 represented the relation between OM sorption efficiency % and temperature. From the Figure, it is clear that increasing the temperature had a slightly effect on OM sorption efficiency, where the increase of temperature from 20 to 60OC, increase OM sorption efficiency from 40 to 42.8% and from 60 to 62.6% respectively for R-C, A-C respectively, This behavior indicates that organic matter sorption from commercial phosphoric acid onto the presented carbon structures is an endothermic process.
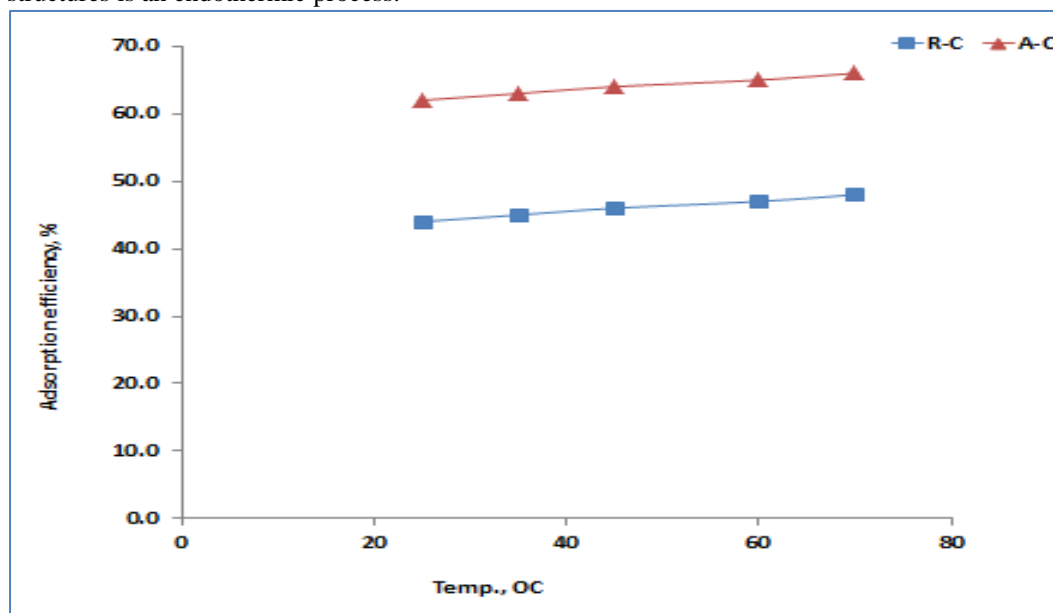

Figure (4): Effect of temperature on OM sorption efficiency, % (shaking time 180 min; 1 g sorbent/ 50ml commercial phosphoric acid; 400 rpm).

3.2.3. Effect of phosphoric acid concentration:

Various experiments were conducted to study the effect of varying phosphoric acid concentrations ranging from 15-44% P2O5 on the sorption of OM by R-C, A-C as an adsorbent while the other parameters were kept constant at room temperature, sorbent dose of 1g/ 50ml, mechanical stirring speed of 400 rpm and shaking time of 180 min. The experimental results are given in Figure (5) as a relation between OM sorption efficiency % and phosphoric acid concentration. From the Figure, it is clear that, as phosphoric acid concentration increased from 15 to 44% P2O5, sorption % dramatically decreased from 60 to 40.5% in case of R-C sorbent, and decreased from 88.4 to 60.0% in case of A-C adsorbent.
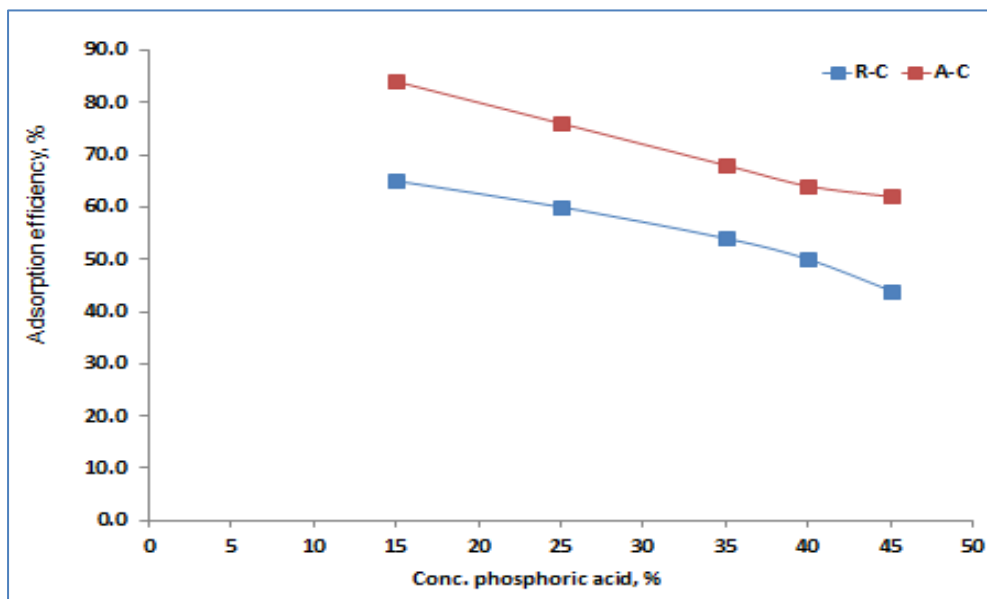
Figure (5): Effect of phosphoric acid concentration on OM sorption efficiency using R-C and A-C (Shaking time 180 min; sorbent dose 1g/ 50ml phosphoric acid; room temperature; 400 rpm).

3.2.4. Effect of Mechanical stirring speed:

To investigate the effect of stirring speed on organic matter recovery from di-hydrate phosphoric acid, 44% P_2O_5, several experiments have been carried out at room temperature, sorbent dosage, 1g/ 50ml, and time of 180 min; however, the stirring speed was ranged from 100 to 1000rpm. The experimental results given in Figure (6) as a relation between OM sorption efficiency and mechanical stirring speed show that, as the stirring speed increased from 100 to 1000rpm, the O.M. sorption efficiency changed from 12 to 50% for R-C and from 20 to 70% for A-C. Thus the change in mechanical stirring speed has slight effect on organic matter sorption onto introduced carbon-based adsorbents. Therefore, 800 rpm was the chosen stirring rate.
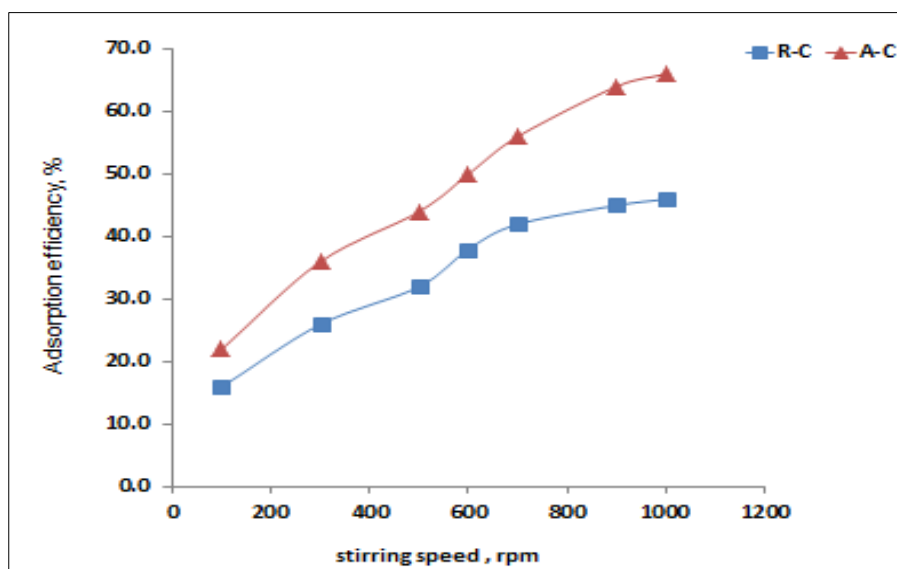

Figure (6): Effect of mechanical stirring speed on the organic matter sorption efficiency, % (Shaking time 180 min; R-C and A-C sorbents dose of 1 g/ 50 ml; room temperature).

3.2.5. Effect of carbon amount of addition

To explore the optimal dosage of adsorbents, the effect of sorbents amount of addition, ranging from 0.1 to 2g/ 50 ml on the sorption efficiency of OM from industrial phosphoric acid, 44 % P_2O_5, onto R-C, A-C was studied. The operating conditions used were, a shaking time of 180 min, room temperature and a stirring speed of 800 rpm. The results are plotted in Fig.7 as a relation between sorption efficiency % and sorbent amount of addition. The results show that the increase of sorbent amount of addition from 0.1 to 2g/ 50ml enhanced the adsorption ability of R-C, A-C for OM. Numerically, as the sorbent amount of addition increased from 0.1 - 2g/

50ml, OM sorption efficiency increased from 5.8 to 46.8% and from 20.6 to 63% respectively in the case of R-C, and A-C respectively. Therefore, the solid/ liquid ratio, g/ ml, was kept at 1g/ 50 ml during all the other experiments.
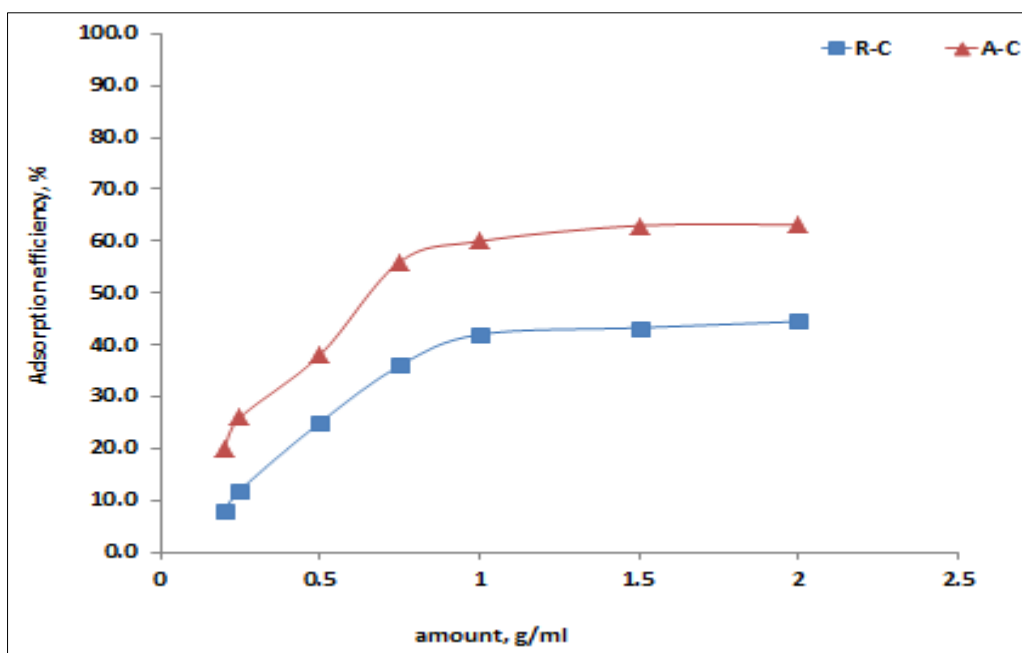

Figure 7: Effect of solid/ liquid ratio, ml/ g, on the O.M. sorption efficiency % from phosphoric acid using R-C, A-C (mixing temperature $25 \pm 1°$C, 800 rpm).

3.3. Adsorption Isotherm Models

The Langmuir isotherm considers the adsorption as a chemical phenomenon with the formation of an energetically monolayer with a maximum adsorption capacity of qmax (mg/g) through the following Equation (4): [11-12] and as table (2).

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}} \quad \ldots\ldots (4)$$

Kf and n are the Freundlich constants which represent the adsorption capacity and the adsorption intensity respectively. Kf and n can be determined from a linear plot of Log qe against Log Ce as shown in table (2), Equation (5):

$$Log q_e = Log K_f + \frac{1}{n} Log C_e \quad \ldots\ldots\ldots (5)$$

The results of the Langmuir and Freundlich isotherm constants are given in Table (2) where it is found that O.M. adsorption on carbon charcoal correlates quite well ($R^2 > 0.9$) with the Langmuir equation as compared with the Freundlich equation under the studied concentration range. Langmuir model is thus suitable for the description of the adsorption equilibrium of O.M. onto carbon charcoal. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor [13], RL, which is used to predict if an adsorption system is favorable or not.

Table 2: Adsorption Isotherm Models

	Freundlich isotherm model			Langmuir isotherm model		
	n	Kf (mg/ g)	R2	Qm (mg/ g)	b (L/ mg)	R2
R-C	2.51	3.42	0.91	28.01	0.04	0.99
A-C	2.86	3.48	0.92	22.17	0.05	0.99

4. CONCLUSIONS

R-C, A-C have been used for O.M. sorption from commercial phosphoric acid, 44% P2O5. The obtained results clarify that, the sorption Parameters: Shaking time 180 min; R-C and A-C sorbents dose of 1 g/ 50 ml; room

temperature. The sorption process is applicable for the high strength phosphoric acid and diluted phosphoric acid but it preferred to the diluted phosphoric acid. Adsorption capacity is 14 and 29 mg/g for R-C and A-C respectively.

5. References

[1] US Energy Information Administration, 'International Energy Outlook 2013'.

[2] Pachauri, R. K., Edenhofer, O. and Minx, J. C. "Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change." (2014): 151.

[3] Sophie G., Anne B., Gilles M., Tommy E., Florian F., "A critical assessment of global uranium resources, including uranium in phosphate rocks, and the possible impact of uranium shortages on nuclear power fleets" Annals of Nuclear Energy journal 58 (2013) 213-220.

[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] Ahmed M. Masoud; Walid M. Youssef and Mostafa I. Amin, "applicable technique for decreasing the content of iron, cadmium, copper, zinc and manganese from wet process phosphoric acid using synergistic organic mixture of methyl isobutyl ketone (mibk) and butanol", Nuclear Sciences Scientific Journal, 8A, 243-256, 2019.

[7] Mostafa Ibrahim Amin , Hady S. Gado, Walid M. Youssef, Ahmed M. Masoud "Precipitation of iron from wet process phosphoric acid using oxalic acid and potassium hexyl xanthate (PHX)", J. Chemical Papers, https://doi.org/10.1007/s11696-019-00735-8

[8] Amir Elzoghby, Hager Fahmy,Mohamed Taha,, Saber Ibrahim; Active carbon-based waste packaging materials for uranium sorption from aqueous solution, Environ Sci Pollut Res Int. 2023; 30(30): 74726–74741

[9] Amir A. Elzoghby , El Sayed A. Haggag ,Osama E. Roshdy , Islam G.Alhindawy and Ahmed M. Masoud,Kaolinite/thiourea-formaldehyde composite for efficient U(VI) sorption from commercial phosphoric acid, journal Radiochimica Acta, https://doi.org/10.1515/ract-2022-0091, 21, 2022

.[10] Paddison, S. J., & Elliott, J. A. (2005). Molecular modeling of the short-side-chain perfluorosulfonic acid membrane. The Journal of Physical Chemistry A, 109(33), 7583-7593.

[11] Langmuir, "The adsorption of gases on plane surfaces of glass, mica and platinum", American Chemical Society, 40, 1361-1368, (1918).

[12] H., Freundlich; "Adsorption in solution". Physical and Chemical Society 40, 1361 (1906).

[13] Li, G.; Wang, X. S.; Guo, X. W.; Liu, S.; Zhao, Q.; Bao, X. H.; Lin, L.W. "Titanium species in titanium silicalite TS-1 prepared by hydrothermal method", Mater. Chem. Phys. 2001, 71, 195–201.