Experimental study of competitive adsorption of heavy metals and organic matter for the phosphoric acid purification

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Abstract

The program articulated around the experimental study of the effect of several parameters on the elimination of the cations: copper, cadmium and zinc, and the organic matter present in the phosphoric acid by using the bentonite, activated carbon and carbon of olives as supports, and on the other hand to show the effect of several parameters on this keeping back such as: the effect of the time (kinetic) of contact, speed of excitement, initial concentration of the pollutant, Solid report / liquid, the isotherms. At selected best parameters for better one capacity we calculated the capacity of purification for the different supports, the sawdust and the waste of cereal. The kinetic study of the keeping back of existing pollutants in the phosphoric acid is still presented.

Keywords: purification of H₃PO₄; adsorption; kinetics; Bentonite; Activated carbon, Characterization of adsorbents.

1. Introduction

The removal of impurities existing in the phosphoric acid is an important step both for fertilizer production and recovery of uranium knowing that the phosphoric acid contains 60 to 100 mg / l of uranium is that the presence of DBP can be a major difficulty for the production of uranium by liquid-liquid extraction to avoid foams and emulsions [1]. To remove impurities existing in phosphoric acid, several researchers presented their work in order to find an efficient adsorbent among the works found in the literature include: Mellah A. et al [2] used the extraction method with kerosene as a solvent is used, the results show that the removal efficiency of ion Titanium>chromium>cadmium concentrations ≥ 7M H₃PO₄ and performance removal of chromium >Titanium for concentrations ≤5M H₃PO₄. MENOUD Philip et al [3] studied the adsorption on a chelating resin allows the treatment of water containing small amounts of heavy metals (Cu⁺², Ni⁺², Co⁺², Zn⁺²) (<0,3 mol.m⁻³) . For this study they used the resin Chelamine standard. These experiences highlight the importance of packaging resin on its ability to balance. El ASSK's motorcade, Laachacha, Azzim et al [4] studied the combination of sorption isotherms (Mono-metal, and competitive) and sequential extractions, which has enabled the evaluation of the sorption and determination of the distribution of Cd, Cu, Pb and Zn in different geochemical phases of soil irrigated by polluted water. B. Serpaud, R.Al-Shukry, M. and G. Matejka Casteignau et al [5]
studied the adsorption of heavy metals Cu, Cd, Zn and Pb in sediments of a stream polluted by industrial discharges, by examining the role of pH, temperature, and sediment composition.

2. Adsorbents and solutions

2.1. Adsorbents

The materials used are: activated carbon, coal from olive pits, which are (washed, dried, charred 300 °C for 2 h in an oven, crushed), Maghnia bentonite as natural. The grading is done by sedimentation to a uniform diameter equal to 0.5 mm.

2.2. Preparation of the main

The contaminated solutions (stock solutions) of 1M phosphoric acid (85% purity, density = 1.57 and molecular weight M = 98 g / mol. (Produce by Merck, Darmstadt)) are prepared by adding heavy metals (Cu, Cd, Zn) respectively prepared from the salts (CuSO₄, 5H₂O, 3CdSO₄, and ZnSO₄ 8H₂O, 7H₂O, (Panreac Quimica, Spain)) organic matter and DBP (manufactured by Alfa Aesar (A. Johnson Matthey company)) with a purity of 99% and a molar mass M = 278.35g / mol), depending on the concentrations of these constituents in each type of phosphate rock (Algerian, Tunisian and Morocco rocks).

Table 1. The composition of the phosphoric acid of various phosphate rocks of ore

<table>
<thead>
<tr>
<th></th>
<th>Cu (mg/l)</th>
<th>Cd (mg/l)</th>
<th>Zn (mg/l)</th>
<th>DBP (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algerian rock</td>
<td>26</td>
<td>11</td>
<td>87</td>
<td>370</td>
</tr>
<tr>
<td>Tunisien rock</td>
<td>1</td>
<td>25</td>
<td>123</td>
<td>50</td>
</tr>
<tr>
<td>Morocco rock</td>
<td>35</td>
<td>9</td>
<td>183</td>
<td>50</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Effect of pH of the solution of phosphoric acid

The results shown in Fig. (1) showed that the performance of competitive adsorption of heavy metals (Cu²⁺, Cd²⁺, Zn²⁺) and organic matter (DBP) increased with increasing pH of the solution, which means that at very low pH values (pH = 1.15, [H₃PO₄] = 5M) removal rate is very negligible. We can
explain it by the high concentration of hydrogen ions in solution, which results in competition for H with the molecules of impurities for free sites that exist at the surface of the adsorbent, after there is an electrostatic repulsion between adsorbed molecules and the surface acquired a positive charge at a pH value of (1.44, [H₃PO₄] = 1 M) concentration of H decreases and the molecules of (Cu⁺², Cd⁺², Zn⁺²) and (DBP), which explains the increased retention rates. Following the results found were selected to work the following experiments with an initial concentration of H₃PO₄ equal to 1 M. The competitive retention of heavy metals (Cu⁺², Cd⁺², Zn⁺²) and organic matter (DBP) existing in the phosphoric acid is as follows: V = 500 rpm, T = 23 °C, pH = 1.44, d = 0.5 mm, C₀ depending on the composition of the rocks of Algeria.

3.2. Effect of contact time

Fig. 2. The effect of contact time on the retention competitive using activated carbon: (A) r = 1 g/l, (B) r = 2 g/l, (C) r = 3 g/l

According to the Fig. (2) shows that the efficiency of adsorption (Cu⁺², Cd⁺², Zn⁺²) and (DBP) on activated carbon is more important (r = 2 and 3 g/l) than in the case of (r = 1 g/l) this is due to the availability of support sites for impurities adsorbed at the same time we note that the results for r = 2 and 3 mg/l are almost the same this is due to the saturation of adsorbent where the explanation of small quantities of adsorbed heavy metals (Cu⁺², Cd⁺², Zn⁺²) and organic matter (DBP). On the other hand, the adsorption equilibrium is reached after 30 min in all cases the ratio (r). Furthermore we note that the returns on the adsorption of different elements are weak, because a contact time of 30 min, the rate of adsorption is in the range of 21.9 to 19.1 - 25.7 - 54.4% for r = 3 g/l. This is probably the hydration of activated carbon. On the other hand, the kinetics of competitive adsorption of these impurities on activated carbon trading is very fast.

3.3. Effect of the nature of the adsorbent

Fig. 3. The effect of the nature of support on competitive retention using: (A) The activated carbon, (B) bentonite, (C) coal from olive pits
The results of comparison of performance against the three types of media (activated carbon, bentonite, charcoal from olive pits) are shown in Fig. (3). By comparing the percentages of elimination from the three media can be seen that the thermal activation of coal from olive pits gives the higher yield compared to bentonite and activated carbon. We also note that the equilibrium time differs from one element to another both in the case of coal than in the case of bentonite or olive pits. However, in the case of coal from olive pits equilibrium is reached in a relatively short time it is 10 minutes for cadmium, zinc and DBP and 20 minutes for copper.

3.4 Effect of solid-liquid ratio

Fig. 4. The effect of the nature of support on competitive retention using:
(A) The activated carbon, (B) bentonite, (C) coal from olive pits

The study of the influence of solid-liquid ratio on the performance of competitive adsorption is shown in Fig. (4). The analysis shows that the yield curves of the competitive adsorption of cations (Cu$^{+2}$, Cd$^{+2}$, Zn$^{+2}$) and organic matter (DBP) is important for (r) greater than 0.5 g / l all the elements that is due to the existence of active sites to adsorb the pollutants media. But beyond this value of solid-liquid ratio the effect of the latter is almost negligible. Performance is changing at 60 minutes (equilibrium time) this could be interpreted by the fact that at the beginning of adsorption the number of active sites are available on the surface of the adsorbent material is much larger than the remaining sites after some time. Following the results found were fixed the solid-liquid 1g / l for the following experiments.

3.5 Effect of stirring speed

Fig. 5. The effect of stirring speed using activated carbon:
(A) 30 minutes of contact, (B) 60 minutes of contact, (C) 90 minutes of contact,
The results of Fig. (5) we note that in our case the performance of competitive adsorption is not influenced by the stirring speed. In fact the curves are nearly parallel, however, the curve corresponding to 500 rpm gives the best results we see four medium speed agitation retention is better supported: Low stirring speed does not promote better contact between the adsorbate and the adsorbent, and a high stirring speed can have an adverse effect on performance is explained by the father of a quantity of adsorbent important that transferring the solution to the walls of the beaker by speed effect.

3.6 Effect of initial concentration of pollutants (composition of rock phosphate)

Based on these results in Fig. (6) we notice that the performance of competitive adsorption to the cation (Cu^{+2}) and organic matter (DBP) is more important in rock Algeria, while the yield respectively larger for cations (Cd^{+2} and Zn^{+2}) in the rocks of Tunisia and Morocco. The curves show that the rate of adsorption can be divided into two phases: rapid and slow reaction. During the first 25 minutes, more than 20, 19, 25, 50% of cations (Cu^{+2}, Cd^{+2}, Zn^{+2}) and DBP were respectively removed from the solution of phosphoric acid. After 25 minutes, the speed is slightly slower to 30 minutes corresponding to the equilibrium time with 65% of impurities removed.

3.7 Selectivity of adsorption

In order to study the influence of the initial concentration of pollutants are considered the following values: $C_0 = 30, 40, 50,$ and $70$ mg / l. The results are shown in Fig. (7) for the equilibrium time equal to 60 minutes From the results we see that the competitive adsorption is more active for high initial
concentrations. For the selectivity of adsorption was found that retention rates from one element to another in the following order: Zn > DBP > Cu > Cd

3.8. Isothermal equilibrium

L’adsorption des matières organiques en solution est modélisée avec succès par les modèles simples de Langmuir, Freundlich et BET ou le pH de la solution et la force ionique sont constants et la concentration de l’adsorbant ionique est la seule variable.

![Graphical representation of isotherms](image)

Fig. 8. Linearity of the isotherms using olive stones:

(A) Langmuir isotherm (B) Freundlich isotherm (C) BET

The results give the following constants:

Table 2. Constants of adsorption isotherms of elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>BET</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\frac{C_e}{q_e} = \frac{Ce}{a} + \frac{1}{ab}$</td>
<td>$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$</td>
<td>$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{K - 1}{q_m K} [\frac{C_e}{C_0}]$</td>
</tr>
<tr>
<td></td>
<td>$a$ (mg/g)</td>
<td>$b$ (l/mg)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>Cu</td>
<td>0.8142</td>
<td>-0.0544</td>
<td>0.6974</td>
</tr>
<tr>
<td>Cd</td>
<td>0.0670</td>
<td>-0.0317</td>
<td>0.6462</td>
</tr>
<tr>
<td>Zn</td>
<td>-206.20</td>
<td>-0.0139</td>
<td>0.9437</td>
</tr>
<tr>
<td>DBP</td>
<td>-176.99</td>
<td>-0.0077</td>
<td>0.7666</td>
</tr>
</tbody>
</table>

Based on the values of $R^2$ we find that the competitive adsorption of copper, cadmium, zinc and DBP in existing phosphoric acid follows the Freundlich model, and are expressed respectively by the following relations:

$$q_e = 0.00225.Ce^{1.8138}, \quad q_e = 0.03680.Ce^{0.9691}, \quad q_e = 2.2795.Ce^{1.1753}, \quad q_e = 2.3312.Ce^{0.8119}$$

(1)

3.9. Determination of the order of the kinetics of binding cations and DBP

The determination of the order of the kinetics of pollutant removal for various media is important, why it is necessary to study three hypotheses as follows [2]:
Tables 3. Kinetic Constants: Testing of kinetic : (a) (Phosphate Rock of Algeria) (b) (Phosphate Rock of Algeria) (c) (Phosphate Rock of Algeria)

<table>
<thead>
<tr>
<th></th>
<th>First order</th>
<th>Intra particle diffusion</th>
<th>Second order order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \ln (q_e-q)=\ln q_e-K_1t )</td>
<td>( q=K_{int}t^{1/2} )</td>
<td>( t/q=1/K_2.q_e^{2}+t/q_e )</td>
</tr>
<tr>
<td>( R )</td>
<td>( K_1 ) (min(^{-1}))</td>
<td>( K_{int} ) (mg/g.min(^{1/2}))</td>
<td>( K_2 ) (g.mg(^{-1}).min(^{-1}))</td>
</tr>
<tr>
<td>Cu(a)</td>
<td>0.1024</td>
<td>0.8043</td>
<td>0.980</td>
</tr>
<tr>
<td>(b)</td>
<td>0.1821</td>
<td>0.8537</td>
<td>0.981</td>
</tr>
<tr>
<td>(c)</td>
<td>-0.8380</td>
<td>0.8385</td>
<td>0.908</td>
</tr>
<tr>
<td>Cd(a)</td>
<td>-0.2020</td>
<td>0.7891</td>
<td>0.960</td>
</tr>
<tr>
<td>(b)</td>
<td>-0.1418</td>
<td>0.7451</td>
<td>0.955</td>
</tr>
<tr>
<td>(c)</td>
<td>-0.9238</td>
<td>0.8928</td>
<td>0.971</td>
</tr>
<tr>
<td>Zn(a)</td>
<td>-0.4491</td>
<td>0.9342</td>
<td>0.972</td>
</tr>
<tr>
<td>(b)</td>
<td>-0.2141</td>
<td>0.8530</td>
<td>0.820</td>
</tr>
<tr>
<td>(c)</td>
<td>-0.9020</td>
<td>0.8629</td>
<td>0.808</td>
</tr>
<tr>
<td>DBP(a)</td>
<td>-0.3450</td>
<td>0.8709</td>
<td>0.961</td>
</tr>
<tr>
<td>(b)</td>
<td>-0.4797</td>
<td>0.8294</td>
<td>0.955</td>
</tr>
<tr>
<td>(c)</td>
<td>-0.4273</td>
<td>0.8812</td>
<td>0.939</td>
</tr>
</tbody>
</table>

From linear regressions of the three tests, one can conclude the mode of retention of cations (Cu\(^{+2}\), Cd\(^{+2}\), Zn\(^{+2}\)) and DBP organic matter by activated carbon from olive pits for each type of rock:

A - Phosphate rock in Algeria: the model of retention is that of intra-particle diffusion.
B - Phosphate rock in Tunisia: the model of retention is that of intra-particle diffusion, but the retention of the cation Zn\(^{+2}\) is of 2nd order.
C - Phosphate rock from Morocco: retention follows the intra particle diffusion model, while that of the cation Zn\(^{+2}\) is the first order.

4. Conclusion

The phosphoric acid usually contains several heavy metals (copper, cadmium, zinc etc ....) And an organic compound which is Dibutylphthalate (DBP). However, most studies on its purification were carried out on the contamination of a single component such as DBP. To get closer to the actual composition of effluent and quantify the adsorption competition between different derived compounds, we chose to study a mixture of four constituents: copper, cadmium, zinc, and DBP. In this study, we first carried out experiments of the adsorption of these elements independently, prior to the competitive adsorption by testing several physicochemical parameters (initial concentration of the acid and the pollutants, solid-liquid ratio, stirring speed, nature of supports, selective adsorption). We also obtained the dynamics of adsorption at different concentrations (depending on the composition of phosphate rocks of Algeria, Tunisia and Morocco), at room temperature, these four components exhibit dynamic adsorption significantly different when their chemical structure is similar. These first results allowed us to make a comparison between the yields of the independent adsorption of pollutants and of the competitive adsorption and to estimate the optimal values of physicochemical parameters to better purification of phosphoric acid and establish the adsorption isotherms. For the four components, depending on the type of coal from olive pits, the isotherm follows the Freundlich model prediction is more suitable than the Langmuir and BET. So the adsorption of DBP and heavy metals quickly reaches equilibrium adsorption suggesting a multi - layered, mainly limited by diffusion in the pores. The study of kinetics showed that the order of it differs At the other component and that for all the rock phosphates
studied. For the selectivity of adsorption was found that retention rates of an element to another in the following order: Zn > DBP > Cu > Cd.

References


