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Simple synthesis of highly selective and fast Hg(II) removal polymer from aqueous solution

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Among the toxic metals, mercury (Hg) is a highly toxic element, and hence, a suitable technology is required to remove it. An imprinted polymer exhibiting a high sensitivity for mercury (II) in aqueous solution is presented. Polymer particles imprinted with mercury (II) were synthesized by polymerizing aminothiophenol. The imprinted polymer was characterized by Fourier transform infrared spectroscopy, UV–vis spectroscopy, X-ray diffraction analysis, and scanning electron microscopy. Relative selective coefficients (k') of the imprinted polymer evaluated from selective binding studies between Hg^{2+} and Cu^{2+} or Hg^{2+} and Cd^{2+} were 64 and 27, respectively. These values indicated highly favored Hg^{2+} extractions over the two competing ions. The polymer has high analytical potential for selective extraction and pre-concentration of mercury (II) ions in the presence of closely related ions. Here we report simple synthesis of polymer with high selectivity and fast adsorption capability of Hg (II) ion over similar charge cations such as Cd (II) and Cu (II). The study shows that the polymer has a potential intern of reusability and high stability.

Keywords: mercury (II); toxic metal; polymer; polyaminothiophenol; conducting polymers; selective adsorption

Introduction

New methods for the reduction and remediation of hazardous wastes such as carcinogenic organic solvents, toxic materials, and nuclear contamination are vital to environmental health. Procedures for effective waste reduction, detection, and removal are important components of any such methods. Toward this end, polymeric smart materials are finding useful applications. Polymer-bound smart catalysts are useful in waste minimization, catalyst recovery, and catalyst reuse. Polymeric smart coatings that are capable of both detecting and removing hazardous nuclear contaminants have been developed. Such applications of smart materials involving catalysis chemistry, sensor chemistry, and chemistry relevant to decontamination methodology are especially applicable to environmental problems.[1–3] In recent years, there has been an increase interest in the metal complexation behavior of polymer-supported ligand as analytical reagents, catalysts, and in pollution control. Chelating resins and water-soluble chelating polymers have been used for the selective removal and recovery of heavy metal ions from drinking water and industrial wastes. Previously, liquid–liquid extraction, sorption, ion exchange, precipitation, and other methods have been used. The complexation behavior of polymer-supported ligand is different from the corresponding low molecular weight analogue. Thus, the complexation parameters of polymeric ligand are decided by the polymeric matrix and are governed by the nature of the polymeric backbone, the nature and extent of the cross-linking agent,

the nature of the ligand and its distribution and accessibility in the polymer. In the case of cross-linked polymers, due to their insolubility, accessibility of metals to functional groups is diffusion controlled.

The number of chelating ligands available for the selective interaction with aqueous metal ions is very wide, and most of them have been bound to polymers. Many reviews [4–6] cover recent attempts to incorporate a vast number of different chelating groups into various synthetic and natural polymeric networks. Different functional groups such as thiols, pyridine, 8-hydroxyquinoline, and dioxime have been immobilized on styrene–divinylbenzene copolymer, glycidyl methacrylate–divinylbenzene copolymer, phenol–formaldehyde resins, and cellulosic materials. Chelating resins are, as mentioned above, very useful in removing heavy metal ions from water, but they often suffer from insufficient chelation speed, because they must work in a nonhomogeneous environment due to their hydrophobic character (water-insoluble cross-linked resins); furthermore, the steric hindrance of polymeric backbone can limit the intrinsic chelating properties of the functional groups.

All mercury compounds are known to be highly toxic chemicals. Their presence in municipal water is prohibited by health authorities almost everywhere in the world. Removal of toxic metals, in general, has been given great attention for environmental cleanup and hydrometallurgical applications. Conventional ion exchangers have limited success in the extraction of trace

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quantities, and the removal of toxic metals requires more efficient sorbent materials. Selective extraction of any desired metal ion is important not only for the isolation or removal of one chemical component but also for the effectiveness of the sorbent material because, during the extraction of any metal ion targeted, a waste amount of ligating groups should be spent for the extraction of common abundant metal ions such as Ca(II) and Mg(II) at the same time. In that case, only a few percent of the ligating groups of the sorbent serve in the removal of a target chemical, and this greatly reduces the effectiveness of the sorbent. In some cases, selective metal ion removal can be achieved to some extent by the proper choice of conditions, such as pH adjustment. [7] However, those polymeric sorbents described are applicable only for binary or ternary mixtures, and even in those cases, clear-cut selectivity has never been attained so far.

A more general approach for selective metal ion removal is template methodology, in which a complexed polymer ligand is post-cross-linked with a suitable reagent. Removal of the metal ion by any means gives rise to a product with microholes having high complexing affinity for the template metal ion. The template methodology has been extended to organic and biomolecules by the groups of Wulff [8] and Mosbach [9] and has been termed molecular imprinting. The subject is now becoming a new area of research and is being exploited in the development of new term selective membranes [10] and chiral membranes.[11] In this technique, the success of the selectivity depends strictly on the cross-linked density of the material, and this makes the separation process slow. Because of this limitation, the technique is applicable only in small-scale separations for the time being, and it needs further improvements.

Three steps are involved in ion-imprinting process. The complexation of metal ions to a polymerizable ligand, then the polymerization of complex monomer, and finally the removal of template produces the ion-imprinted polymer. The monomers are chosen according to their ability to interact with the functional groups of the template molecule. Since the affinity of ligand affects directly on selectivity for an ion template, the right selection of the functional monomer is important.[12] There are some commercial monomers such as 4-vinyl pyridine (VP), styrene, and methacrylic acid that have been used extensively in ion-imprinted polymers. These monomers are used by themselves or with another compound for complexing the ion template before or during the polymerization.[13] Liu et al. [14] have reported Hg (II)-imprinted copolymers by copolymerizing mercury chloride, diazoaminobenzene (DAAB), and 4-VP using ethylene glycol dimethacrylate as a cross-linker in the presence of 2,2-azobisisobutyronitrile (AIBN) as an initiator. Their Hg (II)-imprinted copolymers have high adsorption capacity and good selectivity for Hg (II) compared with

non-imprinted copolymers but their thermal stabilities have not been reported. 5,7-dichloroquinoline-8-ol is another compound that has been used for complexing many ion templates in ion-imprinted polymers.[15–20] Although these compounds increase the selectivity in ion-imprinted polymers, as they do not involve the polymerizable group, they cannot be copolymerized with the functional monomers and will be physically trapped into the bulk of polymer after removing the template that can cause thermal instabilities and they will decompose before thermal decomposition of polymer. Since heavy metals in general and mercury in particular show very great affinity to sulfur, the functional monomers containing the sulfhydryl group can produce a good stable complex with mercury. On the other hand, an amine as a nucleophilic element can react with an activated acryl donor such as methacryloyl chloride and produce the acryl-type monomers. The aminothiols have both amine and sulfhydryl groups; therefore, they are good candidates for producing thiols functional monomers for imprinting the mercury ions.

Mercaptoethylamine (MEA) or cysteamine is the simplest stable aminothiols without additional reactive functional group that is able to form the stable complex with some metal ions.[21] Recently, Mahmoud Firouzzare et al. [22] used this compound for synthesizing N-Methacryloyl-2-mercaptoethylamine (MMEA) and then complexing the mercury ion. The produced complex monomer copolymerized with methacrylic acid and ethylene glycol. After removing the mercury ions, the obtained Hg (II)-imprinted polymer shows high selectivity to Hg (II) ions in comparison with non-imprinted polymers and in competition with other metal ions such as Cd(II), Zn(II), and CH_3HgCl . The synthesis procedure is quite lengthy and too many chemicals are involved. In addition to the existing problem, 4-aminothiophenol (4-ATP) has been used for complexing the mercury ion and the produced complex monomer polymerized by oxidative polymerization. The prepared material in this study is good and obtained in a two-step reaction. Further, its applicability used for the removal of mercury ion from the aqueous solution was studied. The obtained imprinted polymer shows high selectivity and fast removal of Hg (II) ions in comparison with other metal ions such as Cd(II), Zn(II), and Cu(II) presented here.

Experimental

All used solutions were prepared with ultrapure water produced by a Milli-Q system (Millipore Filter Co., Bedford, MA, USA). All reagents used in this work were of the highest purity available and at least of analytical grade. 4-ATP supplied by Sigma-Aldrich; ammonium and persulfate from HiMedia; dimethyl sulfoxide, toluene, tetrahydrofuran, hydrochloric acid, thiourea,

CdCl₂, ZnCl₂, and CuCl₂ were from Qualigen (Glaxo, India). The pH was adjusted with the following buffer solutions: NaCH₃COO/CH₃COOH for pH 4.0–6.0; Na₂HPO₄/NaH₂PO₄ for pH 7.0–7.5; and Na₂B₄O₇/HCl for pH 8.0–9.0

Hg (II)–ATP complex monomer (0.4 M) was dissolved in ethanol and water (80 and 120 ml, respectively) mixture and then homogenized ultrasonically for 30 min. Polymerization of the monomer was initiated by the dropwise addition of the oxidizing agent (ammonium persulfate) under constant stirring at 0–4 °C. After complete addition of the oxidizing agent, the reaction mixture was kept under constant stirring for 24 h at 0–4 °C. Afterward, the obtained polymer was separated and washed with distilled water and then with ethanol until the filtrate was colorless to remove any unreacted monomer, initiator, and solvent. Finally, it was dried in an oven at 60 °C for 12 h, grounded in a mortar and sieved to acquire the powdered particles, and then stirred with the solution of 2 M HCl and 5% thiourea at 40 °C for 36 h for complete removal of Hg (II) from polymer. Hg (II)-imprinted polymer was washed with ultrapure water and dried again in an oven at 60 °C. The non-imprinted polymer particles were prepared in a similar way but without the imprinted ion Hg (II). It was observed that the soluble product was obtained when polymerization carried out without Hg (II) ion.

The FTIR spectra of the polymer were taken on a Bruker FTIR-8101A spectrophotometer between 400 and 4000 cm⁻¹. The samples were prepared in pellet form using spectroscopic grade KBr powder. X-ray diffractogram was recorded on a Philips PW1710 automatic X-ray diffractometer. Scanning electron micrographs were taken with small amounts of dry samples on disk covers coated with gold. The analyses were performed with a JEOL JSM-840 scanning microscope. The particle sizes of the beads were determined by a comparison of the particles to the bar in the right-hand corner of the images. The BET surface areas were measured by the Brunauer–Emmett–Teller method using nitrogen gas as absorbent (BET, ASAP 2420) at 77 K. The resultant polymer was expected to show water absorbency. The water sorption ability was simply determined by a mass increase in the polymer sample (0.2 g) soaked in distilled water in a crucible. After contact for 24 h, the mass of the filtered sample (0.93 g) indicated a 465% (w/w) water sorption.

The mercury sorption capacity of prepared polymer was determined by mixing (0.50 g) with 50 ml aqueous Hg (II) solution (0.08 M). The concentration of Hg (II) in the solution was measured calorimetrically using diphenyl carbazide [11]. The mercury loading capacities were calculated from the initial and final Hg (II) contents of the solution. The data were also verified by analysis of some sample using atomic absorption spectrometric technique.

Results and discussions

Characterization of imprinted polymer particles

The functional group can be introduced in two ways. It is introduced either via the polymerization of a functional monomer or by chemical modification of a polymer. The most important problem is preventing oxidation of the thiols group. Moreover, in the first method, if we try to polymerize the thiols-supported monomer, the SH functions can add to the double bond.[23] So it is necessary to protect the thiols group before its use. Protection can be achieved by the use of a thioester function or an ethyl dithiocarbonate group.[24] Hence, in order to solve the said problem, we assume that the 4-ATP will be a best precursor having thiols group which can be protected first by complexing with Hg (II) ion while –NH₂ group is free, which is used for further polymerization. The interaction of functional group with Hg (II) and formation of polymer was studied by FTIR spectroscopy. The results are shown in Figures 1–3.

FTIR spectra of 4-ATP show band at 3433 cm⁻¹, which is due to N–H stretching. The absorption peaks observed at 1654 and 1637 cm⁻¹ were attributed to C=C stretching in aromatic nuclei. Absorption bands at 1476.12 and 1491.15 cm⁻¹ evidenced C=N stretching in aromatic compounds. The double peaks of S–H were found at 2312 and 2381 cm⁻¹. [21] The absorption bands that lie below 1000 cm⁻¹ are the characteristics of substituted benzene. The same finding has been reported earlier.[19,20] The 4-ATP was dissolved in ethanol and then Hg (II) salt was added slowly and allowed to further reaction for 2 h with stirring. Formed complex (Hg (II)-ATP) was filtered and washed with water, ethanol, and acetone and then dried in vacuum desiccators. The S–H stretching vibration band at 2312 and 2381 cm⁻¹ is absent from the spectrum of Hg (II)–ATP complex monomer (Figure 2), which confirms the formation of complex while band corresponding to –NH₂ group is seen. This indicates that the Hg (II) ion forms a complex using S–H group while NH₂ group remains free. The careful observation of Figure 3 shows the formation of polymeric compound. The presence of two bands in the vicinity of 1500 and 1600 cm⁻¹ is assigned to the non-symmetric C₆ ring stretching modes. The higher frequency vibration 1600 cm⁻¹ has a major contribution from quinoid rings, and lower frequency mode at 1500 cm⁻¹ depicts the presence of benzenoid ring unit. The presence of these two bands clearly shows the formation of polymer having the amine and imine units. The presence of characteristics vibration bands confirms the formation of polymer in the conducting emeraldine salt phase. Strong peaks near to 500 cm⁻¹ are a characteristic peak of metal–sulfur bond present in the polymer, which is shown in Figure 3.

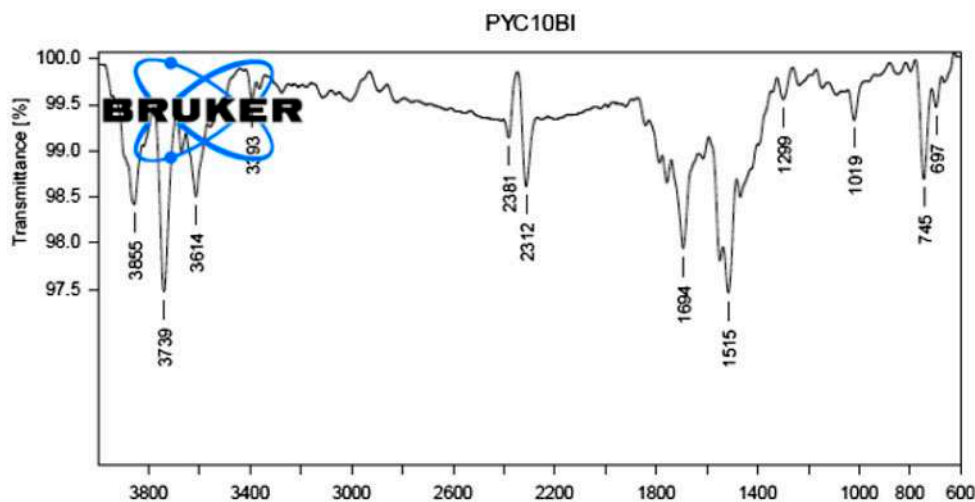


Figure 1. FTIR spectra of p-aminothiophenol.

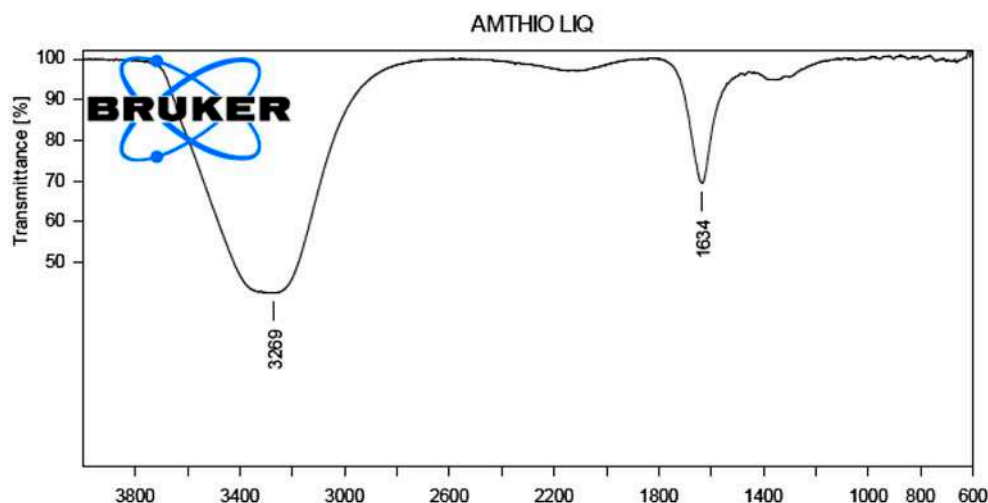


Figure 2. FTIR spectra of p-aminothiophenol-Hg (II) complex.

The material may be used for the removal at higher temperature, and hence in order to study it, the thermogravimetric analysis was carried out as shown in Figure 4. The thermogravimetric analysis shows that the leached and unleached polymers are quite stable at higher temperature up to 20 °C, and incorporation of Hg (II) in polymer network increases the thermal stability of the material. This shows that the prepared polymeric material can be used for the removal of Hg (II) at higher temperature, which was an inherent problem associated with the earlier reported materials.

XRD of prepared imprinted polymer is shown in Figure 5. Generally, PANI and its derivatives are amorphous and exhibit a broad diffraction band around 250 that corresponds to periodicity parallel to polymer chain. The XRD pattern of prepared material is typical of PANI

derivative showing the amorphous band around 27°. No significant difference was observed for the imprinted polymer after the complete extraction of Hg (II) ion, which shows that extraction does not alter the structure of polymer.

Figure 6 shows the UV-vis absorption spectra of the synthesized polyaminothiophenol samples. Normally, in UV-vis of PANI samples, the spectrum of emeraldine base (EB) form presents two absorption peaks, one is located around 634 nm (1.96 eV) and another one is around 320 nm (3.75 eV).[19] The former peak is due to the excitation formation in the quinoid rings (oxidized unit), and the latter one is assigned to the $\pi-\pi^*$ transition in the benzoid structure (reduced unit).[25] The prepared sample having both oxidizing and reducing units indicates that the prepared sample is in EB form.

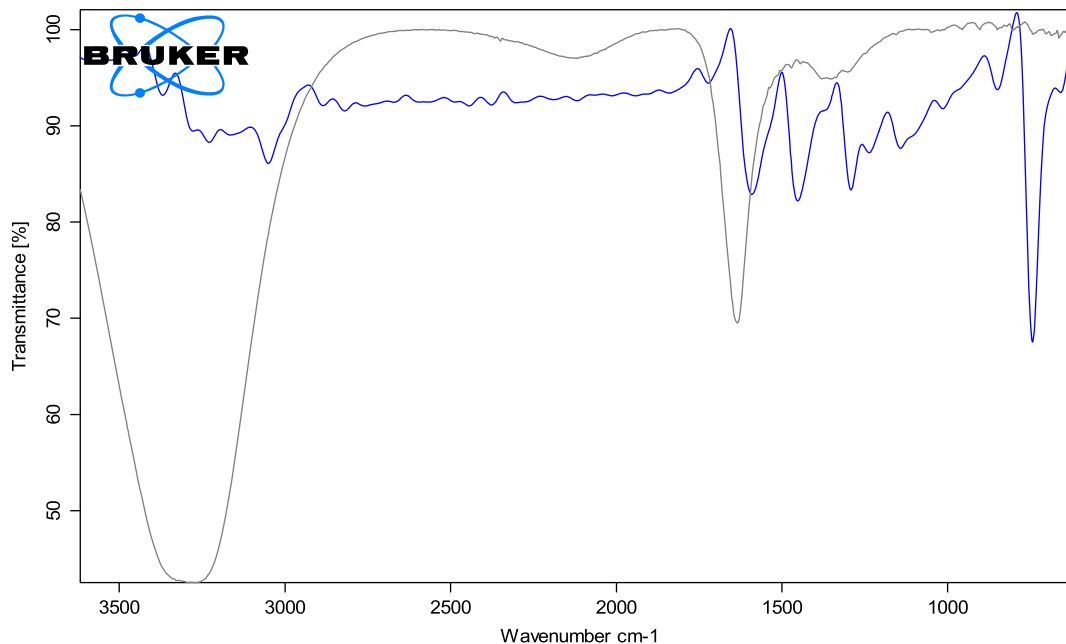


Figure 3. FTIR spectra of polyaminothiophenol without leaching in with comparison with p-aminothiophenol-Hg (II) complex.

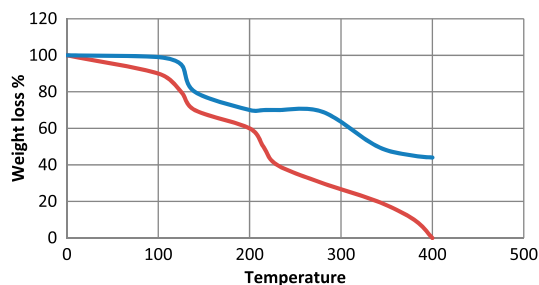


Figure 4. TGA curves of leached and unleached polymer (4-aminothiophenol).

The morphological study of prepared polymer was carried out, and images are shown in Figure 7. The SEM images of polyaminothiophenol show globular morphology having a globular size of 200–300 nm. The unique morphology may play important role during the removal of metal ions from aqueous solution. Further EDS study shows that after leaching, the complete removal of Hg (II) takes place and sulfur atom as a $-SH$ group remains with polymer.

The N_2 adsorption isotherms at $-196\text{ }^\circ\text{C}$ of material prepared are shown in Figure 8 and Table 1. Nitrogen adsorption desorption isotherms display the stereo IV type isotherms with an obvious hysteric loop in the relative pressure (P/P_0) range of 0.0–1.00. This finding indicates that the sample contains both the ordered mesopores and the disordered larger pores because the loop in range of 0.7–1.0 indicates the mesopores, whereas those

in higher relative pressure originated from the larger and usually disordered pores, which are often constructed by the inter-particle holes. The loops located in the range of higher relative pressure, that the amount of adsorbed nitrogen rise very steeply in the high relative pressure, suggesting the presence of relative large and nonuniform pores and the multilayer adsorption of N_2 in the meso- and macro-pores. The detail about the characteristic feature of materials is given in Table 1.

Metal ion separation behaviors of imprinted polymer particles

All mercury compounds are known to be highly toxic chemicals. Their presence in municipal water is prohibited by health authorities almost everywhere in the world. Removal of toxic metals, in general, has been given great attention for environmental cleanup and hydrometallurgical applications.

The effect of pH on Hg^{2+} ion adsorption by the polymer powder is shown in Figure 9. The polymer exhibited low affinities for Hg^{2+} ion extraction in highly acidic and alkaline conditions, as indicated by the low q_{pH}, with the highest calculated being 37 ± 0.1 at pH 6.4 and same for pH at 6.9 and 7.3. Low pH (acidic) solutions have a greater affinity for metal ions such as the Hg^{2+} ion; hence, the ion may be distributed more in the acidic solution than on the polymer particles. Thus, the low q_{pH} were recorded at low pH. Under alkaline conditions (high pH), it was likely that the Hg^{2+} ion complexed with the hydroxide ions forming soluble

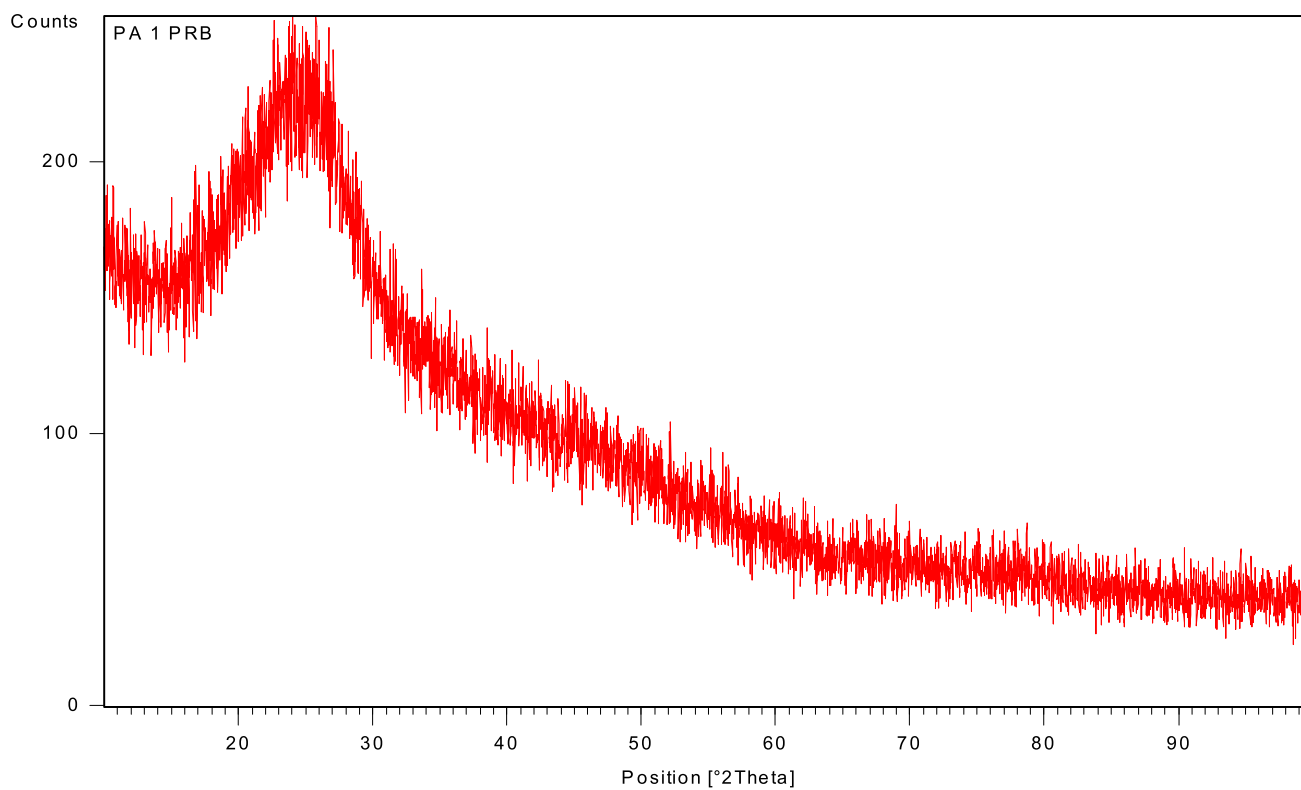


Figure 5. XRD of polyaminothiophenol.

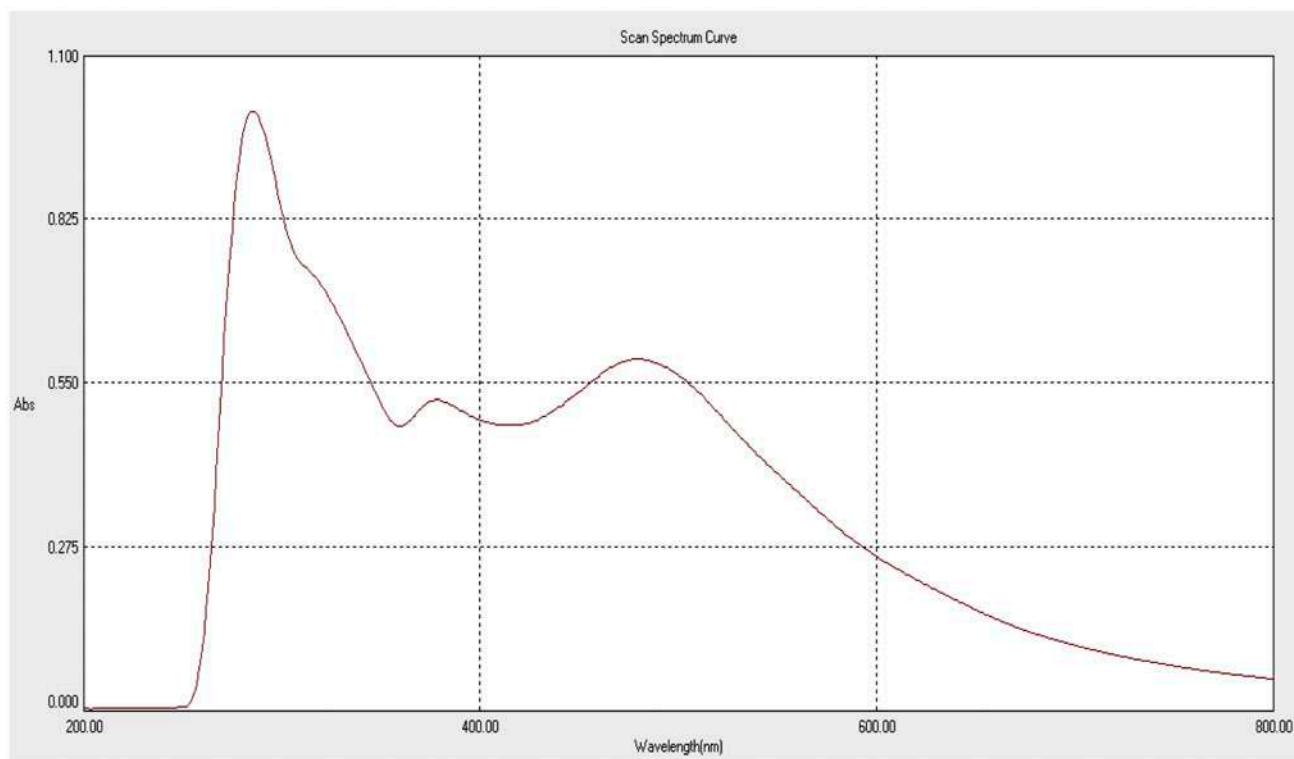


Figure 6. UV-vis spectra of polyaminothiophenol after leaching.

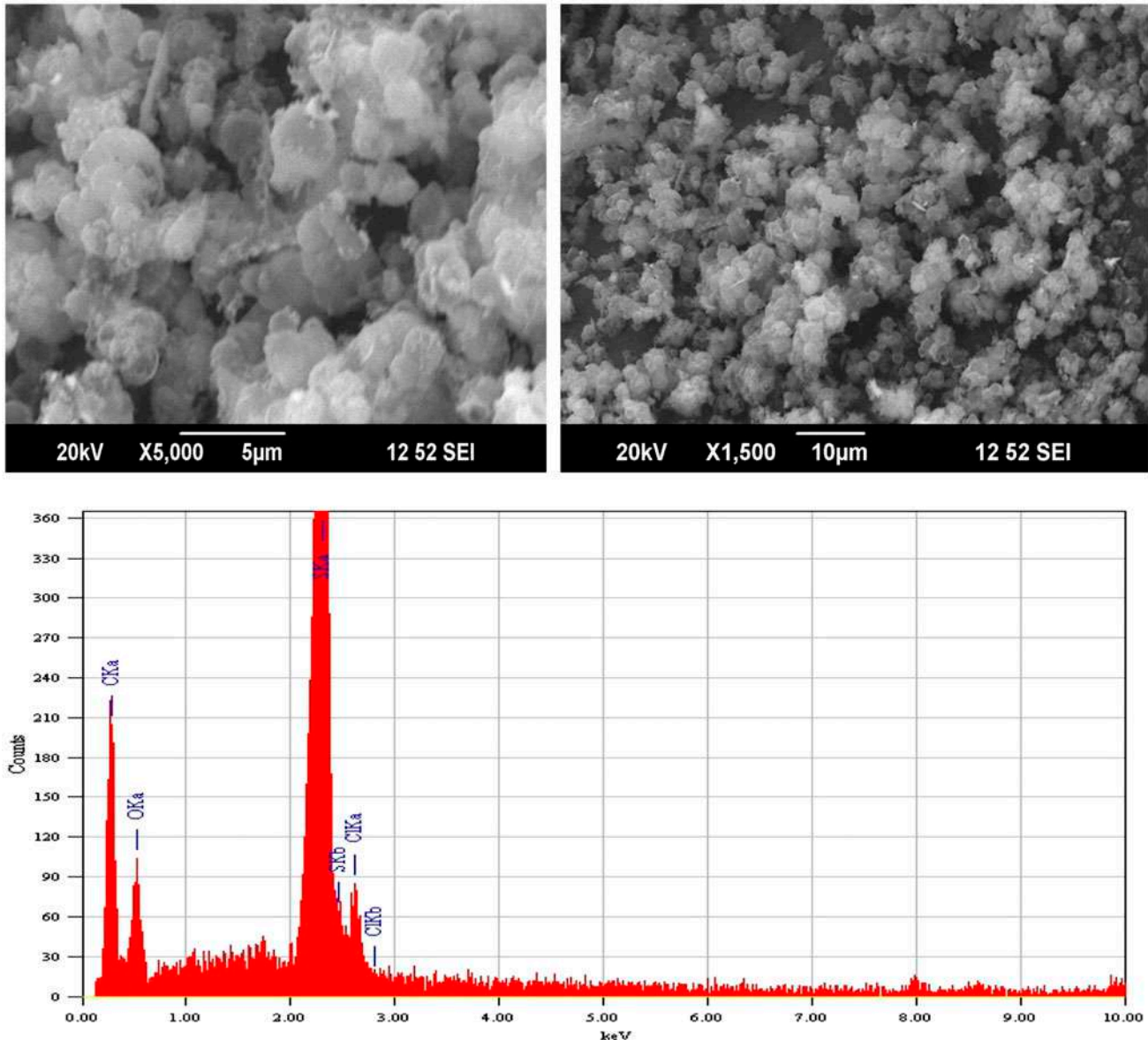


Figure 7. SEM images of polyaminothiophenol after leaching.

amphoteric hydroxides instead of being adsorbed on the polymer particles. As a result, low qpHs were recorded. Figure 10 shows the time dependence of the adsorption capacities of Hg^{2+} ions on the polymer powder as a function of time. The following parameters were used in the study: amount of polyaminothiophenol polymer (1000 mg), pH (pH 7.3), initial metal concentration (400 mg/L), and stirring speed (200 rpm). Hg^{2+} ion adsorption increases with time during the first 06 min, after which it levels off (Figure 10), exhibiting fast kinetics for binding the Hg^{2+} ions. Good removal efficiency (%) of the bound ions was recorded ($100 \pm 0.1\%$), even at these short equilibration-adsorption times.

The polymer amount is also one of the important parameters to obtain the quantitative uptake of metal ion. The dependence of metal sorption on resin input amount was studied by varying the amount of polyaminothiophenol polymer (200–2000 mg), while the other parameters such as pH (pH 7.3), initial metal concentration (400 mg/L), and stirring speed (200 rpm) remained constant. The percentage of Hg^{2+} extracted increased with the quantity of polymer from 200 to 1000 mg, after which further increase in the quantity of the polymer did not yield any increase, as shown in Figure 11. This marked the optimum quantity of the polymer powder (1000 mg) needed to bind maximally. The highest

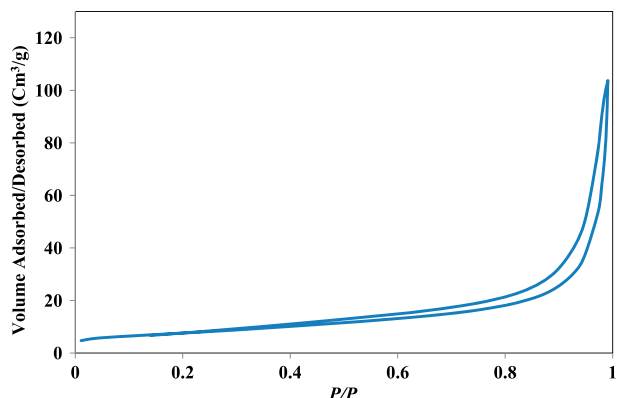


Figure 8. The N₂ adsorption-desorption isotherms at -196 °C of imprinted polymer.

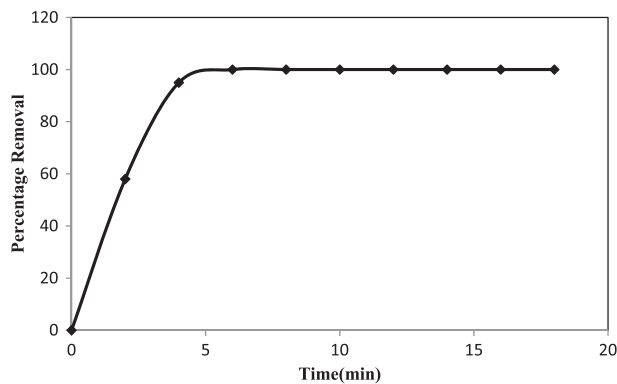


Figure 10. The dependence of removal efficiency with agitation time.

Table 1. Various surface textural parameters of polymer from N₂ adsorption isotherm at -196 °C.

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Surface area

Single point surface area at $P/P_0 = 0.249627923$	57.0310 m ² /g
BET surface area	58.1098 m ² /g
Langmuir surface area	80.4304 m ² /g
t-Plot micropore area	6.5904 m ² /g
t-Plot external surface area	51.5193 m ² /g
BJH adsorption cumulative surface area of pores between 1.7000 and 300.0000 nm width	64.532 m ² /g
BJH desorption cumulative surface area of pores between 1.7000 and 300.0000 nm width	70.8610 m ² /g

Pore volume

Single point desorption total pore volume of pores less than 90.9236 nm width at $P/P_0 = 0.978233983$	0.269075 cm ³ /g
t-Plot micropore volume	0.002729 cm ³ /g
BJH adsorption cumulative volume of pores between 1.7000 and 300.0000 nm width	0.310102 cm ³ /g
BJH desorption cumulative volume of pores between 1.7000 and 300.0000 nm width	0.309300 cm ³ /g

Pore size

Desorption average pore width (4 V/A by BET):	18.52185 nm
BJH adsorption average pore width (4 V/A):	19.2215 nm
BJH desorption average pore width (4 V/A):	17.4596 nm

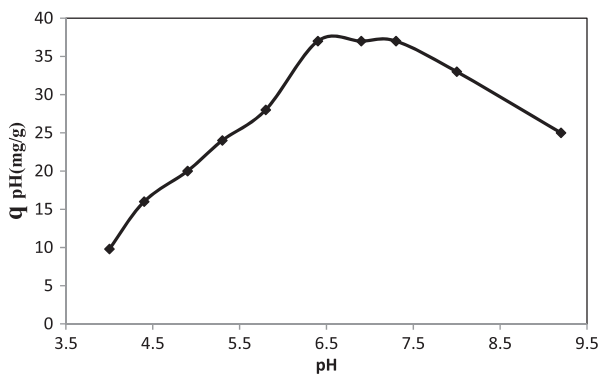


Figure 9. The effect of pH on Hg²⁺ ion adsorption by the polymer powder.

removal efficiency (%) of Hg²⁺ achieved was calculated as 100 ± 0.1%. The amount of Hg (II) ions adsorbed per unit mass of the polymer (i.e. adsorption capacity)

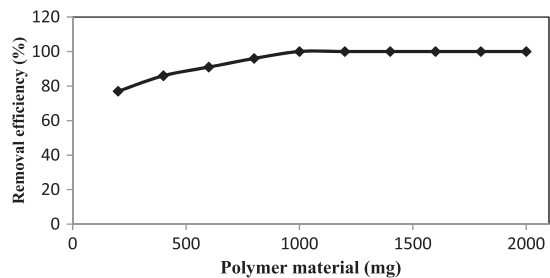


Figure 11. Effect of polymer dosages on removal efficiency of Hg (II).

increases with increasing the initial concentration of Hg (II) ions. The maximum adsorption, which represents saturation of active points on the polymer by Hg (II) ions, was 400 mg Hg (II) per g of polymer.

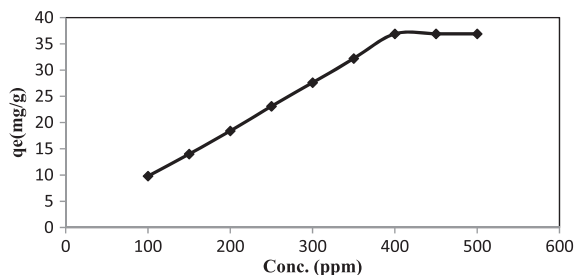


Figure 12. Amount adsorbed q_e as a function of the initial concentrations of Hg (II) in solution.

The Langmuir and Freundlich equations are most widely used to study the adsorption of metal ion in the various adsorbents.[26,27] The Langmuir model assumes that the adsorption of metal ions is a process occurring on a homogenous surface without any interaction between adsorbed ions homogenous surface, and without any interaction between adsorbed ions. The adsorption proceeds until a complete monolayer is formed. To get the equilibrium data, sample with different initial concentrations of Hg (II) and constant adsorbent mass in each sample was studied. The Langmuir and Freundlich equations were used to describe the isotherm data obtained for the adsorption of Hg (II) ions over the entire concentration range. The characteristics of Langmuir and Freundlich equations are shown in Figures 12 and 13 and Table 2.

The regression coefficients in Table 2 show that the experimental data reasonably well fitted the linearized equation of the Langmuir isotherm over the whole Hg (II) concentration range studied. Data in Table 2 show that the Freundlich isotherm was also representative for

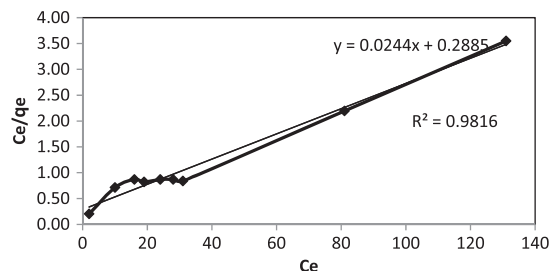


Figure 13. Verification of Langmuir–Hinshelwood mechanism.

heavy metal adsorption. However, Freundlich isotherm could be considered as a better fitting model than Langmuir isotherm. It has been stated that the magnitude of the exponent $1/n$ gives an indication of the favorability of adsorption capacity of the solid adsorbent for the studied adsorbate. The values $n > 1$ represent the favorable adsorption conditions for the removal of Hg (II) ions from aqueous solution by prepared material.

Competitive adsorption of $\text{Hg}^{2+}/\text{Cd}^{2+}$ and $\text{Hg}^{2+}/\text{Cu}^{2+}$ couples was investigated in an equilibration-adsorption batch system. Cd^{2+} ion was chosen as a competing ion because, like Hg^{2+} , it binds well with amine ligands, while Cu^{2+} has a higher affinity for the same type of ligand. Additionally, both of the competing ions have the same charge, have comparative ionic radii, and often coexist with Hg^{2+} ions, exhibiting certain interference properties in aqueous environments. Table 3 summarizes the distribution coefficient (K_d), the selectivity coefficient (k), and the relative selectivity coefficient (k') values of the competing ions with respect to the target ions, i.e., Hg^{2+} ions. The K_d values are the ratio of the concentra-

Table 2. Parameters for the Langmuir adsorption isotherms and Freundlich adsorption isotherms for Hg (II) removal by imprinted polymer.

Langmuir isotherm	Hg (II) removal	Freundlich isotherm	Hg (II) removal
q_m (mg/g)	288	k (l/g)	5.93
K (l/mg)	0.409	n	3.52
Correlation coefficient r^2	0.981	Correlation coefficient r^2	0.993

Table 3 Showing the distribution coefficient (K_d), the selectivity coefficient (k), and the relative selectivity coefficient (k') values.

Metal ions	K_d (ml g ⁻¹)		k		k'	
	Hg (II) polymer	Non-Hg polymer	Hg (II) polymer	Non-Hg polymer	Hg (II) polymer	Non-Hg polymer
Hg	1190	11				
Cd	0.50	0.13				
Cu	0.25	0.15				
Mix Hg/Cd			2369	89	27	
Mix Hg/Cu			4749	74	64	

tion of a particular ion between the imprinted polymer and the aqueous environment. It signifies the extraction ability of a unit quantity of the polymer for a particular ion in a unit volume of solution. K_d values for the imprinted polymer for all ions were higher than those for the non-imprinted polymer, indicating that even the non-imprinted polymer has nonselective sites which any ion may bound to. The K_d value for the imprinted polymer used to extract Hg^{2+} ions in the samples was significantly higher, more than one thousand times, than that of Cd^{2+} and Cu^{2+} . This demonstrated the ability of the imprinted polymer to bind Hg^{2+} ions as they perfectly fitted the fabricated recognition sites, and to a far greater extent than the competing ions. The selectivity coefficient (k) for Hg^{2+} binding in the presence of Cd^{2+} ions was found to be 2369, that is, the polymer will extract Hg^{2+} 2369 times more than it can extract Cd^{2+} ions. For Cu^{2+} , this is 4749 times more, making Cu^{2+} the less interfering ion, as the Hg^{2+} ion out-competes it by a large k value. The k values for the non-imprinted polymer were of the same order of magnitude: 89 for the $\text{Hg}^{2+}/\text{Cd}^{2+}$ and 74 for the $\text{Hg}^{2+}/\text{Cu}^{2+}$ competition systems. The closeness of these values shows that the non-imprinted polymer had similar if not the same affinity for all of the ions, as there were no recognition sites that were originally created for any particular ion in its structure. From the k' values, the effect of imprinting on selectivity can be estimated. The high values of k' exhibited by the prepared imprinted polymer powder between $\text{Hg}^{2+}/\text{Cd}^{2+}$ (27) and $\text{Hg}^{2+}/\text{Cu}^{2+}$ (64) indicate that the prepared polymer is highly selective to Hg^{2+} even in the presence of its closely related analogues.

Conclusion

In conclusion, polyaminothiophenol is synthesized via a chemical route. The polyaminothiophenol shows highly selective adsorption capacity for Hg^{2+} as well as kinetics is very fast. The adsorbent (polyaminothiophenol) is stable and environmentally friendly with a high Hg^{2+} adsorption capacity and extremely high desorption capacity showing practical utility for wastewater treatment. A mercury (II) ion-imprinted functionalized polymer with exceedingly high performance, which is marked by the fast equilibration-adsorption kinetics, the very large relative selectivity coefficients, high extraction efficiency percentages of the targeted ion (Hg^{2+}), even in the presence of other closely related ions, was successfully prepared. The polymer was simple and relatively easy to prepare. The polymer has high analytical potential for selective extraction and pre-concentration of mercury (II) ions in the presence of closely related ions. Its use as a solid-phase extraction sorbent can be further evaluated in the future.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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