Adsorption and Separation of Mercury (II) on Synthetic Two Component Ion Exchange Material

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Abstract:- A Method has been developed for the quantitative adsorption and spectrophotometric determination of Hg (II) by employing antimony phosphate as two component adsorbing material and Dithizone (1, 5-Diphenylthiocarbazone) as spectrophotometric reagent. Antimony phosphate was prepared, processed and characterized. Antimony phosphate found to be stable towards acids, weak bases and most of the common chemical reagents. The effect of different parameters such as time of contact, amount of absorbent etc in the adsorption of 10 µg of Hg (II) have been studied. It has been observed that 100 mg of antimony phosphate is sufficient for maximum adsorption (92.62 $\underline{+}$ 1.29 %) of 10 µg Hg (II) at pH 3.5 and contact time of 3 min. Under the optimum condition of adsorption, effect of various anions and cations in the adsorption of Hg (II) has been studied. Interfering cations has been masked by using suitable masking agent or reducing the amount of cations so as to make the process more selective. The distribution coefficient values for various cations were also evaluated.

Keywords:- *Antimoney phosphate, seperation, Mercury(II), Adsorption, 1-5-diphenylthiocarbazone, Specrophotometry.*

I. INTRODUCTION

The compounds of mercury are used extensively in insecticides and bactericides for agricultural purposes. Mercury amalgams find various applications in diverse fields such as Zn-Hg as a reducing agent in synthesis, Cd-Hg in the Weston cadmium cell, Au-Hg in dental fillings etc. In most of these applications a simple, rapid and accurate analytical method for determining the mercury content in the samples is often essential. Determination of Mercury & its compounds have a long history in medicine. Certain metal salts and its compounds are used in the skin ointment, eye ointment and lotions.

Adsorption is a process in which atom or molecules move from a bulk phase onto a solid or liquid surface. At the molecular level, adsorption is due to attraction interaction between a surface and the species being adsorbed. Antimony phosphate is two component ion exchange material which is thermally and chemically stable. It shows selective adsorption towards Hg (II). Literature Survey reveals that Dithizone has been used for spectrophotometric determination of Hg (II) in environmental samples, biological sample, water samples, soil samples, etc. A very simple, sensitive and selective spectrophotometric method for Hg (II) has been reported in the literature by Humaria Khan etal. [2] The method obeys Beer Lamberts Law in the range of 0.05 µg to 10µg. In the present investigation the method has been developed for the maximum adsorption of 10µg of Hg (II) on antimony phosphate. The interference of various anions and cations in the adsorption of Hg (II) also have been studied. Ideal conditions in the adsorption of Hg (II) on antimony phosphate has been investigated.

II. EXPERIMENTAL

A. Hg (II) standard solution

1 mg per cm^3 Hg (II) was prepared by dissolving required amount of mercury chloride in deionized distilled water containing nitric acid. The solution was standardized by complexometirc titration.

B. 1,5-diphenylthiocarbazone

1.95 x 10^{-4} M solution was prepared by dissolving required amount of diphenylthiocarbazone in known volume of isoamyl alcohol

C. Sodium dodecyl sulfate

0.6 M solution of pure sodium dodecyl sulfate was prepared in deionised distilled water.

All other reagents and chemical used were AR grade

D. Synthesis of Antimony Phosphate

Antimony phosphate was prepared as per the method [3] by mixing the solution of potassium pyro antimonate (1 M) and Ortho Phosphoric Acid (0.05 M) in 1:1 volume ratio. The pH of the solution was maintained by adding aqueous ammonia with constant stirring. The gel obtained was kept for 24 hrs at room temperature and filtered under suction. The excess acid was removed by washing with deionized water and then material was dried in the oven at 50° C. The material was converted into H^+ form by treating with 1 M nitric acid for 24 hrs. It was washed with deionized water to remove excess acid and finally dried at 50° C. After grinding, required quantity of the material was taken for batch adsorption studies. FTIR spectra (Figure I) was also recorded to characterize the material synthesized.

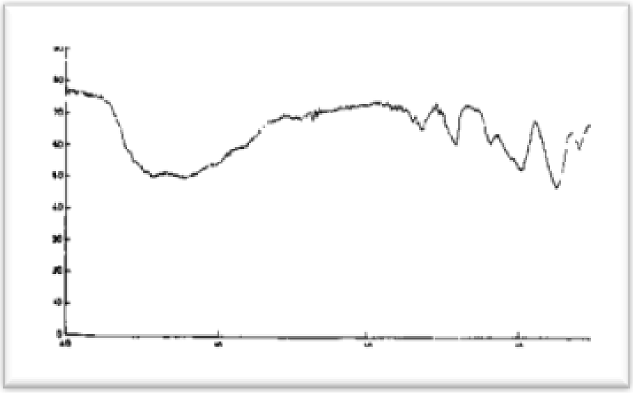

Fig 1:- IR spectra of antimony phosphate

IR spectra (Figure 1) show the various peaks at around 750, 1050, 1200, 1400,1600 and 3300 cm^{-1}.The peaks observed at 750 and 1050 cm^{-1} are indicative of the metal-oxygen stretching vibrations while those at 1200 and 1400 cm^{-1} are due to the presence of phosphate groups. The presence of water of crystallization is indicated by the peaks at 1600 and 3300 cm^{-1}. The peaks at 1600 $^{\text{cm-1}}$ are also indicative of the strongly hydrogen - bonded - OH groups or extremely strongly coordinated H_2O molecules. [4,5]

III. MEHOD

A. Batch Adsorption Method

10 cm^3 solution containing 10 μg of Hg (II) whose pH adjusted at 3.5 was added to 100mg of Antimony phosphate in a cone of capacity 25 cm^3. Mixture was equilibrated for 3minutes, centrifuged for 5 minutes and supernatant liquid was collected in 25cm^3 standard measuring flask. 5cm^3 of 0.6 M Sodium dodecyl sulfate and 1cm^3 of 1 M H_2SO_4 was added followed by 1.5 cm^3 of 1.95x10^{-4}M Dithizone solution. The mixture was diluted to the mark with deionized water. The absorbance spectra was recorded (Figure II) using spectrophotometer (Equip-Tronics EQ-825).In all further adsorption studies absorption was measured at 490nm against reagent blank. The percentage of Hg (II) adsorbed and unadsorbed was calculated using standard formula.

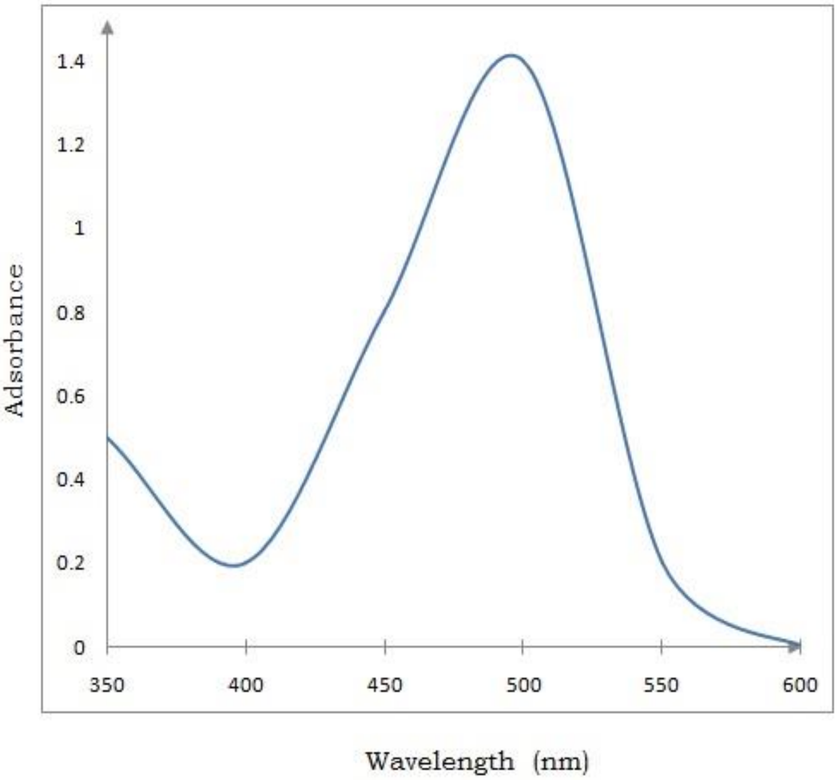

Fig 2:- Absorbance Spectra of Hg (II)-Dithizone Complex

IV. RESULTS AND DISCUSSION

A. *Effect of pH*

Effect of pH in the adsorption of 10 µg Hg (II) on 100mg of antimony phosphate was studied for contact time of 3 minutes. It was observed that adsorption of Hg (II) was increased upto pH 3.5 and remained constant thereafter. From the Figure III, it is cleared that percentage adsorption of Hg (II) on 100mg of antimony phosphate is maximum at pH 3.5. Hence all further adsorption studies were carried at pH 3.5

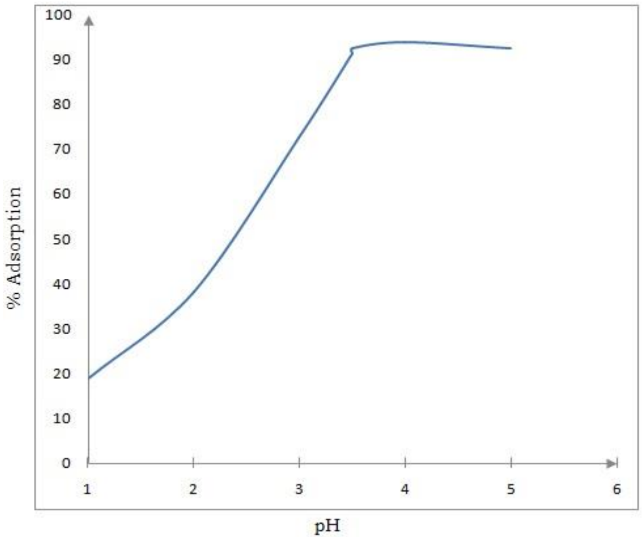

Fig 3:- Effect of pH
(Amount of Hg (II) 10 µg, amount of antimony phosphate 100mg, time of contact 3 min, temperature 28 ± 2^0 C)

B. *The Effect of Amount of Antimony Phosphate*

The effect of amount of antimony phosphate in the adsorption of 10 µg Hg (II) was studied at pH 3.5. Amount of antimony phosphate was varied from 50mg to 200mg. From Figure 4 it is revealed that 100mg of antimony phosphate is sufficient for the maximum adsorption of 10 µg of Hg (II) at pH 3.5 and contact time of 3 minutes.

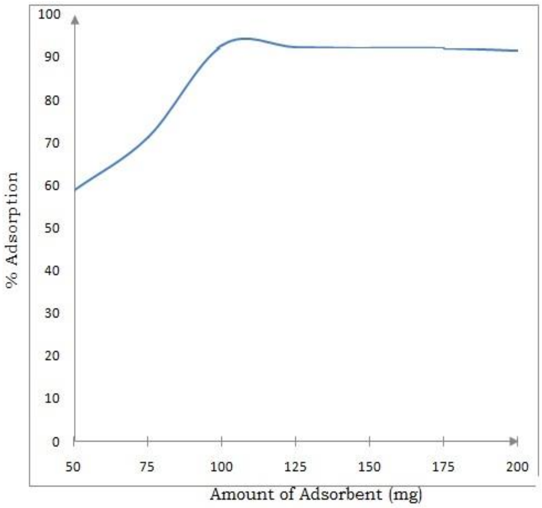

Fig 4:- Effect of Amount of Adsorbent
(Amount of Hg (II) 10 µg, pH 3.5, time of Contact 3 min, temperature 28 ± 2^0)

C. *Effect of Time of Contact*

The effect of time of contact in the adsorption of 10 µg of Hg (II) on 100mg of antimony phosphate was studied. From figure 5 it is clear that 3 minutes of contact time is sufficient for the maximum adsorption of 10 µg Hg (II) over 100mg of antimony phosphate at pH 3.5.

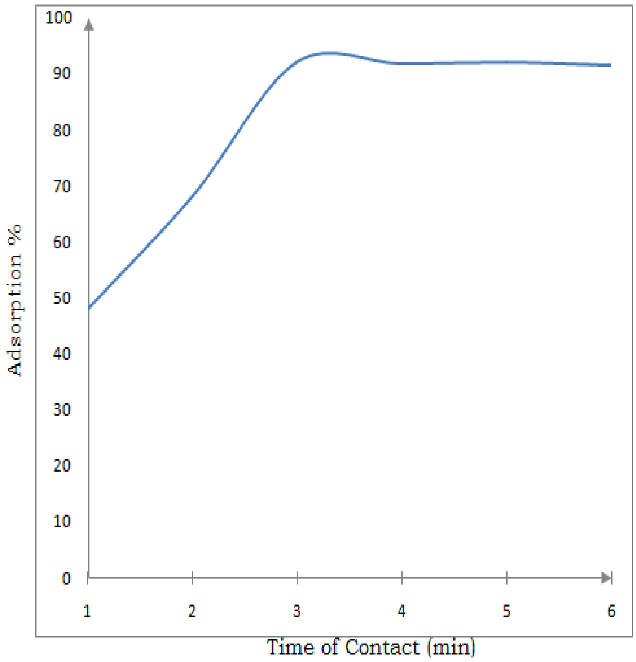

Fig 5:- Time of Contact
(Amount of Hg (II) 10 µg, pH 3.5, Amount of Antimony Phosphate 100mg, Temperature 28 ± 2°C)

From the study of above parameter in the adsorption of Hg (II) over antimony phosphate, it is cleared that 100mg of antimony phosphate is sufficient for maximum adsorption of 10 µg Hg (II) at pH 3.5 and contact time of 3 minutes.

D. *Reproducibility*

Reproducibility of the method was evaluated by repeating the batch adsorption method at ideal conditions in the adsorption of Hg (II). From table 1 it is observed that the reproducibility of the method is 92.62 ± 1.29 %

pH	% Adsorption
1	38.3
2	72.66
3	91.33
3.5	91.33
3.5	92.67
3.5	93.88
4	92.65
5	92.82
6	91.88

Table 1:- Reproducibility
(Hg (II) ion concentration 10mg, Amount of antimony phosphate 100mg, pH 3.5, Time of Contact 3 min, Temperature 28 ± 2°C)
Reproducibility of the method = 92.62 ± 1.29 %

E. Interference of anions

Effect of different anions in the % adsorption Hg (II) was investigated by taking the anion as salt of K$^+$ or NH4$^+$. It has been observed that 1mg of EDTA, tartrate; 0.5mg of Acetate; chloride; oxalate, bromide, citrate, carbonate, iodide, nitrate, phosphate, persulfate, sulfite, thiocyanate do not interfere in the adsorption Hg (II) on antimony phosphate. During Interference studies the ppt formed (if any) was centrifuged prior to the Adsorption.

F. Adsorption of other elements and Distribution Coefficient (Kd) values

0,1mg of Sb (III), Ce(IV), Zr(IV), La(III),Al (III), As (III), As (V), Be (II), Ba (II), Bi (III), Cd (II)*,Zn(II)*, Ni (II)*,Ag(I)*,Na(I), Cr (III), Cr (VI), Co (II), Co (III), Ca (II), Cu (II), Fe(II), Cs (I), In(II), Tl(I), Fe(III) was adsorbed to the extent of less than 17 %. 0.05mg of Mn (II), Mo (VI), Mg (II), Ni (II), K (I), Sr (II), Tl (I), was adsorbed to the extent of less than 10 % and did not interfere in the adsorption of Hg (II). Whereas 0.01mg of Zn(II), , Cd (II), Ni(II) interfere in the adsorption of Hg (II). The interference were masked by using suitable masking agents so as to make the separation process more selective. The distribution coefficient (Kd) in presence of Hg(II) which gives affinity of various cations towards adsorbent under experimental conditions also have been evaluated and as given in Table 2.

Metal Ion	Kd Value	Metal Ion	Kd Value
Sr(II)	0.82	Fe(II)*	8.24
Ba(II)	1.23	Cr(VI)	8.57
Zr(IV)	1.77	Ca(II)	8.86
Mg(II)	2.46	Mn(II)*	9.10
Co(II)	2.77	Fe(II)*	9.46
Mo(II)	3.34	Tl(I)	11.28
La(III)	3.47	Al(III)	12.63
Ce(II)*	3.86	In(III)	16.77
Fe(III)*	4.77	Ce(II)	38.84
Be(II)	4.89	Mn(II)	42.44
K(I)	4.98	Ag(I)	48.73
Na(I)	5.56	Fe(III)	58.57
Ag(I)*	6.52	Fe(II)	116.54
Ni(II)*	6.86	Zn(II)	164.34
Zn(II)*	6.88	Cd(II)	176.44
Cd(II)*	7.56	Ni(II)	241.08

Table 2:- Distribution Coefficient (Kd) Values On Antimoney Phosphate In The Presence Of Hg(Ii)
(Hg (II) ion concentration 10mg, Amount of antimony phosphate 100mg, pH 3.5, Time of Contact 3 min, Temperature 28 ± 2°C)

The method thus developed for the separation of Hg(II) by adsorbing it on the Antimony phosphate is selective, rapid and will be applied for the determination of mercury in water samples, soil samples, synthetic mixtures etc.

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