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# Adsorption Profile and Complexing Behavior of Hg(II) Ions onto Polyurethane Foam from Acidic Mixed Solvent System ($H_2O + $Ethanol) Containing Dithizone

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**A new method has been developed to remove Hg(II) metal ion by preconcentrating onto polyurethane foam (PUF) from acidic mixed solvent system (0.5 N $HNO_3 + 25\%$ ethanol) containing dithizone. Batch experiments were carried out to assess adsorption equilibrium and kinetic behavior by varying parameters such as acid concentration, agitation time, aqueous- ethanol ratio, and metal ion concentration. These facilitated the computation of kinetic parameters and adsorption behavior. The optimum conditions of sorption of mixed solvent system are 0.5 mol $L^{-1}$ $HNO_3 + 25\%$ ethanol containing $1.95 \times 10^{-4}$ mol $L^{-1}$ of dithizone with 40 minutes of equilibrium time. The kinetic parameters indicate that sorption follows the first-order reaction and intraparticle diffusion process. The obtained data followed the adsorption models. i.e., Freundlich, Langmuir, and Dubinin–Radushkevich (D-R) isotherms successfully. The thermodynamics studies indicate that sorption increases with rise in temperature, entropy driven, and endothermic chemisorption. The nature of the sorption mechanism of Hg(II) ions with dithizone and PUF has been discussed and the composition of the adsorbed complex has been predicted. The effect of different foreign cations and anions has been investigated. The data indicates that only EDTA, thiosulphate, and cyanide are interfering. The method was applied on different synthetic mixtures and saline solution to test the selectivity of the new method for the abatement of Hg(II) ions from mixed solvent system.**

**Keywords** adsorption; dithizone; Hg(II); kinetics; polyurethane foam; thermodynamics

## INTRODUCTION

Mercury is considered as a highly dangerous element because of its accumulation and persistent character in the environment and biotic. The major source of mercury pollution in the aquatic environment is industries such as chloroalkali, paint, pulp, and fertilizes industries. Methyl mercury is neurotoxic and more dangerous to the human body. The conversion of inorganic mercury into methyl mercury by the action of microorganisms under aerobic conditions, has received considerable attention to control and for the removal of the mercury from industrial waste (1,2).

Preconcentration and separation methods for modern analytical chemistry are very important prior to instrumental analysis. These separations/preconcentration methods are based on liquid-liquid extraction, sorption on metal oxides, ion exchange resins, and solid-liquid extraction, etc. and with immobilized reagents such as dithiozone, diethyldithocarbamats, 8 hydroxyquinolin, etc. onto solid support (3–11).

Dithiozone (DZ) is widely used for the separation/preconcentration of mercury in liquid liquid extraction or on liquid solid support. Similarly at trace level concentration for the rapid collection of this dangerous inorganic pollutant for the quantitative separation of mercury ions from different matrices, the dithizone loaded polyurethane foam packed column based on an analytical point of view were reported in the literature (12,13).

PUF is a cheaper and widely used sorbent for the separation and preconcentration of trace metal ions that reflects its potential in the environmental and analytical chemistry (8,13,14). The sorption properties of PUF can be altered with immobilization of different organic reagents towards trace metal ions. A number of mechanisms such as ion exchange, ligand addition, ion association, surface sorption, etc. have been reported depending upon the nature of the chemical species sorbed and sorption conditions (13).

In our laboratory the sorption behavior of a number of elements including Hg(II), Sb(V), Tm(III) onto PUF has been studied in details which clearly indicated that accumulation of trace metal ions via adsorption phenomena (15–17). However, in many instances the reagent loaded foam gives insoluble flakes. To avoid this, the mixed solvent system is selected to study the sorption behavior of toxic metal ions onto virgin PUF. This communication describes the results of the sorption behavior of Hg(II) onto unloaded PUF from mixed solvent system containing dithiozone.

## EXPERIMENTAL

The radiotracer of $^{203}$Hg(II) was prepared by the irradiation of specpure HgO in PARR-I reactor of this institute at the flux of $7 \times 10^{13}$ n cm$^{-2}$ sec$^{-1}$. The irradiated oxide ($\sim$30 mg) was dissolved in concentrated $HNO_3$,

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heated to dryness and the residue was dissolved in 25 mL of 0.1 M $HNO_3$ solution for further use. The radionuclide purity was checked on 4 K series 85 Canberra (USA) multichannel analyzer coupled with 25 $cm^3$ Ge(Li) detector.

All other regents used were of analar grade. Laboratory grade dithiozone and HPLC grade ethanol from Merck (Darmstadt, Germany) were used as such. The polyurethane foam plugs were prepared and washed as described elsewhere (18). The total pore area of PUF was measured using a Micrometeric porosimeter was 67 $m^2\,g^{-1}$, total intrusion volume was 0.14 $cm^3\,g^{-1}$ and average pore diameter was 8.3 nm. The stock solution of $7.8 \times 10^{-4}$ mol $L^{-1}$ of dithizone in ethanol was prepared and used for further studies.

## PROCEDURE

The 4.5 mL of known concentration of acid solutions were mixed with 1.5 mL of $7.8 \times 10^{-4}$ mol $L^{-1}$ dithizone ethanol stock solution in a Pyrex glass culture tube with a polyethylene cap. A known amount of radiotracer $^{203}$Hg(II) was added and the contents were mixed thoroughly. An aliquot of 2 mL was taken in a vial for gross gamma – counts ($A_o$). The remaining solution was equilibrated with 29 mg of washed PUF for 30 minutes on a Stuart Scientific Wrist – action shaker. Thereafter, 2 mL of aliquot was assayed ($A_e$) radiometrically on Tennelac (USA) counting assembly equipped with a well- type NaI(Tl) crystal.

For thermodynamic studies the solution was taken in a culture tube and dipped in the Gallenkamp thermostirrer-100 Model BKL; 234, water bath at constant temperature and the same procedure was adopted as described above. During shaking about 70% length of the culture tube remained dipped in the water bath so that the solid-liquid contents immersed completely in water at the controlled temperature.

The percentage of sorbed Hg(II) ions at equilibrium was calculated from the difference in the activity of an aliquot drawn before ($A_o$) and after shaking ($A_e$). The net gamma – activity of the $3.48 \times 10^{-5}$ mol $L^{-1}$ solution of Hg(II) ions was in the range of 35,000–40,000 cpm $mL^{-1}$. The percentage sorption and distribution coefficient ($K_d$), which is the molar ratio of the adsorbate in the solid and liquid phases, were calculated as:

$$\%\text{Adsorption} = \frac{A_o - A_e}{A_o} \times 100 \tag{1}$$

$$K_d = \frac{\%\text{Adsorption}}{100 - \%\text{Adsorption}} \times \frac{\text{Volume of solution in mL (V)}}{\text{Weight of PUF in g (W)}} \tag{2}$$

The % adsorption and the distribution coefficient ($K_d$) can be correlated as

$$\%\text{Adsorption} = \frac{100K_d}{K_d + \frac{V}{W}} \tag{3}$$

All the experiments were performed at 25 ± 2°C or at a temperature specified otherwise. The results are the average of at least triplicate independent measurements and overall precision in most cases is with in ±2%. The linear regression and slop analyses for the statistical data were carried out.

## RESULTS AND DISCUSSION

The effect of different electrolytes on the sorption of $3.48 \times 10^{-5}$ mol $L^{-1}$ of $^{203}$Hg(II) solution in the presence of arbitary chosen 25% (V/V) ethanol containing $1.95 \times 10^{-4}$ mol $L^{-1}$ of dithizone on PUF was investigated. The results of sorption in different electrolytes, namely HCl, $HNO_3$ $H_2SO_4$, and $HClO_4$ acids of varied concentration are tabulated in Table 1. The sorption of Hg(II) ions in the absence of dithizone from mixed solvent system was negligible. Table 1 indicates that sorption was quantitative in all acids in the concentration range 0.01–1.5 mol $L^{-1}$ investigated. The nitric acid seems to be a better mixed solvent system

TABLE 1

The effect of different electrolytes on the sorption of $^{203}$Hg(II) ($3.48 \times 10^{-5}$ mol $L^{-1}$) onto PUF in the presence of 25% ethanol containing $1.95 \times 10^{-4}$ mol $L^{-1}$ of dithizone after 40 minutes shaking time

| | $HClO_4$ | | $HNO_3$ | | $H_2SO_4$ | | HCl | |
|---|---|---|---|---|---|---|---|---|
| N | Sorption (%) | $K_d$ (mL $g^{-1}$) | Sorption (%) | $K_d$ (mL $g^{-1}$) | Sorption (%) | $K_d$ (mL $g^{-1}$) | Sorption (%) | $K_d$ (mL $g^{-1}$) |
| 1.5 | 98.13 | 7197 | 99.34 | 21046 | 97.29 | 4953 | 95.05 | 2448 |
| 1.0 | 96.23 | 3525 | 99.43 | 25692 | 93.85 | 2107 | 82.62 | 656 |
| 0.5 | 98.10 | 7091 | 99.88 | 78953 | 85.34 | 803 | 82.38 | 645 |
| 0.1 | 97.76 | 5754 | 99.33 | 19747 | 85.25 | 727 | 85.48 | 812 |
| 0.01 | 97.55 | 5504 | 94.86 | 2545 | 85.1 | 787 | 87.63 | 977 |

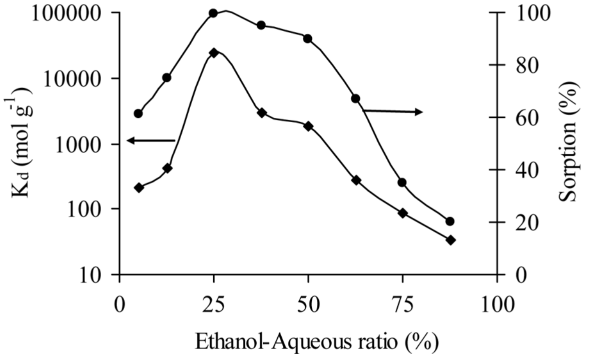


FIG. 1. Effect of ethanol ratio on the sorption of Hg(II) ions onto PUF from (0.5 M $HNO_3$ + ethanol) aqueous medium containing $1.95 \times 10^{-4}$ mol $L^{-1}$ of dithizone.

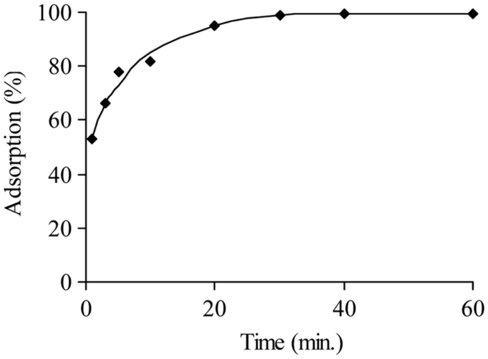


FIG. 2. Effect of shaking time on the sorption of Hg(II) ions onto PUF from (0.5 M $HNO_3$ + 25% Ethanol) aqueous medium containing $1.95 \times 10^{-4}$ mol $L^{-1}$ of dithizone.

because of the maximum distribution coefficient of Hg(II) ions. The maximum sorption and distribution was found in 0.5 mol $L^{-1}$ $HNO_3$ aqueous – ethanol system and was therefore selected for further studies.

Dithizone is insoluble in aqueous solution but with the addition of ethanol in aqueous phase, its solubility increases. In order to find out the maximum ratio of 0.5 mol $L^{-1}$ $HNO_3$ – ethanol aqueous phase, the sorption of Hg(II) ions was studied with different aqueous ethanol ratios containing dithizone and results are shown in Fig. 1. The 25% (V/V) ethanol aqueous ratio was found to be optimum. This optimum ratio was selected for further experiments. The decrease in sorption with the increase in the ethanol ratio (>25%), is due to high solubility of Hg – dithizone complex in mixed solvent system rather then sorption onto PUF.

## EFFECT OF SHAKING TIME

The effect of equilibrium time on the sorption of $3.48 \times 10^{-5}$ mol $L^{-1}$ of Hg(II) ions form mixed solvent containing $1.95 \times 10^{-4}$ mol $L^{-1}$ of dithizone was carried out in the range of 1–60 minutes. The maximum equilibrium time was observed to be 40 minutes and above (Fig. 2). This data was subjected to the kinetic modeling. PUF is an inert porous medium with spherically symmetric macropores and micropores. Adsorption in macropores is rapid and characteristic of film diffusion. The sorption in micropores is slow and hindered due to the small size of the pores and similar in size to the solute molecule. Diffusion in such pores would be characteristic of intraparticle diffusion. In this regard the standard Weber Morris (19) equation was tested in the form as:

$$q_t = R_d\sqrt{t} \tag{4}$$

where $q_t$ is the sorbate concentration in mol $g^{-1}$ at time t, and $R_d$ is the rate constant of intraparticle diffusion coefficient in mol $g^{-1}$ $t^{-1/2}$. Figure 3 shows that the plot $q_t$ vs. $t^{1/2}$ is not linear indicating that the entire data did not follow the Weber Morris equation. However, for intraparticle diffusion process, Reichenberg equation was also tested in the form:

$$F = (1 - 6/\pi^2)e^{-Bt} \tag{5}$$

The value of Bt is the mathematical function of F and can be calculated from the following relationship:

$$Bt = -0.4977 - 2.303 \log (1 - F) \tag{6}$$

The plot of Bt vs time is linear and passing through the origin as shown in Fig. 4. This indicates that sorption is strongly favored in the intraparticle diffusion process and controls the kinetics of Hg(II) dithizone complex sorption on PUF.

Based on the mass action process, regardless of the mechanism used, there is a correlation between q, the number of Hg(II) – dithizone complex adsorbed per unit area at a given pressure and temperature in time "t" required to complete the adsorption process as shown by Lagergren in the form of first-order reaction equation:

$$q_t = q_{max}(1 - e^{-k_1 t}) \tag{7}$$

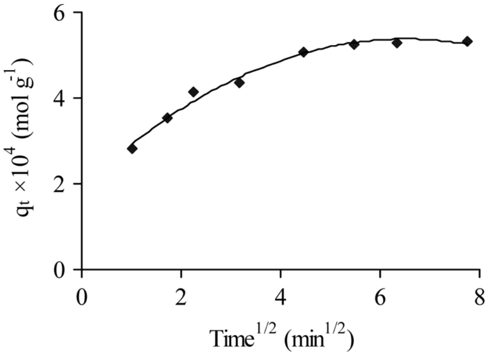


FIG. 3. Concentration of Hg(II) adsorbed as function of time onto PUF from (0.5 M $HNO_3$ + 25% Ethanol) aqueous medium containing $1.95 \times 10^{-4}$ mol $L^{-1}$ of dithizone, shaking time 40 minutes.

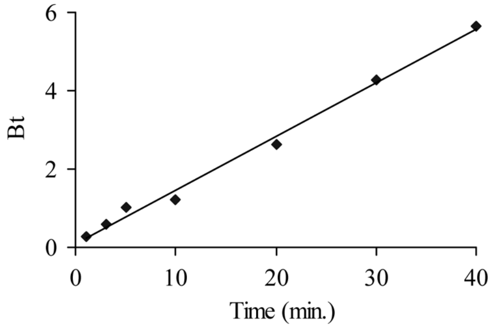


FIG. 4. Reichenberg plot of the sorption of Hg(II) ions onto PUF from (0.5 M $HNO_3$ + 25% Ethanol) aqueous medium containing $1.95 \times 10^{-4}$ mol $L^{-1}$ of dithizone, shaking time 40 minutes.

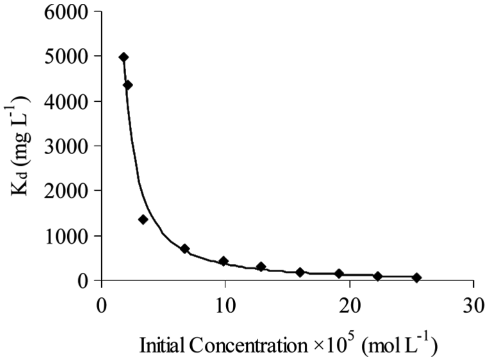


FIG. 6. Variation of $K_d$ of sorption with initial Hg(II) ions concentration onto PUF from (0.5 M $HNO_3$ + 25% Ethanol) aqueous medium containing $1.95 \times 10^{-4}$ mol $L^{-1}$ of dithizone, shaking time 40 minutes.

or

$$\ln(1 - F) = -kt \tag{8}$$

where $F = q_t/q_{max}$, $q_t$ is the amount of solute adsorbed in mol $g^{-1}$ at time t, $q_{max}$ is the maximum amount of solute adsorbed in mol $g^{-1}$ at equilibrium and k is the adsorption rate constant. The plot of $\ln(1 - F)$ vs. time is shown in Fig. 5. The straight line indicates that the adsorption process follows the first-order reaction with respect to adsorbed concentration. The numerical value of the first-order rate constant k of the sorption was calculated from the slope of the graph and was found to be $0.136 \pm 0.005\ \text{min}^{-1}$.

## EFFECT OF METAL ION CONCENTRATION

The variation of the distribution coefficient ($K_d$) relative to the concentration of mercury(II) ions itself was examined about 15-fold in the concentration range from $1.7 \times 10^{-5}$ to $2.5 \times 10^{-4}$ mol $L^{-1}$, utilizing 40 minutes shaking time under the optimized conditions. The results are shown in Fig. 6. A rapid decrease in the $K_d$ value occurred with the increase in the initial concentration of mercury(II) ions. The similar trend has also been observed for the sorption of Ag(I) ions and Hg(II) ions onto PUF (15,20). This can be explained by the fact that at lower metal ion concentration, sorption occurs preferentially at the most energetically favorable sites. At higher metal ion concentration, these strong active sites are fully occupied and sorption decreases. The sorption data was subjected to the different adsorption isotherms to describe the sorption equilibrium i.e., Frendulich, Langmuir, and D-R isotherms (19). The Frendulich isotherm was used for the heterogeneous surface in energy term. The Frendulich equation is widely used in environmental engineering practice to model the adsorption of metal ions from an aqueous medium empirically. The linear form of Frendulich isotherm is:

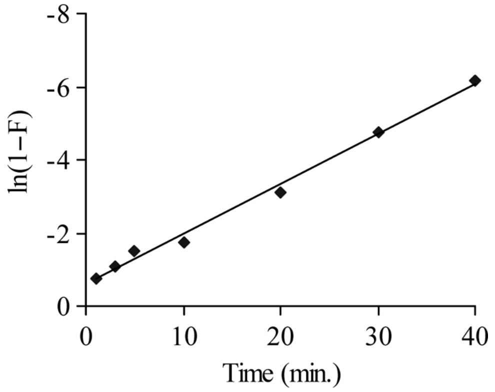


FIG. 5. Lagergern plot of Hg(II) ions sorption onto PUF from (0.5 M $HNO_3$ + 25% Ethanol) aqueous medium containing $1.95 \times 10^{-4}$ mol $L^{-1}$ of dithizone, shaking time 40 minutes.

$$\log C_{ads} = \log K_F + \frac{1}{n}\log C_e \tag{9}$$

where $C_{ads}$ is the amount of Hg(II) adsorbed in mol $g^{-1}$, $C_e$ is the amount of Hg(II) in solution at equilibrium in mol $L^{-1}$ and $K_F$ and $1/n$ are constants incorporating all factors affecting the adsorption capacity and an indication of the favorability of Hg(II) ions adsorption onto the adsorbent. The numerical values of $K_F$ and $1/n$ are given in Table 2.

The Langmuir model was originally developed to represent the chemisorption of a set of well-defined localized adsorption sites having the same energy of sorption, independent of surface coverage, and no interaction between adsorbed molecules. The maximum sorption is noticed when the surface of the sorbent is covered with a monolayer of the adsorbate. The familiar linear form of the Langmuir isotherm based on kinetic consideration is expressed as:

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{10}$$

TABLE 2
Different parameters of Hg(II) ions sorption onto PUF from mixed solvent system

| Constants | Values |
|---|---|
| Freundlich isotherm constants | |
| $1/n$ | $= 0.36 \pm 0.02$ |
| $K_F$ | $= (4.4 \pm 0.12) \times 10^{-4}\,\mathrm{mol\,g^{-1}}$ |
| $R^2$ | $= 0.9852$ |
| Langmuir isotherm constants | |
| Q | $= (1.21 \pm 0.04) \times 10^{-5}\,\mathrm{mol\,g^{-1}}$ |
| b | $= (5.19 \pm 0.16) \times 10^{5}\,\mathrm{L\,mol^{-1}}$ |
| $R^2$ | $= 0.9921$ |
| D-R isotherm constants | |
| $\beta$ | $= -0.00241 \pm 0.00012$ |
| $X_{DR}$ | $= (5.02 \pm 0.49) \times 10^{-5}\,\mathrm{mol\,g^{-1}}$ |
| E | $= 14.40 \pm 0.35\,\mathrm{kJ\,mol^{-1}}$ |
| $R^2$ | $= 0.9865$ |
| Thermodynamics parameters | |
| $\Delta H$ | $= 35 \pm 2\,\mathrm{kJ\,mol^{-1}}$ |
| $\Delta S$ | $= 147 \pm 6\,\mathrm{J\,mol^{-1}\,K^{-1}}$ |
| $\Delta G$ | $= -8.01 \pm 0.55\,\mathrm{kJ\,mol^{-1}}$ |
| $-T\Delta S$ | $= 44 \pm 3\,\mathrm{kJ\,mol^{-1}}$ |
| $\Delta G_{ads}$ | $= -42 \pm 1\,\mathrm{kJ\,mol^{-1}}$ |

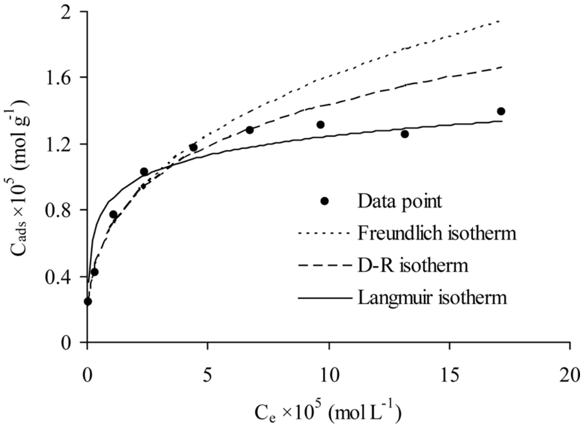


FIG. 7. Adsorption isotherm of Hg(II) ions onto PUF from (0.5 M $HNO_3$ + 25% Ethanol) aqueous medium containing $1.95 \times 10^{-4}$ mol L$^{-1}$ of dithizone, shaking time 40 minutes.

where $C_e$ and $C_{ads}$ are expressed as above, Q is the constant related to the maximum amount of solute adsorbed in mol g$^{-1}$, and b is the constant related to the binding energy of solute. The numerical values of the constants are given in Table 2.

In order to evaluate the physio-chemical properties of adsorption of Hg(II) ions onto PUF in the presence of dithizone, the data were applied to the D–R isotherm model which assumes that there are small regions on the sorption surface that are uniform in structure and energetically homogenous and compatible to the adsorbate. The linear form of D–R isotherm is:

$$\ln C_{ads} = \ln X_{DR} - \beta\varepsilon^2 \tag{11}$$

where $X_{DR}$ is the maximum amount of solute adsorbed in mol g$^{-1}$, $\beta$ is the net adsorbate – adsorbent affinity coefficient in kJ$^2$ mol$^{-2}$ and $\varepsilon$ is Polanyi potential $(\varepsilon) = RT \ln(1 + 1/C_e)$, where R is the gas constant in J mol$^{-1}$ K$^{-1}$, and T is the temperature in Kelvin. The numerical values of $\beta$ and $X_{DR}$ are given in Table 2.

The equilibrium plot of $C_{ads}$ vs $C_e$ is shown in Fig. 7. This figure indicates that the data point of the sorption of Hg (II) ions in the presence of dithizone onto PUF strictly followed the adsorption isotherm models. The sorption of Hg(II) ions followed the Langmuir model over the entire range of metal ion concentration under investigation while the sorption of D–R isotherm and Frendulich isotherm satisfied this sorption behavior at lower metal ions concentration i.e., upto $1.9 \times 10^{-4}$ mol L$^{-1}$.

In order to study the nature of bonding, the affinity coefficient β of D–R isotherm can be related to mean sorption energy (E) as

$$(E) = (-2\beta)^{-1/2} \tag{12}$$

which is the free energy transfer of one mole of adsorbate to the surface of the adsorbent in solution from infinity. The numerical value of E in the range 1–8 kJ mol$^{-1}$ and 9–16 kJ mol$^{-1}$ represents the physical sorption and chemical sorption respectively. The numerical value of E comes out to be $14.4 \pm 0.35$ kJ mol$^{-1}$ indicating that chemisorption phenomena is predominant for the present system. Moreover, the high value of sorption free energy reflects the strong bonding between the adsorbate and the adsorbent.

The numerical values of the constants of the above adsorption isotherms were evaluated from slops and intercepts of the linear graphic forms of adsorption isotherms and are summarized in Table 2. This table clearly indicates that the sorption affinity $(1/n)$ constant of the Frendulich isotherm is $< 1$ indicating favorable adsorption and encompassing the exponential distribution of active sites in their energy. According to the correlation coefficient ($R^2$) obtained, we deduced that the Langmuir model is correlated the experimental data very well as compared to the other adsorption models for Hg(II) ions. Moreover, the experimental maximum sorption capacity of PUF under the optimum sorption conditions of Hg(II) ions was found to be $(1.25 \pm 0.1) \times 10^{-5}$ mol g$^{-1}$ which is near to the theoretical sorption capacity (Q) of Langmuir isotherm $(1.21 \pm 0.04) \times 10^{-5}$ mol g$^{-1}$ (Table 2).

## EFFECT OF TEMPERATURE

The variation of sorption behavior of $3.48 \times 10^{-5}$ $\mathrm{mol\,L^{-1}}$ of Hg(II) ions on PUF from mixed solvent system ($0.5\,\mathrm{mol\,L^{-1}}$ $HNO_3 + 25\%$ ethanol) containing $1.95 \times 10^{-4}$ $\mathrm{mol\,L^{-1}}$ of dithizone using 40 min shaking time from 5 to 45°C has been studied. Different thermodynamic parameters have been evaluated using the following equations.

$$\log K_c = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \tag{13}$$

and

$$\Delta G = -RT \ln K_c \tag{14}$$

The equilibrium constants ($K_c$) is simply the distribution ratio of the Hg(II) ions between solid – liquid phase. The numerical values of "$K_c$" was worked out as reported earlier (19). The plot of log $K_c$ vs. $1/T$ is shown in Fig. 8. From the slop and intercept of the plot the numerical values of the heat of enthalpy ($\Delta H$) and entropy ($\Delta S$) were calculated and are given in Table 2. The Gibb's free energy ($\Delta G$) was determined using above Eq. (14) and given in Table 2. The positive values of $\Delta H$ and negative value of $\Delta G$ indicate that sorption process is endothermic and spontaneous in nature. The high value of $\Delta S$ reflects that the stability of sorbed species is entropy driven. Similarly, the numerical value of the term $-T\Delta S$ is $44 \pm 3\,\mathrm{kJ\,mol^{-1}}$ which is greater than $\Delta H$ (Table 2), supports the entropy driven sorption due to decrease in the randomness of the system that results is the positive entropy change (21).

The adsorption free energy ($\Delta G_{ads}$) related to the micropores filling of the PUF as pore width approaches to the adsorbate dimensions has been evaluated using the following relationship.

$$\Delta G_{ads} = -RT \ln(b\omega) \tag{15}$$

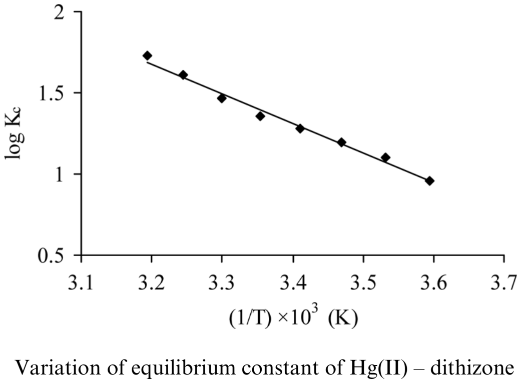


FIG. 8. Variation of equilibrium constant of Hg(II) – dithizone complex sorption onto PUF with temperature from ($0.5\,M$ $HNO_3 + 25\%$ Ethanol) aqueous medium containing $1.95 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ of dithizone, shaking time 40 minutes..

where b is the Langmuir constant, $\omega$ is the molal concentration of the sorption medium. Hence in our system, the sorption medium was the mixed solvent system, therefore, necessary corrections have been carried out using the molal concentration. The large negative value of $\Delta G_{ads}$ as shown in Table 2, indicates the strong affinity of Hg(II) ions sorption onto PUF and related to the pore filling of the PUF sorbent which is energetically homogenous and close to the size of the Hg(II) complex (22).

## SORPTION MECHANISM

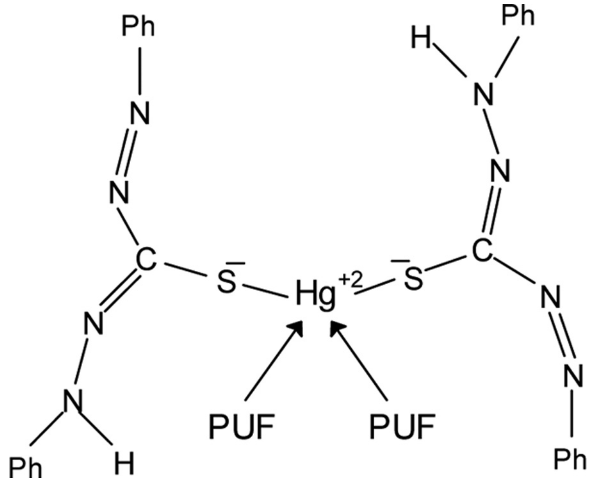
Although dithizone is a common reagent for the colorimetry determination of certain metals, the structure of the metal derivatives has remained uncertain. In fact this ligand has two active sites for bonding i.e., sulfur and nitrogen atoms of the azo group of dithizone (23). The X-ray study indicates that when nitrogen atom is bonded strongly to the central metal ions, it forms a tetrahedral structure and the isolation of the metal–dithizone complex is possible such as Ni(II), Zn(II), and Co(II) complexes of dithizone (24,25). However, when charge neutralization and coordination took place by sulfur atom of dithizone and there was a weak bonding of the nitrogen atom with the central metal atom, which then resulted in a complex of metal dithizone which in turn was ended with a distorted tetrahedral or linear structure such as Hg(II)-dithizone complex. Hg(II) dithizone complex was isolated from aqueous pyridine as deep red solvated needles. The arrangement of the isolated complex is $Hg(DZ)_2$ 2Py and was best described as a distortion of linear bicovalent mercury. As there was no internal hydrogen bonding, the pyridine molecules occupy the space like a channel parallel to the z-axis (26).

Similarly, in this system, the light red coloration of PUF produced on the sorption of Hg(II) – dithizone indicates that PUF plays an important role in the sorption of the $Hg(DZ)_2$ molecules. Since mercury is a soft metal, it can satisfy its coordination of number four by interaction with nitrogen atom of the isocyanates group present in PUF via a ligand addition mechanism. The charge of Hg(II) ion is neutralized by the interaction of the sulfur atom of the dithizone. The overall mechanism is as follows.

$$Hg^{+2} + 2HDZ \rightleftharpoons Hg(DZ)_2 + 2H^+$$

$$Hg(DZ)_2 + \overline{2PUF} \rightleftharpoons \overline{Hg(DZ)_2 2PUF}$$

where DZ is dithizone and the bar quantities indicates the reaction in PUF. The possible structure of $Hg(DZ)_2 \cdot 2PUF$ complex is as follows:



The thermodynamic parameters support the stability of the sorbed complex. The distorted tetrahedral geometry contributes to the high positive value of enthalpy. The high value of entropy indicates that the sorbed complex is more oriented as compared to the hydrated state of Hg(II) ions in mixed solvent system and stability of the sorbed complex is entropy driven. Moreover, there is no chelate group of dithizone affecting the system but the high value of entropy as compared to the other reported systems strongly supports the stability and interaction of PUF with Hg(II) – dithizone complex and subsequently the proposed mechanism (15,27). The numerical value of the sorption free energy (E) of the system is $14.40 \pm 0.35\,\mathrm{kJ\,mol^{-1}}$ derived from the DR isotherm also supports the ligand addition type chemisorption in the present investigation.

## EFFECT OF FOREIGN IONS

The sensitivity of PUF for the preconcentration of Hg(II) – dithizone complex from mixed solvent system has been checked under the optimum conditions of sorption. The addition of foreign ions may change the environments of the sorption medium and the solution chemistry of central metal ions that effects on the sorption behavior. In Table 3, the effect of different anions on the sorption behavior of Hg(II) – dithizone complex onto PUF from a mixed solvent system is given. This table indicates that cyanide and EDTA anions masked the sorption of Hg(II) ions completely. This behavior can be explained through the coordination chemistry of these ions. The acidic form of cyanide and EDTA anions have very low dissociation constants, chemically stable but labile. These anions have a strong tendency to replace the hydrogen ions with metal ions through substitution reaction and formed more stable and inert complexes with Hg(II) ions. The stability constant of $[Hg(CN)_4]^{-2}$ and $Hg(EDTA)^{-2}$ complexes are $10^{41}$ and $10^{22}$, respectively (28). Thiosulphate and thiourea reduce the Hg(II) to Hg(I) ions that may not sorb onto PUF. However, the effect of chloride anions is interesting.

TABLE 3
Effect of different anions on the sorption of $^{203}$Hg(II) ($3.48 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$) ions onto PUF from mixed solvent system containing $1.95 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ of dithizone, 40 minutes shaking time

| Anions | Compound added | Concentration ($\mathrm{mol\,L^{-1}}$) | $K_d$ ($\mathrm{mL\,g^{-1}}$) | Percent sorption |
|---|---|---|---|---|
| Nil | Nil | Nil | 78953 | 99.8 |
| Chloride | NaCl | $1.7 \times 10^{-1}$ | 6396 | 97.8 |
| Bromide | NaBr | $9.2 \times 10^{-2}$ | 1791 | 92.9 |
| Fluoride | NaF | $2.4 \times 10^{-1}$ | 1693 | 92.5 |
| Iodide | NaI | $6.7 \times 10^{-2}$ | 10188 | 98.6 |
| Perchorate | $NaClO_4$ | $8.2 \times 10^{-2}$ | 3525 | 96.2 |
| Sulphate | $Na_2SO_4$ | $7.0 \times 10^{-2}$ | 8616 | 98.4 |
| Cyanide | NaCN | $2.1 \times 10^{-1}$ | <1 | <1 |
| EDTA | $Na_2C_{10}H_{18}N_2O_{10}$ | $2.7 \times 10^{-2}$ | <25.3 | <15.5 |
| Ascorbate | $C_6H_8O_6$ | $5.7 \times 10^{-2}$ | 595 | 81.2 |
| Thiourea | $H_2NCSNH_2$ | $1.3 \times 10^{-2}$ | 798 | 58.9 |
| Phosphate | $Na_2HPO_4$ | $7.1 \times 10^{-2}$ | 4157 | 96.7 |
| Oxalate | $Na_2C_2O_4$ | $7.4 \times 10^{-2}$ | 2870 | 95.4 |
| Acetate | $CH_3COONa$ | $1.2 \times 10^{-1}$ | 10314 | 98.6 |
| Thiocyanate | NaSCN | $1.2 \times 10^{-1}$ | 4729 | 97.2 |
| Tartrate | $Na_2C_4H_4O_8 \cdot 2H_2O$ | $4.4 \times 10^{-2}$ | 1773 | 92.3 |
| Citrate | $C_6H_5Na_3O_7 \cdot 2H_2O$ | $3.4 \times 10^{-2}$ | 7441 | 98.1 |
| Nitrite | $NaNO_2$ | $1.4 \times 10^{-1}$ | 776 | 84.9 |
| Thiosulphate | $Na_2S_2O_3 \cdot 5H_2O$ | $1.2 \times 10^{-1}$ | 145 | 51.2 |

TABLE 4
Effect of different cations on the sorption of $^{203}$Hg(II) ($3.48 \times 10^{-5}$ mol L$^{-1}$) ions onto PUF from mixed solvent system containing $1.95 \times 10^{-4}$ mol L$^{-1}$ of dithizone, 40 minutes shaking time

| Cations | Compound added | Concentration (mol L$^{-1}$) | K$_d$ (mL g$^{-1}$) | Percent sorption |
|---|---|---|---|---|
| Hg(II) | Nil | Nil | 78953 | 99.8 |
| Li(I) | LiCl | $2.3 \times 10^{-1}$ | 903 | 86.5 |
| Ag(I) | $AgNO_3$ | $5.9 \times 10^{-2}$ | 627 | 82.1 |
| Tl(I) | TlCl | $4.2 \times 10^{-2}$ | 3693 | 96.4 |
| Sr(II) | $SrCl_2 \cdot 6H_2O$ | $3.7 \times 10^{-2}$ | 1736 | 92.6 |
| Ba(II) | $BaCl_2 \cdot 2H_2O$ | $4.1 \times 10^{-2}$ | 2015 | 93.5 |
| Cd(II) | $CdSO_4 \cdot 8H_2O$ | $4.0 \times 10^{-2}$ | 2496 | 94.8 |
| Mg(II) | $Mg(NO_3)_2 \cdot 6H_2O$ | $3.9 \times 10^{-2}$ | 1713 | 92.5 |
| Ca(II) | $Ca(NO_3)_2 \cdot 4H_2O$ | $4.2 \times 10^{-2}$ | 1583 | 92.0 |
| Pb(II) | $Pb(NO_3)_2$ | $3.0 \times 10^{-2}$ | 2759 | 95.2 |
| Ni(II) | $NiSO_4 \cdot 6H_2O$ | $3.8 \times 10^{-2}$ | 13485 | 98.9 |
| Co(II) | $CoCl_2 \cdot 6H_2O$ | $4.2 \times 10^{-2}$ | 5298 | 97.5 |
| Mn(II) | $MnCl_2 \cdot 4H_2O$ | $5.1 \times 10^{-2}$ | 3047 | 95.7 |
| Cu(II) | $CuSO_4 \cdot 5H_2O$ | $4.0 \times 10^{-2}$ | 1528 | 91.7 |
| Al(III) | $Al(NO_3)_3 \cdot 4H_2O$ | $2.6 \times 10^{-2}$ | 3025 | 95.6 |
| Ce(III) | $CeCl_3 \cdot 7H_2O$ | $2.7 \times 10^{-2}$ | 1053 | 88.4 |
| Bi(III) | $Bi(NO_3)_3 \cdot 5H_2O$ | $2.1 \times 10^{-2}$ | 156 | 53.1 |
| Y(III) | $Y(NO_3)_3 \cdot 6H_2O$ | $2.6 \times 10^{-2}$ | 6325 | 97.7 |
| Cr(III) | $CrCl_3 \cdot 6H_2O$ | $3.7 \times 10^{-2}$ | 8036 | 98.3 |
| Fe(III) | $Fe(NO_3)_3$ | $4.1 \times 10^{-2}$ | 3624 | 96.3 |

Although mercury(II) ions form a stable complex with chloride ions, but in a mixed solvent system this phenomena was not observed, even in 10% chloride solution, which may be due to the solvent effect.

The effect of about a 100-fold concentration of different cations on the sorption behavior of Hg(II) dithizone complex onto PUF are summarized in Table 4. This table indicates that except Bi(III) ions all the metal ions under investigation do not hinder the sorption of Hg(II) dithizone complex. The interference of the Bi(III) could probably be due to competitive reaction of bismuth with dithizone in acidic solution (29).

The sensitivity and selectivity of the developed method was tested by applying the separation of Hg(II) – dithizone complex from synthetic mixtures of different compositions using batch method. The PUF was separated, washed with 0.5 mol L$^{-1}$ $HNO_3$ solution, and assayed radiometrically on a multi-channel analyzer both the $^{203}$Hg(II) complex loaded PUF and the aqueous phase. The results of the separation of Hg(II) complex by the spiking method are given in Table 5. This table indicates that the Hg(II) ions are easily and quantitatively separated/removed from different matrices and saline solutions etc. without an extensive treatment of samples.

TABLE 5
Determination of Hg(II) ions from different synthetic mixtures

| | Concentration of Hg(II) ions (μg mL$^{-1}$) | |
|---|---|---|
| Composition of synthetic mixtures (μg mL$^{-1}$) | Added (μg mL$^{-1}$) | Found (μg mL$^{-1}$) |
| Al(25), Zn(25), Cu(25), Ag(25), Cd(25), | 7 | 6.92 ± 0.21 |
| Pb(25), Ni(25), Mn(25), Co(25), | 7 | 6.89 ± 0.19 |
| Ca(25), Mg(25), Ba(25) | 7 | 7.11 ± 0.22 |
| Eu(25), Tb(25), Y(25), Sc(25), Ce(25), | 7 | 7.08 ± 0.17 |
| Tape water | 7 | 6.87 ± 0.21 |
| 10% NaCl | 7 | 7.15 ± 0.25 |

## CONCLUSION

The developed procedure for the removal of Hg(II) ions is rapid, quantitative, and efficient. It can be used with high certainty for the removal of Hg(II) ions from its associated ions in different matrices in a single stage operation. The sorption equilibrium of Hg(II) ions can be explained by different adsorption models presented in the paper. The Langmuir model as evidence is followed with a better correlation coefficient value as compared to others. The maximum sorption capacity (Q) was found to be equivalent to the experimental sorption capacity. The kinetic data and mass transfer phenomena indicates the intraparticle diffusion process and first order reaction respectively. The thermodynamics values indicate that sorption is spontaneous and endothermic chemisorption in nature. The stability of the sorbed complex is entropy driven. The sorption mechanism is the ligand addition and the direct interaction of the active sites of PUF with central metal ions has been suggested on the basis of the experimental data and the reported models.

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