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# Elimination of Trace Element Ions $Co^{2+}$ and Toxic $Pb^{2+}$ from Wastewater on a Food Waste (Apricot Kernel Shell Treated with Acid)

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## Abstract

The main objective of this manuscript was to investigate the adsorption potential of Apricot Stone Activated Carbone (ASAC) for the removal of Heavy Metals ions from aqueous solution in a batch mode operation. The adsorbent was characterized by FTIR, BET, X-fluorescence and X-ray diffraction. The influence of the operating parameters such as initial concentration, pH, temperature, adsorbent dosage, particle size and contact time on ASAC is explored. A comparison between several models on the overall adsorption rate showed that the kinetic of adsorption was better described by the pseudo-second order model. The Langmuir, Freundlich and Temkin models were used to depict the adsorption of metal ions onto ASAC. The smaller RMSE values obtained for the Langmuir Isotherm model indicate the better curves fitting. The maximum monolayer adsorption capacity of the ASAC were found to be 80.628 mg/g at pH 8 and 25.22 mg/g at pH 9 for $Pb^{2+}$ and $Co^{2+}$ respectively. The thermodynamic results showed that the adsorption process was exothermic and spontaneous in nature.

This work has been undertaken in the field of the environment to evaluate the application potential of activated carbon prepared from apricot stone as a low-cost adsorbent for the removal of toxic pollutants. Pollutant wastewater has long been a major environmental problem all over the world. The problem is further aggravated by rapid industrialization, population growth and unskilled use of natural water resources.

This study has given encouraging results, and we wish to carry out column adsorption tests under the conditions applicable to the treatment of industrial effluents.

***Keywords:*** *Heavy Metals; Isotherm; Equilibrium; Adsorbent; Modeling; Thermodynamic; Apricot Stone*

## Introduction

The effects of heavy metals like lead, copper, zinc, cobalt on the human health have been extensively studied and well documented. Excessive ingestion of such metals can cause accumulative poisoning, cancer, nervous system damage, etc [1]. Cobalt is an oligo element that is essential for human health since it is a part of vitamin B12. However, higher concentration of cobalt may cause low blood pressure, paralysis, diarrhoea, lung irritation and bone defects. Lead is a common industrial metal that has become widespread in air, water and soil. He is widely used in the storage batteries, gasoline additives and other chemicals, ammunition, solder, and other uses and the world production exceeds 3 million tons per year. The presence of heavy metals in the aquatic environment has been of great concern for the scientists and engineers because of their increased discharge, toxic nature, and other adverse effects on receiving waters. In this respect, the excessive utilization of lead has dramatically raised its concentration in blood. We are interesting by Pb and Co and which are ubiquitous in the environment and hazardous at high level. It is a general metabolic poison and enzyme inhibitor and can accumulate in bones, brain, kidney and muscles. Long-term drinking water containing lead causes serious disorders, like anemia, kidney disease and mental retardation. In order to insure a better quality of life and protect the environment, removing lead from industrial wastes is of vital importance. Unlike organic compounds, lead is non-biodegradable and, therefore, must be removed from water. A wide variety of inexpensive materials, have been exploited for the cobalt and lead removal from aqueous medium, including, apricot stone [2-6]. Apricot stone is a cheap precursor for activated carbon source.

### Batch mode adsorption studies

The effects of the experimental parameters such as, the initial $Pb^{2+}$ and $Co^{2+}$ concentration (20 - 100 $mgL^{-1}$), pH (2 - 14), adsorbent dosage (5 - 45 $gL^{-1}$) and temperature (298 - 323 K) on the adsorptive removal of $Pb^{2+}$ and $Co^{2+}$ is studied in batch mode for a specific period of contact time (0 - 40 minutes). The stock solution is prepared by dissolving the accurate amount of $PbSO_4.7H_2O$ and $CoSO_4.7H_2O$ (99 %, Merck) in distilled water and other solutions are prepared by dilution). The amount of $Pb^{2+}$ and $Co^{2+}$ adsorbed on activated carbon $q_t$ ($mgg^{-1}$) is calculated by using the following equation (A1):

$$q_e = \frac{(c_0 - c_e).V}{m} \quad \text{Eq. (A1)}$$

where $C_o$ is the initial $Pb^{2+}$ and $Co^{2+}$ concentration and $C_t$ the $Pb^{2+}$ and $Co^{2+}$ concentrations ($mgL^{-1}$) at any time, V the volume of solution (L) and m the mass of the activated carbon (g).

Due to the inherent bias resulting from linearization of the isotherm models, the non-linear regression Root Mean Square Error (RMSE) equation (A2), the Sun of Error Squares (SSE) equation (A3) and Chi-Squares (X2) equation (A4) test are employed as criterion for the quality of fitting.

$$\text{RMSE} = \sqrt{\frac{1}{\text{N-2}}.\sum_1^N (q_{e,exp} - q_{e,cal})^2} \quad \text{Eq. (A2)}$$

$$\text{SSE} = \frac{1}{N}\sum_{n=1}^{\infty} (qe_{cal} - qe_{exp})^2 \quad \text{Eq. (A3)}$$

$$X^2 = \sum_1^N \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \quad \text{Eq. (A4)}$$

Where, $q_{e(exp)}$ ($mg.g^{-1}$) is the experimental value of uptake, $q_{e(cal)}$ the calculated value of uptake using a model ($mg.g^{-1}$), and N the number of observations in the experiment (the number of data points). The small the RMSE values, the better the curve fitting.

## Results and Discussion

### Characterization of ASAC

The FTIR spectrum of ASAC displays a number of adsorption peaks, indicating that many functional groups of the adsorbent are involved in the adsorption. The peak at 1732 $cm^{-1}$ is assigned to C=O in carboxylic groups. Such results clearly indicate that the functional groups including carboxylic and hydroxyl groups contribute to $Pb^{2+}$ adsorption on the binding sites. The prepared activated carbon was characterized by selected physical properties (bulk density and surface area), chemical properties and adsorption properties (pH of the point of zero charge: $pH_{pzc}$). The elemental analysis was performed by using an elemental analyzer LECO-CHNS 932. The specific surface area of the activated carbon was achieved by using the BET-Technic, as a sorption phenomenon of nitrogen gas on the adsorbent surface, at 77K. The measurements were made using a Pore Size Micrometric-9320, USA equipment. The ash content Ash (%) of the activated carbon was determined by using a muffle furnace over 3 hours at 450°C. Conductivity measurements were carried out by using a conductimeter type Erwika. The $pH_{pzc}$ of the ASAC was determined by using potassium nitrate (Cerovich Method).

## Optimization study of operating conditions

Significant variations in the uptake capacity and removal efficiency are observed for different particles sizes; indicates that the best performance is obtained with smaller sizes (315 - 800 µm). The adsorption capacity of ions increases over time and reaches a maximum after 20 minutes of contact time and thereafter, with a constant value indicating that no more $Pb^{2+}$ ions are further removed from the solution. The equilibrium times averages 40 minutes but for practical reasons the adsorption experiments are run up to 40 min. With raising the initial ions concentration ($C_o$) from 20 to 40 mgL$^{-1}$, the amount of $Pb^{2+}$ and $Co^{2+}$ adsorbed increases from 8.38 to 16.8 and from 3.94 to 7.94 mgg$^{-1}$ respectively Figure 1.

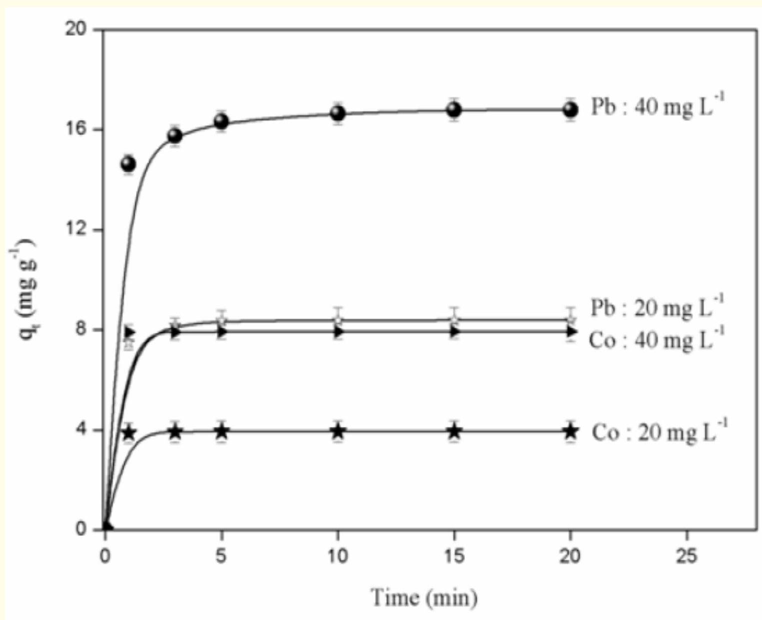


***Figure 1:*** *Effect of contact time and concentration.*

The effect of the stirring speed in the range (100 - 1250 rpm) on the adsorption capacity onto ASAC is also investigated. The optimal adsorption capacity is obtained for a speed of 300 rpm which gives the best homogeneity of the mixture suspension. The first stage of batch experiments on ASAC and the effect of adsorbent dosage on the $Pb^{2+}$ and $Co^{2+}$ adsorption are examined.Significant variations in the uptake capacity and removal efficiency are observed at different adsorbent dosage (5 - 45 gL$^{-1}$), indicating that the best adsorption is obtained with an adsorbent dosage of 5 gL$^{-1}$. This result was subsequently used in all isotherms adsorption experiments. The pH (ZPC) is determined by Cerovitch method (Figure 2).

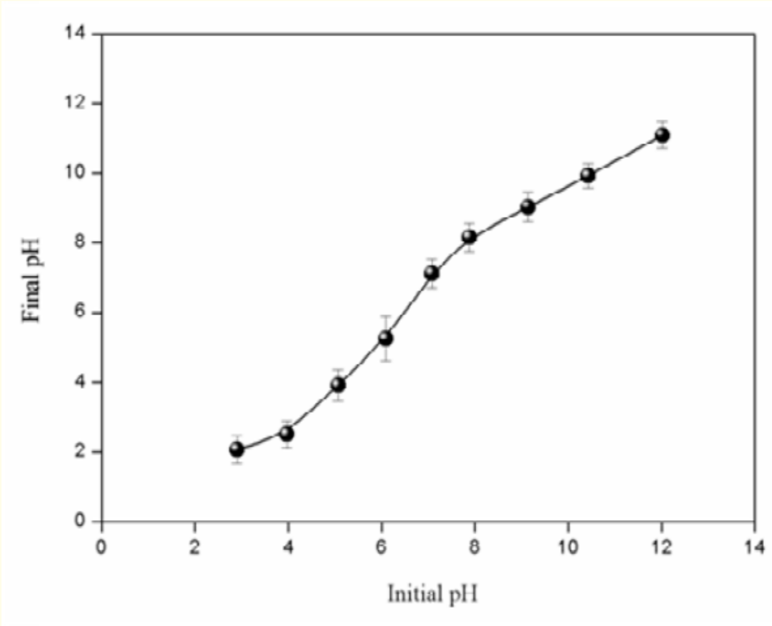


***Figure 2:*** *Determination of pH ($_{ZPC}$).*

### Adsorption Isotherms

The shape of the isotherms is the first experimental tool to diagnose the nature of a specific adsorption. The isotherms are generally classified in four main groups: L, S, H, and C shapes according to of [6]. In our case the isotherm of $Pb^{2+}$ and $Co^{2+}$ on ASAC displays an L shape figure 3 and 4. The constants models parameters are summarized in (Table 1).

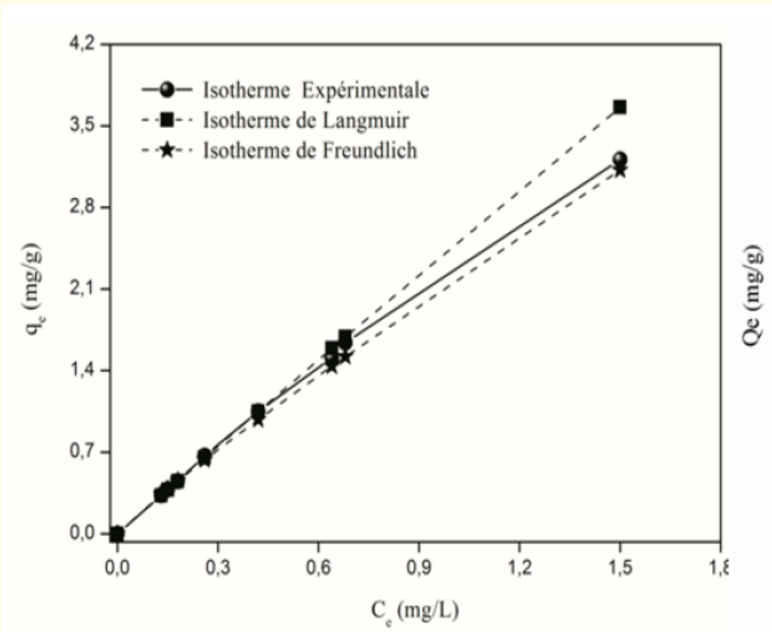


***Figure 3:*** *Adsorption Isotherm of Cobalt.*

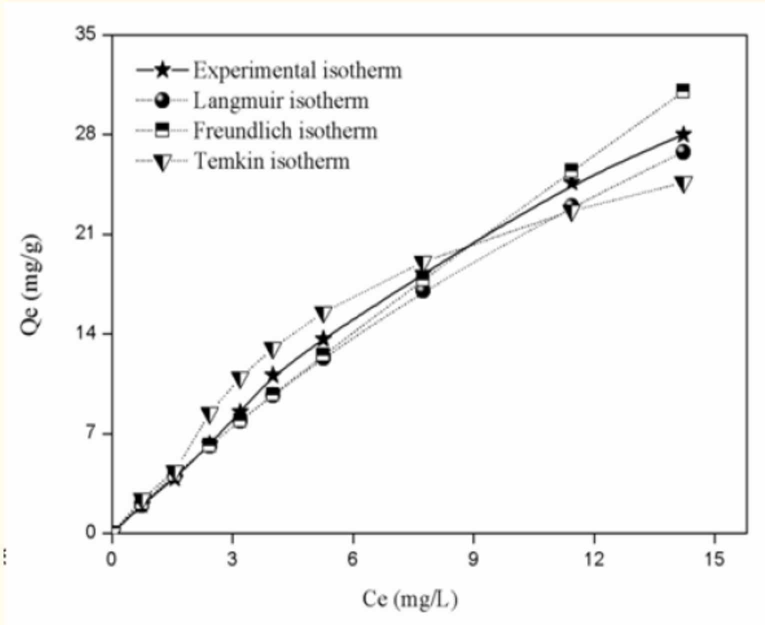


***Figure 4***: *Adsorption Isotherm of Lead.*

| Model | Langmuir | Freundlich | Temkin |
|---|---|---|---|
| | $q_{max}$ = 80.628 $mgg^{-1}$ | 1/n = 0.859 | B = RT/ΔQ = 6.588 |
| $Pb^{2+}$ | $K_L$ = 0.034 $Lmg^{-1}$ | $K_F$ = 2.849 $mgg^{-1}$ | ΔQ = 375.89 $Jmol^{-1}$<br>BLnA = 2.008<br>A = 1.356 |
| $R^2$ | 0.995 | 0.998 | 0.894 |
| RMSE | 3.0032 | 2.81354 | 3.4907 |
| SSE | 9.0191 | 7.91601 | 18.1849 |
| $X^2$ | 0.1011 | 0.1026 | 0.2072 |
| | $q_{max}$ = 25.22 $mgg^{-1}$ | 1/n = 0.909 | B = RT/ΔQ = 1.079 |
| $Co^{2+}$ | $K_L$ = 0.102 $Lmg^{-1}$ | $K_F$ = 2.16 $mgg^{-1}$ | ΔQ = 2295.06 $Jmol^{-1}$<br>BLnA = 2.107<br>A = 8.22 |
| $R^2$ | 0.995 | 0.998 | 0.954 |
| RMSE | 0.1874 | 0.0738 | 5.658 |
| SSE | 0.1623 | 0.0639 | 39.14 |
| $X^2$ | 0.1101 | 0.0423 | 1.321 |

***Table 1:*** *Sorption isotherms coefficients of Langmuir, Freundlich and Temkin models.*

## Adsorption kinetics

Two kinetic models namely the, pseudo first order and pseudo second-order are selected in this study for describe the adsorption process. The pseudo first order equation is given by [7]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}.t \qquad \text{Eq. (B1)}$$

While the pseudo second order model [8] is given by:

$$\frac{t}{q_t} = \frac{1}{k_2 . q_e^2} + \frac{1}{q_e}.t \qquad \text{Eq. (B2)}$$

where qt ($mgg^{-1}$) is the amount of ions adsorbed on ASAC at the time t (min). $K_1$ ($min^{-1}$) and $K_2$ (g $mg^{-1}min^{-1}$) are the pseudo-first order and pseudo-second order kinetics constants respectively (Table 2).

| | | **Pseudo-second order kinetic** | | | **Pseudo-first order kinetic** | | |
|---|---|---|---|---|---|---|---|
| | **$q_{e,exp}$($mgg^{-1}$)** | **$q_{e,cal}$($mgg^{-1}$)** | **$K_2$($gmg^{-1}min^{-1}$)** | **$R^2$** | **$q_{e\,cal}$($mgg^{-1}$)** | **$K_1$($mn^{-1}$)** | **$R^2$** |
| $C_0$ ($mgL^{-1}$) | | | | | | | |
| **$Co^{2+}$** | | | | | | | |
| 20 | 3.94 | 3.945 | 21.42 | 1.00 | 5 $10^{-9}$ | 1.28 | 0.758 |
| 40 | 7.95 | 7.94 | 1.38 | 1.00 | 0.43 | 0.511 | 0.367 |
| **$Pb^{2+}$** | | | | | | | |
| 20 | 8.39 | 8.44 | 1.38 | 0.999 | 2.32 | 0.625 | 0.805 |
| 40 | 16.80 | 16.80 | 0.86 | 0.999 | 5.759 | 0.408 | 0.778 |

***Table 2:*** *Pseudo-first order and pseudo-second order kinetic model constants.*

The mechanism of the adsorption reaction of metals has been proposed to interpret the phenomenon [9].

$M^{2+} + H^2O \rightleftharpoons M(OH)^+ + H^+$ ($M^{2+}$: $Co^{2+}$, $Pb^{2+}$ )

$M(OH)^+ + X^- \rightleftharpoons XMOH$ with $X^-$ : Surface (negative sites of the adsorbent)

The adsorption capacity of ASAC increases with raising temperature over the range (298-323 K), above, the vaporization becomes increasing problem The insights of the adsorption mechanism can be determined from the thermodynamic parameters: the free energy (G°), the enthalpy (H°) and the entropy (S°) [10].

## Conclusions

The present study has shown that the activated carbon prepared from apricot stone can be employed as effective and low cost adsorbent for the removal of $Pb^{2+}$ and $Co^{2+}$ in aqueous solution. Increasing the initial concentration and pH led to an improved adsorption capacity of ASAC. The Freundlich and Langmuir models provides the best fit of the equilibrium adsorption data with a maximum adsorption capacity of 80.628 $mgg^{-1}$ at pH ~ 8 and 25.22 $mgg^{-1}$ at pH ~ 9 for $Pb^{2+}$ and $Co^{2+}$ respectively. The thermodynamic parameters indicate that the $Pb^{2+}$ and $Co^{2+}$ adsorption onto ASAC are exothermic and spontaneous in nature. The $Pb^{2+}$ and $Co^{2+}$ uptake follows the pseudo-second-order kinetic model, which relies on the assumption that the chemisorption is the rate-limiting step. The results of the present investigation showed that ASAC is a potentially useful adsorbent for the adsorption of metals, an issue of environmental concern and the natural abundance of this food waste can provide an adsorption medium which contributes to the treatment of wastewater. The comparison of the adsorption capacity of the prepared adsorbent with other adsorbents shows its attractive properties from industrial and economic interests. This work has been undertaken in the field of the environment to assess the application potential of a low-cost prepared activated carbon for the removal of toxic pollutants. Wastewater has long been a major environmental problem in the world. The problem is further aggravated by rapid industrialization and unskilled use of natural water resources. This study has given encouraging results, column adsorption tests re envisaged.

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