

# Applications of Mercaptomethyl Crosslinked Polystyrene Resin for extraction of Mercury and Arsenic ions from wastewater

Archana Gupta

Assistant Professor

Dept. of Applied Sciences, College of Engineering  
Chandigarh Group of Colleges, Landran, Mohali (Punjab)  
Email: agupta271984@gmail.com

## Abstract

A chelating resin with mercaptan groups has been prepared. The mercury and arsenic sorption capacity was around 0.62  $\mu\text{mol/g}$  and 0.219  $\mu\text{mol/g}$  of resin. The effect of pH on the adsorption performance was examined in the pH range of 1-6 for mercury and 3-10 for arsenic at an initial metal ion concentration of mercury and arsenic ions. The uptake of Hg(II) and As(III) ions on resins was investigated by using batch technique. The adsorption of Hg(II) and As(III) ions on resins was found to follow Langmuir adsorption isotherm and pseudo second order kinetics.

**Keywords:** Mercaptomethyl crosslinked polystyrene resin, Arsenic and mercury, adsorption isotherm, kinetics study.

## 1. INTRODUCTION

The occurrence of heavy metals in the environment is hazardous because of their harmful nature. Among the heavy metals arsenic and mercury are well known for their extremely high toxicity to human life and natural environment<sup>1</sup>. Arsenic is worldwide pollutant in ground and surface waters with serious health effects upon long term intake of even low concentration through portable water consumption<sup>2</sup>. Arsenic is released into the air by volcanoes and is a natural contaminant in some deep water wells. Arsenic exposure is common in smelting industry where arsenic is byproduct of ores containing lead, gold, cobalt, nickel and in microelectronic industry due to gallium arsenide. People who are Exposed by inorganic arsenic may cause nausea, vomiting, diarrhea, decreased production of white and red cells, abnormal heart rhythm, blood vessel damage, shock, convulsions, irritation, inflammation, ulceration of mucous membrane and skin, kidney damage, coma and finally death<sup>2,3</sup>. Similarly Mercury is one of the most dangerous heavy metals.

Mercury is discharged into the earth by number of commercial ventures in particular paper, paints, beauty care products, additives, thermometers manometers, fluorescent lights and mercury batteries and so on. Inorganic and organic mercury compounds might be available in normal water and can be accumulated in different life forms like fish. Mercury metal itself is also harmful. It is widely known that mercury (II) compounds are converted into more dangerous methyl mercury species by aquatic organisms. This poisonous compound aggregates in the blood has a prompt and lasting impact on the brain and central nervous system leading to health hazards<sup>2,3</sup>. It is therefore very necessary to remove these toxic metal ions from the aquatic systems. The common methods adopted for the treatment of arsenic and mercury contaminated water include flotation, precipitation with sulfide, coagulation, filtration and ion exchange methods<sup>4,5</sup>. These synthetic strategies are simple, but disadvantages associated with them are that they produce large amounts of toxic sludge, which needs facilitate treatment before disposal into environment. Adsorption using polymer resins having chelating ligands has been reported to be good technique for removal of toxic metal ions from water system<sup>6</sup>. These chelate resins interact specifically with metal ions forming metal-chelate complexes.

Mercury and arsenic ions in water may be removed using polymer adsorbents modified with ligands containing nitrogen, sulfur donor atoms such as pyridine, polyethyleneimine, thioether, thiourea,



thiozoline, dithiocarbonate and phosphine sulfide etc. Several chelating resins have been reported in the literature by incorporating above mentioned ligands in the polymer matrix and evaluated for the removal of heavy metal ions from water. By the reaction of chloromethylated polystyrene with 4-hydroxy benzoic acid, glycine and the Schiff's base are used to synthesize the polystyrene supported chelating resins for removal of Pb (II), Cd (II) as reported by A.R. Reddy et al<sup>7</sup>.

A novel chelating resin with functional group containing S and N atoms was prepared using chloro methylated polystyrene and 2,5-dimercapto-1, 3, 4-thiadiazole for the removal of mercury (II) ions<sup>8</sup>. Dithiocarbamate-incorporated polystyrene based microsphere were used for selective removal of Hg (II) from aqueous solutions containing different amount of Hg (II) ranging from 10-100 ppm as reported by Denizli et al<sup>9</sup>. Incorporation of 2-aminothiophenol into Merrifield polymer through C-N covalent bond was result into a new stable chelating resin. The resin exhibits no affinity to alkali or alkaline earth metals ions and commons ions. The separation of mercury (II) in the presence of different alkali and alkaline earth metal ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ), commons anions ( $\text{ClO}_4^-$ ,  $\text{SO}_4^{2-}$ ) and other diverse ions ( $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$ ) has been studied<sup>10</sup>. A new resin was synthesized by Mondal et al<sup>11</sup> which was functionalized with 6-mercaptopurine for mercury and silver determination in environmental samples by atomic absorption spectrophotometer. Dutta et al<sup>12</sup> reported the chloromethylated polystyrene-divinylbenzene functionalized with 2-aminothiazole by using microwave irradiation for removal of mercury (II) and cadmium (II) respectively. Selective separation of silver ion at pH 2 using chloro methylated polystyrene-divinylbenzene modified with 2-mercaptobenzothiazole was reported by El-.Menshawy<sup>13</sup>.

A number of chelating resins having heterocyclic functional groups pyridine, thiadiazole, benzothiazole introduced into macro porous chloromethylated polystyrene was synthesized via hydrophilic spacer arm of polyethylene glycol containing sulfur. These functionalised resins were found to show high adsorption capacities for toxic metal ions<sup>14</sup>. Atia et al<sup>15</sup> has reported a synthetic resin containing amine and mercaptan as chelating groups for Selective separation of mercury. Adsorption of arsenate and mercury ions have also been studied using aminated poly(acrylonitrile) fibers in water and found to be effective in removing metal ions at low level for drinking water purification<sup>16,17</sup>. Adsorption of arsenic to the level of 106 mg/g resin at pH 2 for arsenate and 30 mg/g resin at pH 8 for arsenite using thiol resin poly(ethylene mercaptoacetamide) was also reported in the literature<sup>18</sup>. The synthesis of polystyrene thiol resin having properties<sup>19-24</sup> like strong radicals, metals and nucleophiles scavenger is of specific interest. In this research paper synthesis of mercaptomethyl crosslinked polystyrene resin was done by using already reported method<sup>26</sup> and used it for removal of mercury and arsenic ions from aqueous system.

## 2. EXPERIMENTAL

### 2.1 Analysis

Here in this research paper, metal ions concentration in all samples was analyzed with GBS HG 3000 atomic adsorption spectrophotometer. FTIR spectra of this resin were already explained in published paper<sup>26</sup>.

### 2.2 Chemicals

Cross linked polystyrene mercaptomethyl resin was synthesized from merrifield resin (M/s Fluka Analytica, Switzerland as a starting material. It is a gel type cross-linked polystyrene divinyl benzene resin (2% DVB), 200-900 mesh containing 4.3 mmol/g Cl in dry state. *O, O'*-diethyl thionophosphate potassium salt 98% is used as thiolating agent, which is also commercially available (M/s Sigma-Aldrich). Chemicals used for metal ion removal studies were procured from Trade, sodium meta arsenate ( $\text{NaAsO}_2 \cdot 7\text{H}_2\text{O}$ ) and mercury Chloride ( $\text{HgCl}_2$ ) from M/s Merck India.

### 2.3 Synthesis of mercaptomethyl crosslinked polystyrene resin



Mercaptomethyl crosslinked polystyrene beads were synthesized by already reported method in our earlier publication<sup>26</sup>.

### 3. ADSORPTION STUDIES

#### 3.1 Effect of contact time

Adsorption of mercury and arsenic onto mercaptomethyl resin was studied for various time intervals (Fig. 1). Results obtained by AAS show an incremental adsorption of  $\text{Hg}^{2+}$  and  $\text{As}^{3+}$  with enhanced chelation time using mercaptomethyl resins. The maximum uptake of arsenic ion was found to be  $0.62 \mu\text{mol/g}$  of the resin with initial metal ions concentration is  $C_0 = 0.6674 \mu\text{mol}$  for arsenic. The maximum metal ions uptake was achieved within 16h. Similarly it was observed that resin could adsorb maximum amount of  $0.22 \mu\text{mol}$  of  $\text{Hg/g}$  of resin with initial metal ions concentration is  $C_0 = 0.25 \mu\text{mol}$ ,  $30^\circ\text{C}$ ) in same time interval.

#### 3.2 Adsorption isotherm

Arsenic and mercury adsorption mercaptomethyl resin displayed the characteristics of relatively high uptake amount with low equilibrium concentration as given in Fig.2,3. Under identical non competitive conditions, mercaptomethyl polystyrene resin adsorb almost comparable amount of arsenic and mercury ions in water. These adsorption data for arsenic and mercury at equilibrium concentrations over the integrated range have been correlated with Langmuir isotherm using the equation

$$C_e/q_e = 1/q_0K_L + C_e/q_0$$

Where  $C_e$  is the equilibrium concentration of metal ion in solution (mmol/l),  $q_e$  is the adsorbed value of metal ion at equilibrium concentration,  $q_0$  is the maximum adsorption capacity (mmol/g) and  $K_L$  is the binding constant which is related to energy of adsorption.  $C_e/q_e$  vs  $C_e$  plots for arsenic and mercury ions adsorption result into a straight line and Langmuir isotherm parameters were calculated as given in Table 1 and shown in fig 4,5. It was observed that  $q_0$  values are in close agreement with these obtained experimentally. The high values of  $K_L$  which reflect the strength of adsorbed ion-resin binding suggest a strong interaction between metal ions and  $-\text{SH}$  group of mercaptomethyl resin. The values of correlation coefficients are higher than 0.99 suggesting that experimental data are well fitted by the Langmuir model of monolayer coverage of mercury and arsenic ions on the surface of mercaptomethyl polystyrene resin. The maximum adsorption capacities of arsenic and mercury ions were predicted to be  $0.62 \mu\text{mol/g}$  and  $0.219 \mu\text{mol/g}$  respectively for  $\text{As-SH-P}$  and  $\text{Hg-SH-P}$  systems. Adsorption data were also correlation with Freundlich isotherm using the equation.

$$\log q_e = \log K_f + 1/n \log C_e$$

Where  $C_e$  is the equilibrium concentration of metal ion in solution (mmol/g),  $q_e$  the adsorbed value of metal ion at equilibrium concentration, The exponent  $1/n$  is an index of the diversity of free energies associated with the adsorption of the solute by multiple components of a heterogeneous adsorbent. Freundlich isotherm parameters were obtained by plotting  $\log q_e$  vs  $\log C_e$  and results were summarized in Table 2 [Fig 6,7]. The binding constant  $k$  values are low suggesting poor interaction between metal ions and  $-\text{SH}$  group of mercaptomethyl resin. The correlation coefficients values are 0.6275 and 0.8790 respectively for adsorption of arsenic and mercury on mercaptomethyl resin. These values are below 0.99 suggesting that adsorption data are not fitted well by the Freundlich model of multilayer adsorption.

#### 3.3 Effect of pH on uptake of Hg (II) and As (III)

The effect of pH on the adsorption completion was examined in the pH range of 1-6 for mercury and 3-10 for arsenic at an initial metal ion concentration of mercury and arsenic ions. The effect of acidic medium on assimilation of mercury was studied and data are presented in Fig.8. The highest uptake was found at  $\text{pH} = 5.7$  (natural). This may be due to the free lone pair of electron on sulfur atoms (or



deprotonation of –SH group) which form a coordination with metal ions to give the corresponding resin-metal complex. The higher affinity of Hg (II) towards –SH sites may be attributed to soft base nature of S atom which is capable for interaction with Hg (II). The decrease of adsorption in acidic media may be because of protonation of lone pairs of –SH group that retard the complex formation. The adsorption of Hg (II) beyond natural pH is doubtful and may be attributed only to interaction of Hg (II) cations with active the sites on resin but also to formation of metal hydroxides species such as soluble  $\text{Hg}(\text{OH})^+$  or insoluble precipitate  $\text{Hg}(\text{OH})_2$ . Further these findings are in agreement with the reported literature<sup>15</sup>. Similarly effect of pH on arsenic absorption by mercaptomethyl cross linked polystyrene resin was studied in the pH range 3-9 as given in Fig.9. The results show that arsenic adsorption does not vary significantly in the pH range 3-6. With increase of pH to 7-10 arsenic adsorption starts decreasing. When the pH above 9 the predominate species is  $\text{H}_2\text{AsO}_3^{-1}$ ,  $\text{HAsO}_3^{-2}$ ,  $\text{AsO}_3^{-3}$ . At high pH condition led to hydroxylation of sulfur at bead surface, which would repel negatively charge anion such as  $\text{H}_2\text{AsO}_3^{-1}$  (which predominate in this pH condition) resulting into reduced adsorption<sup>25</sup>. The higher attraction of As (III) towards –SH sites may be attributed to soft base nature of S atom which is capable for interaction with As (III). Most toxic metals occur in solution as cations (e.g.  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ) which generally become increasingly insoluble as the pH increases. Near-neutral pH of water, the solubility of most trace-metal cations is severely limited by precipitation or co-precipitation with an oxide, hydroxide, carbonate or phosphate mineral or more likely by their strong adsorption to hydrous metal oxides, clay or organic matter). In contrast, most oxyanions including arsenite tend to become less strongly sorbed as the pH increases.

### 3.4 Kinetic model

The adsorption kinetics of As and Hg ions was modeled using the pseudo second order kinetics which is represented by

$$t/q = 1/k_2 q_e^2 + 1/q_e t$$

Where  $k_2$  is the pseudo second order rate constant (g/mol.min). Where q is the amount of metal adsorbed at any time (mmol/g) and  $q_e$  is amount of metal adsorbed at equilibrium time (mmol/g). Results of the pseudo second order kinetics are given in Fig. 10,11 and Table 3. The theoretical  $q_0$  values were calculated and show some agreement with the experimental data for second order kinetics. Further the correlation coefficients values for both the metal ions are higher than 0.99 suggesting that adsorption of these metal ions on mercaptomethyl polystyrene resin under noncompetitive conditions obeys pseudo second order kinetics. Thus adsorption of arsenic and mercury ions on the above mentioned thiol resin depends on metal ion concentration and characteristics of resin.

## 4. CONCLUSION

All through this paper effect of various parameter like effect of pH, effect of time and effect of concentration on mercaptomethyl resin crosslinked polystyrene resin was studied for removal of heavy metals from wastewater. In single metal species system lead and mercury ions are adsorbed on mercaptomethyl resin crosslinked polystyrene resin. The maximum adsorption capacities for mercury and arsenic ions are found to be 0.62  $\mu\text{mol/g}$  and 0.219  $\mu\text{mol/g}$  respectively.

## Acknowledgements

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## Author



Dr. Archana is working as Assistant Professor of Chemistry in Chandigarh Group of Colleges, Landran, Punjab. Her area of research is Polymer Chemistry. She is a member of American Chemical Society.



Figures Captions

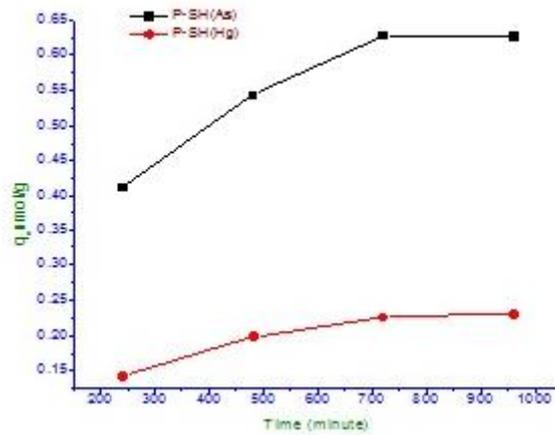


Fig 1. Effect of contact time on adsorption of heavy metal ions on mercaptomethyl resin ( $C_0= 0.6674 \mu\text{mol}$  for arsenic and  $C_0= 0.25 \mu\text{mol}$ ,  $30^\circ\text{C}$ ).

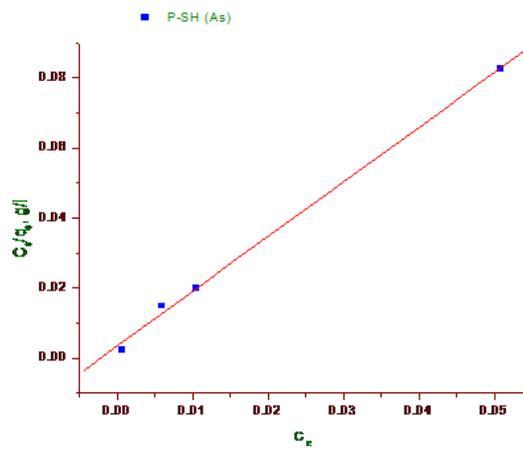


Fig 2. . Equilibrium isotherms curves for adsorption of  $\text{Hg}^{2+}$  on mercaptomethyl resin ( $\text{pH}=6.42$ ,  $30^\circ\text{C}$ ).

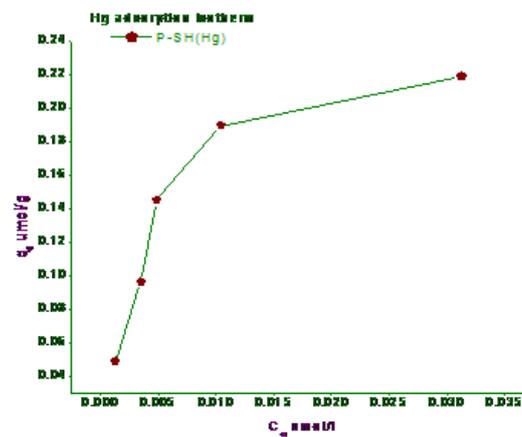


Fig 3. Equilibrium isotherms curves for adsorption of  $\text{As}^{3+}$  on mercaptomethyl resin ( $\text{pH}=5.87$ ,  $30^\circ\text{C}$ )



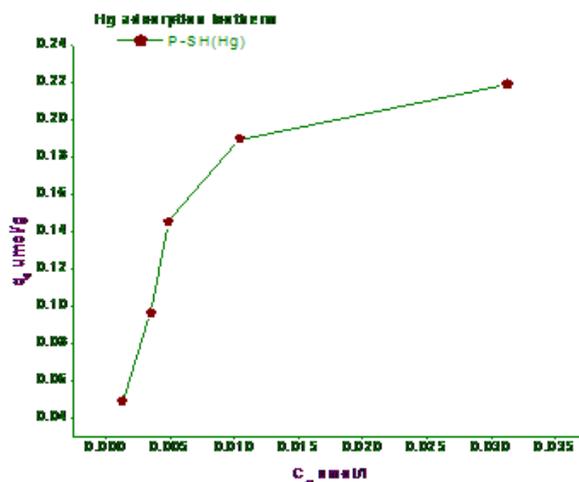


Fig 4 Langmuir adsorption isotherm for adsorption Hg<sup>2+</sup> on P-SH.

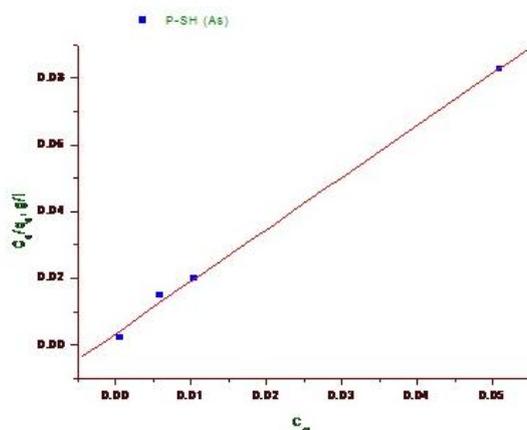


Fig 5 Langmuir adsorption isotherm for adsorption of As<sup>3+</sup> on P-SH.

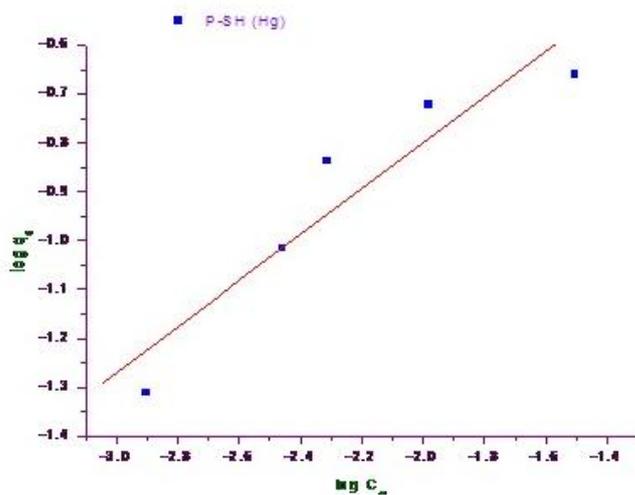


Fig 6 Freundlich adsorption isotherm for adsorption of Hg<sup>2+</sup> on P-SH.



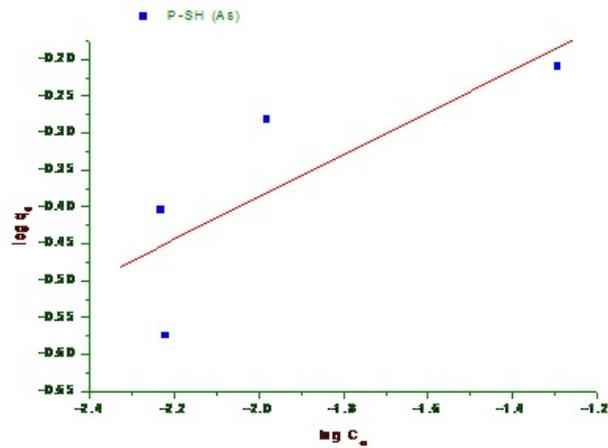


Fig 7 Freundlich adsorption isotherm for adsorption of As<sup>3+</sup> on PSH.

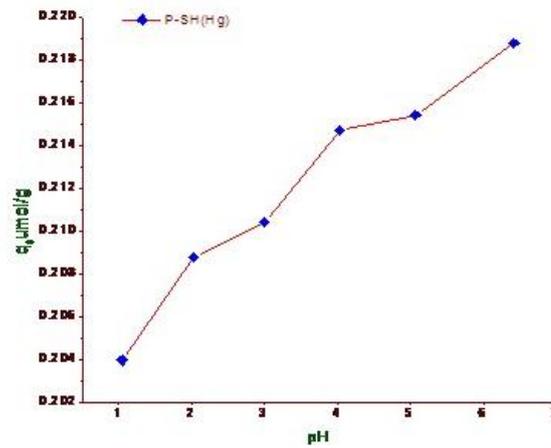


Fig 8 . Effect of initial pH on adsorption of heavy metal ion (Hg) on mercapto methyl resin (C<sub>0</sub>=0.25 μmol, 30<sup>0</sup>C).

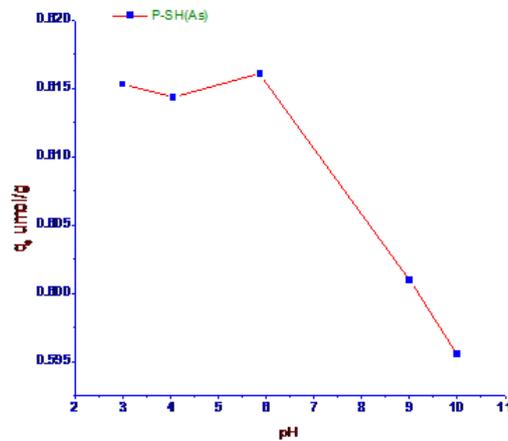


Fig 9. Effect of initial pH on adsorption of heavy metal ion (As) on mercapto methyl resin (C<sub>0</sub>= 0.6674 μmol, 30<sup>0</sup>C).



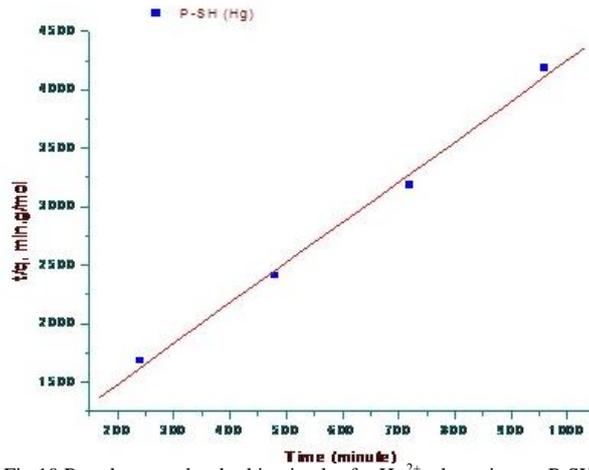


Fig 10 Pseudo second order kinetic plot for  $Hg^{2+}$  adsorption on P-SH.

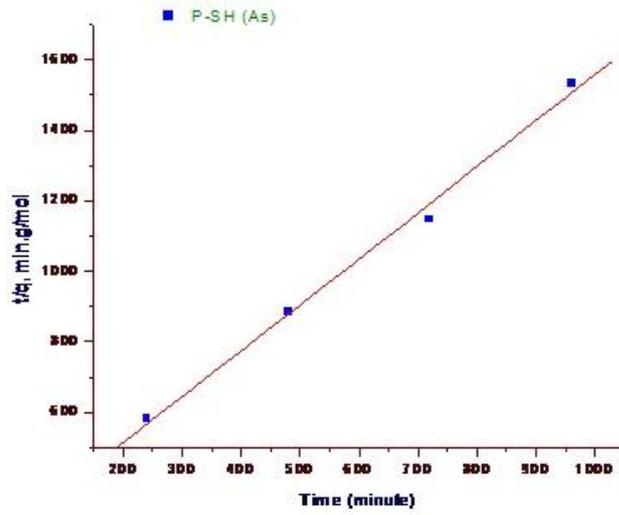


Fig 11 Pseudo second order kinetic plot for  $As^{3+}$  adsorption on P-SH.



## Tables Captions

Table 1: Langmuir isotherms constants for heavy metal ions adsorption onto P-SH

Adsorbent	Metal ion	Langmuir isotherm parameters			
		$K_L$ (l/ $\mu$ mol)	$q_0$ ( $\mu$ molg <sup>-1</sup> ) experimental	$q_0$ ( $\mu$ molg <sup>-1</sup> ) calculated	$R^2$
P-SH	As	448	0.6167	0.6411	0.9975
	Hg	217	0.219	0.2537	0.9936

Table 2: Freundlich isotherms constants for heavy metal ions adsorption onto P-SH

Adsorbent	Metal ion	Freundlich isotherm parameters		
		$K_f$ ( $\mu$ mol/g)	1/n	$R^2$
P-SH	As	1.203	0.2859	0.6275
	Hg	1.1498	0.4698	0.8790

Table 3: Pseudo second order rate constants for the adsorption of Hg<sup>2+</sup>, As<sup>3+</sup> on P-SH

Adsorbent	Metal ion	Pseudo second order kinetics			
		$K$ ( $\mu$ mol <sup>-1</sup> min <sup>-1</sup> )	$q_0$ ( $\mu$ molg <sup>-1</sup> ) experimental	$q_0$ ( $\mu$ molg <sup>-1</sup> ) calculated	$R^2$
P-SH	As	0.00655	0.7706	0.6369	0.994
	Hg	0.01493	0.2899	0.2292	0.994

