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# Sorption potential of impregnated charcoal for removal of heavy metals from phosphoric acid

E.A. El-Sofany*, W.F. Zaher, H.F. Aly

*Hot Laboratory Center, Atomic Energy Authority, P.O. Box 13759, Cairo, Egypt*

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ABSTRACT

The viability of some heavy ions removal from phosphoric acid solution by means of impregnated charcoal with triphenylphosphine sulphide extractant has been demonstrated in this work. Factors affecting removal of $Cu^{2+}$, $Cd^{2+}$, $Zn^{2+}$and $Pb^{2+}$ include initial concentration of ions, volume of the aqueous solution to weight of adsorbent ratio ($V/m$), concentration of the extractant loaded onto charcoal and temperature. The removal percent of these ions is increased by decreasing values of $V/m$ ratio and increasing temperature for all ions. The sorption isotherms data fit Langmuir, Freundlich and Dubinin–Radushkviech (D–R) models. The values of the mean free energy, $E_a$, of sorption is in all cases in the range 9.1–25.6 kJ/mol, which are within the ranges of chemical sorption reaction. The sorption reaction was found to obey a pseudo second-order rate model.



## 1. Introduction

Phosphoric acid is generally produced in Egypt by the wet process method, where the hydroxyl appetite mineral is treated mainly with sulfuric acid. Wet process phosphoric acid (WPA) contains a number of organic and inorganic impurities that affect on the grade of the acid. Some of these inorganic impurities are heavy ions such as copper, cadmium, zinc and lead which are considered as hazardous substances. The presence of these impurities is the reason for about 95% of the acid produced by the wet process is directly used as fertilizers and not in other applications as foodstuff, pharmaceutics and sugar industry [1].

Removal of heavy ions from phosphoric acid has been studied using many techniques, such as precipitation [2], liquid membranes [3], liquid–liquid extraction [4,5] and solid–liquid extraction [6].

This technique provides the best use of advantages of both liquid–liquid extraction and solid–liquid technologies. The solvent impregnated materials are characterized by their high binding capacity, selectivity and enhanced mobility of the extractant in the solid surface [7]. Numerous extractants [8–12] were used by this technique such as organophosphorus extractants like di(2-ethyl hexyl phosphoric acid (HDEHP), CYANEX-272, PC-88A; neutral extractants like tri-*n*-butyl phosphate (TBP) and also basic extractants like tri-*n*-octylamine (TOA). These extractants were impregnated onto different supports like XAD series Amberlite resins, silica gel, kiesselguhr and activated carbons.

In this contribution, the removal of Cu(II), Cd(II), Zn(II) and Pb(II) ions form phosphoric acid solutions by triphenylphosphine sulphide impregnated onto charcoal has been investigated by batch kinetics and equilibrium studies.

## 2. Experimental

### 2.1. Chemical and reagents

All chemicals and reagents used were of AR grade. Copper, cadmium, zinc and lead were prepared using analytical grade $CuSO_4$, $CdSO_4$, $ZnSO_4$ and $PbNO_3$ obtained from Winlab, England. Analytical grade phosphoric acid solution (Adwic) was used. Triphenylphosphine sulphide (TPPS) obtained from Aldrich and chloroform was purchased from Adwic. Activated charcoal supplied by LOBA Chemie. The concentrations of the heavy ions studied were determined using atomic absorption spectrometry (AAS) model Z-8100, Hitachi, Japan.

### 2.2. Preparation of the solid phase

TPPS in (chloroform) solution was impregnated onto charcoal by dry method technique which is widely used [13]. In this concern, 50 mL of the impregnated solutions were mixed with 10 g of

* Corresponding author. Tel.: +20 2 555 3747; fax: +20 2 462 0796.
*E-mail address:* bosycat_19902000@yahoo.com (E.A. El-Sofany).

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charcoal. The resulting slurry is gently stirred for 2 h and chloroform was then evaporated at ambient temperature (25 ± 1 °C). The solid materials were dried at 70 °C before use.

### 2.3. Procedure

Cu, Cd, Zn and Pb solutions were prepared by dissolution of certain weights of their salts in 3.5 M phosphoric acid to obtain solutions containing 1.0 g/L for each ion. Ions concentrations were determined by AAS.

Batch sorption experiments were performed by shaking 0.05 g of the impregnated charcoal with 5.0 mL of the ion solution in a thermostated shaker bath at (25 ± 1°C). All the experiments were carried out in triplicate and the mean values were presented.

The amount of the ion uptake was calculated by the difference between the equilibrium concentration and the initial concentration. The amount of ion retained in the solid phase $q_e$ (mg/g) was calculated using the relation:

$$q_e = (C_o - C_e)\left[\frac{V}{m}\right] \quad (1)$$

where $C_o$ and $C_e$ are the initial and equilibrium concentrations (mg/L) of ions solution, respectively, $V$ is the volume of solution (L) and $m$ is the weight (g) of the adsorbent.

The removal percent of ions from the aqueous phase is calculated from the relation:

$$R\% = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

## 3. Results and discussion

### 3.1. Infrared spectroscopy

The impregnation process of TPPS on charcoal is mainly due to a combination of pore filling as well as surface adsorption i.e. extractants fill almost all porous system for charcoal. This suggestion is confirmed using detailed investigation of quantitative IR spectroscopic characterization of charcoal before and after impregnation step.

The spectrum of untreated charcoal is shown in Fig. 1a, and the spectrum of charcoal loaded with triphenylphosphine sulphide is shown in Fig. 1b.

Fig. 1a shows the characteristic conjugated polynuclear aromatic compounds band at 1567 $cm^{-1}$. This figure also shows C—H and O—H bending bands at 1111 $cm^{-1}$, also, bands in the range of 622–450 $cm^{-1}$ arising from out of plan C—H bending modes of aromatic structures.

As shown in Fig. 1b and comparing with Fig. 1a, It could be observed that addition of triphenylphosphine sulphide shows a new P=S stretching band at 870 and 550 $cm^{-1}$. Also P=Ph bands at 1527 and 1105 $cm^{-1}$ and a stretching band of benzene cycle C—H at 3764 $cm^{-1}$. All of these bands confirmed that TPPS is typically impregnated on charcoal.

### 3.2. Batch investigation

The removal of Cu, Cd, Zn and Pb ions were tested experimentally to investigate the adsorption capacities of the impregnated charcoal. The factors affecting removal percent of the studied ions are, $V/m$, ion concentrations, extractants concentration and temperature.

#### 3.2.1. Removal kinetics

The removal kinetics of Cu, Cd, Zn and Pb ions at a concentration of 50 mg/L for each on the impregnated charcoal are studied as a function of shaking time at different time intervals ranged from 15 min to 2 h. As shown in Fig. 2a and b the equilibrium of the four elements is reached after 60 min for the impregnated charcoal system at different concentration of extractant. From the figures, it was found that the removal of the ions is increased with increasing shaking time until a steady state is attained after 60 min. The kinetic data indicates that no significant change in the removal percent after the 2 h.

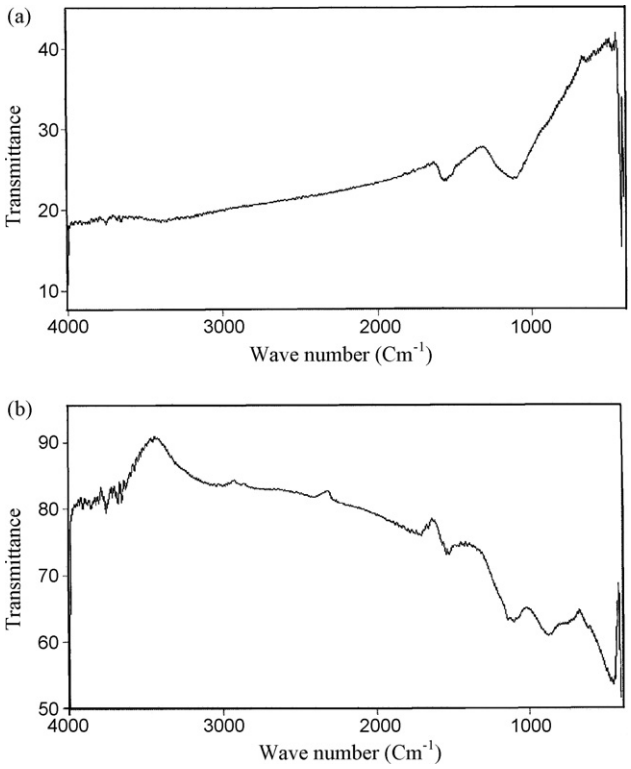


**Fig. 1.** (a) Infra-red spectrum of charcoal. (b) Infra-red spectrum of charcoal impregnated with TPPS.

#### 3.2.2. Volume to weight ratio

The effect of $V/m$ on the removal percent of Cu, Cd, Zn and Pb ions from 3.5 M phosphoric acid is studied in the range from 25 to 200 to evaluate the optimum resin weight to achieve a high removal capability. As shown in Fig. 3a and b the removal percent increases as $V/m$ ratio decrease from 200 to 25. The $V/m$ ratio was kept at 100 during all the experiments whereas there is no increase in the removal percent less than this ratio.

#### 3.2.3. Extractant concentration

The effect of TPPS concentrations on the removal percent of the studied ions is shown in Table 1. It was noticed that as the concentration of TPPS increased from 0.05 to 0.1 M a slight increase in the removal percent was observed. The order of removal is as follow

**Table 1**
Effect of extractant concentration on the removal percent of $Zn^{2+}$, $Cd^{2+}$, $Cu^{2+}$ and $Pb^{2+}$ ions onto impregnated charcoal.

| Metal ion | Removal%, 0.05 M TPPS | Removal%, 0.1 M TPPS |
|---|---|---|
| $Cu^{2+}$ | 25.46 | 27.45 |
| $Cd^{2+}$ | 31.89 | 43.7 |
| $Zn^{2+}$ | 21.8 | 36.74 |
| $Pb^{2+}$ | 8.47 | 9.12 |