

Synthesis of Polyaminothiophenol with Hg(II)-ATP complex and their application in removal of mercury & dye from aqueous solutions

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Abstract

One of the main issues in worldwide public health is severe sickness and environmental contamination from heavy metal ions. Particularly dangerous to living systems is mercury(II), one form of very deadly pollutant that can kill a person's metabolism, central nervous system, and immune system. Thus, it is crucial to use novel techniques for creating eco-friendly, effective, and affordable materials for the selective detection and removal of Hg^{2+} . The polyaminothiophenol has been synthesized and explored their ability to the separation of Hg^{2+} ions and dye in aqueous media.

Introduction

The applications of conducting polymers in various areas such as display devices, microelectronics, chemically modified electrodes and corrosion protection have recently attracted a good deal of attention in the scientific community. Environmental stability of polyanilines makes them important conjugated conducting polymers. Their rigid planar backbone, which is necessary for electrical conductivity leads to a material that is insoluble in most common solvents. However its intractability resulting from the stiffness of the backbone and the hydrogen-bonding interaction between adjacent chains limits not only the industrial applications but also complete understanding of the properties of this conducting polymer. One of the promises of the conducting polymers is that, unlike inorganic metals and semiconductors, both the synthesis and chemical modification of organic materials offer unlimited possibilities. Soon enough it was recognized that few monomers render polymer chains with high conductivity. On the other hand, conjugated polymer backbones could have low conductivity due to electronic and or steric effects. The addition of side groups to polyaniline has enhanced its process ability and has changed its properties. The process ability of polyaniline has been improved by using various groups, usually by modifying the polymer chain with various ring or N-substituent s. Since most conducting polymers with the significant exception of polyacetylene, contain activated aromatic rings it is possible to introduce substituents by electrophilic aromatic substitution. The method has been explored to modify polyanilines. Epstein and co-workers synthesize a partially (up to 50%) sulfonated polyaniline by sulfonation of emeraldine base, dissolved in concentrated sulfuric acid, with sulfur trioxide (SO_3) present in fuming sulfuric acid [1-5]. The resulting polymer (SPAN) is soluble in aqueous base and both the ion exchange during oxidation or reduction and the pH sensitivity were altered. It seems that 100% sulfonation is not feasible because some oxidation of the leucoemeraldine occurs during sulfonation. Interestingly, the conductivity of the resulting polymer is even higher than SPAN but lower than that of PANI. The reaction of PANI with bromine yields brominated PANI, with a bromine content of bromine proportional to the concentration of bromine introduced in the reaction mixture (up to 59.1 wt %) [6]. the reaction reduces the conductivity of the polymer, as expected by electronic and steric effect of the covalently linked bromine atoms [7].

The polymerization of substituted anilines has been studied with an aim to achieve the formation of soluble polymeric films in order to improve processability while maintaining

electric properties [8]. However, the electropolymerization of benzyl monomers containing both $-NH_3$ and $-OH$ groups are more recent and less well explored [9]. O-aminophenol monomer (OAP) is an aniline derivative that has been shown to hold two groups in the benzenic ring: an amine and a hydroxyl group, which supply many more coordination sites. There is controversy in the literature with regard to dimeric structures formed after chemical and electrochemical oxidation of OAP in aqueous medium. Electrophilic reactions may occur at the meta or para position of the $-NH_2$ group of OAP, yielding two types of heteroaminic structures. While chemical oxidation of OAP yields the formation of 2-aminophenoxazine (APZ) [10-13], redox reactions involving the structure (phenoxazine units) have been proposed for electrochemically prepared POAP films [14-17].

Thiophenol is a compound of aromatic thiol which is structurally analogous to phenol, hydroxyl group ($-OH$) bonded to the aromatic ring is replaced by a sulfhydryl group ($-SH$). This structure means that the oxygen atom of hydroxyl group is replaced by a sulfur atom. Thiophenol is also called phenyl mercaptan. Thiophenol is a toxic, flammable clear liquid with a strong and disagreeable odour, boiling at $168^\circ C$. It is insoluble in water but soluble in alcohol and ether. Many chemical reactions of thiophenols are analogous to phenols. The substantial difference between sulfur and oxygen is that sulfur much more readily gets oxidized to higher oxidation states than oxygen. Sulfur in organic compounds is fairly stable in several oxidation states. Thiophenols can form thiophenolate anions by losing sulfhydryl H^+ ions, used as reagents for the simple chemical preparation. The ring closure reaction of *o*-amino thiophenol produces benzothiazole, an important industrial product. Thiophenol itself is used as an antinematodal agent. Thiophenol class compounds have the skeleton of thiophenol as per the literature review. Due to its oxidizing properties, the synthesis of pure polyaminothiophenol is not reported till date.

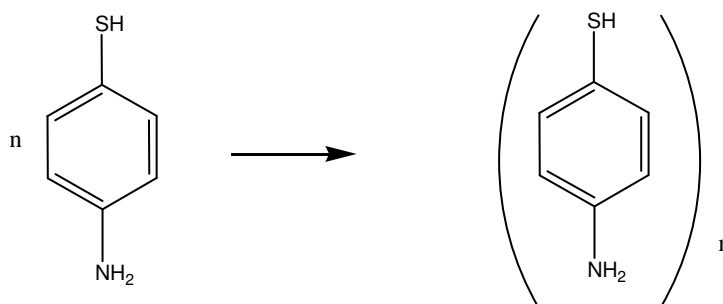


Fig. 1.1 Structure of Polyaminothiophenol

Material and Methods

Synthesis

Hg(II)-ATP complex monomer (0.4 M) were dissolved in the ethanol and water (80ml and 120ml respectively) mixture then homogenized ultrasonically for 30 min. polymerization of the monomer was initiated by the drop-wise addition of the oxidizing agent (ammonium persulphate) under constant stirring at $0-4^\circ C$. After complete addition of the oxidizing agent, the reaction mixture was kept under constant stirring for 24 hours at $0-4^\circ C$. Afterwards, the obtained polymer was separated and washed with distilled water and then ethanol until the filtrate was colorless to remove any unreacted monomer and solvent. Finally, it was dried in an oven at $60^\circ C$ for 12 hours grounded in a mortar and sieved to acquire the powdered particles. The powder material stirred with the solution of 2M HCl and 5% thiourea at $40^\circ C$ for 36 hours for complete removal of Hg(II) from polymer. Hg (II)-imprinted polymer was washed with ultra-pure water and dried again in an oven at $60^\circ C$. The non-imprinted polymer particles were prepared in a similar way but without the imprinted ion Hg (II). It is observed that the soluble product was obtained when polymerisation carried out without Hg (II) ion and hence product was not recovered in aqueous medium.

Characterizations

Characterization of a material is an important step after its synthesis because it gives useful parameters in determining the properties of polymers. Chemical characterization consists of determination of oxidation states. Physical characterization consists of spectroscopic analysis using Fourier Transform Infra- Red (FT-IR) and UV-visible spectrometer, thermal analysis (Thermo Gravimetric Analysis), XRD, SEM, Electrical conductivity, ion exchange and electrochemical properties. The characterization of polyaminothiophenol has been using XRD Analysis, UV-Visible Absorption Spectroscopy, FTIR Analysis, TGA Analysis, SEM Analysis and Electrochemical Analysis

Applications

The material prepared and characterized by the various methods are use for the environmental applications.

Mercury Removal

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 selective metal ion removal can be achieved to some extent by the proper choice of conditions, such as pH adjustment [18] 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.

Recently, Mahmoud Firouzzare et al [19] used this compound for synthesizing N-Methacryloyl-2-mercaptoethylamine (MMEA) then complexing the mercury ion. The produced complex monomer copolymerized with methacrylic acid and ethylene glycol dimethacrylate as a functional monomer and crosslinker respectively. After removing the mercury ions the obtained Hg (II) - imprinted polymer shows high selectivity to Hg (II) ions in comparison to non-imprinted polymers and in competition with other metal ions such as Cd(II), Zn(II) and CH₃HgCl. The synthesis procedure is quite lengthy and too many chemical are involved. In order to above problem the prepared material in this study is good and obtained in a two-step reaction. Further its applicability, used for the removal mercury ion from the aqueous solution.

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.

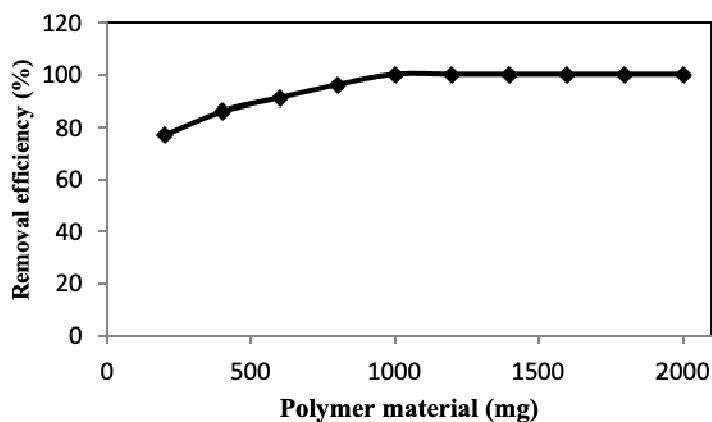


Fig. 1.2 Removal efficiency of Leached 4-ATP

The percentage of Hg^{2+} extracted increased with the quantity of polymer from 200 mg up to 1000 mg, after which further increase in the quantity of the polymer did not yield any increase, as shown in Fig. 1.2 This marked the optimum quantity of the polymer powder (1000 mg) needed to bind maximally. The highest removal efficiency (%) of Hg^{2+} achieved was calculated as $100 \pm 0.1\%$.

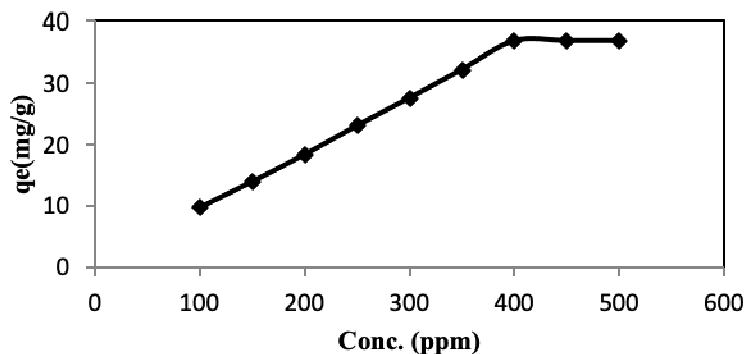


Fig. 1.3 The effect of conc. of Hg^{2+} on removal efficiency of Leached 4-ATP

The amount of Hg (II) ions adsorbed per unit mass of the polymer (i.e. adsorption capacity) 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.

Competitive adsorption of $\text{Hg}^{2+}/\text{Cd}^{2+}$ and $\text{Hg}^{2+}/\text{Cu}^{2+}$ couples were 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 [19]. 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 1 summarizes the distribution coefficient (Kd), 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.

Table 1 Showing the distribution coefficient (Kd), the selectivity coefficient (k) and the relative selectivity coefficient(k') values

Metal ions	Kd (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	

The Kd values are the ratio of the concentration 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. Kd 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 be bound to. The Kd 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 79 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 $\text{Hg}^{2+}/\text{Cd}^{2+}$ is 27 and $\text{Hg}^{2+}/\text{Cu}^{2+}$ is 64 indicate that the prepared polymer is highly selective to Hg^{2+} even in the presence of its closely-related analogues.

Dye Removal

Synthetic dyes represent a relatively large group of organic chemicals which are met in practically all spheres of our daily life. It is therefore possible that such chemicals have undesirable effects not only on the environment, but also on man. In order to minimize the possible damages to man and environment arising from the production and applications of the dyes, several researches were made. The potential toxicity of some dyes has been known for many decades [20]. Dyeing and finishing wastes in the textile industry have high color and organic content. Dyestuff production units and dyeing units have always had a pressing for techniques that allow economical pretreatment for dye removal from wastewater has made it an ideal alternative to other expensive treatment options. Colored waters are also objectionable on aesthetic grounds for drinking and other municipal and agricultural purposes. Some groups have used various adsorbents for the removal of acidic and basic dyes from aqueous solutions [21].

The removal of dyes is important reference to environmental concern and material prepared in this study has an enough potential. The adsorptions of some anionic dyes containing sulfonyl group such as Acid Orange 7 (Orange II) onto polymer from their aqueous solutions have been investigated. Acid orange 7 also known as 2-naphthol orange and Orange II. Acid dyes are water-soluble dyes employed mostly in the form of sodium salts of the sulfonic or carboxylic acids. They are anionic which attach strongly to cationic groups in the fiber directly. They can be applicable to all kind of natural fibers like wool, cotton and silk as well as to synthetics like polyesters, acrylic and rayon. But they are not substantive to cellulosic fibers. They are also used in paints, inks, plastics and leather. Orange acid azo dyes produce an orange-pink color. They are used in coloring foods and drugs and as intermediates for making photosensitive dyes and drugs. They are used as counter stains in histology and cytology and as components of Mallory's acid fuchsin. Acid Orange 7 (acid magenta) is a various mixture of sulfonated fuchsin. There are four of these compounds which have three sulfonic groups each. It is used in Andrade's indicator and in various complex stains to demonstrate collagen fibers red and in smooth muscle in contrast to collagen. It is used as a pH indicator. Its chemical formula is

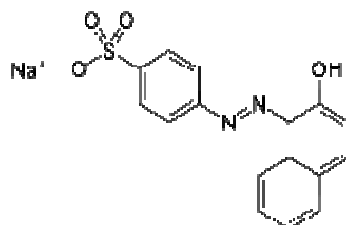


Fig. 1.4 The chemical structure of acid orange 7

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 Acid Orange 7 (40 mg/L) and stirring speed (200 rpm) remained constant.

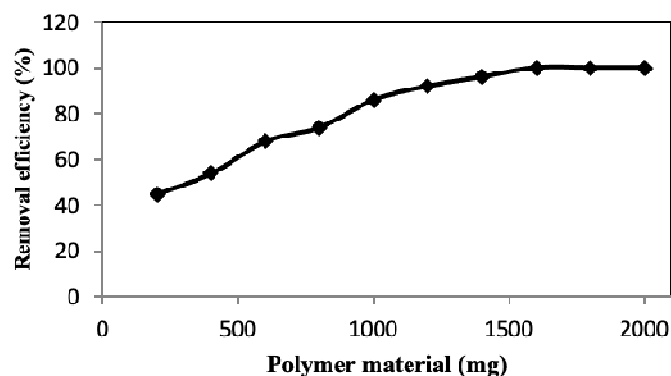


Fig. 1.5 Removal efficiency of polymer material with reference to polymer dosags

The percentage of Acid Orange 7 extracted increased with the quantity of polymer from 200 mg up to 1600 mg, after which further increase in the quantity of the polymer did not yield any increase, as shown in Fig. 1.5. This marked the optimum quantity of the polymer powder (1600 mg) needed to bind maximally. The highest removal efficiency (%) of Acid Orange 7 dye achieved was calculated as $100 \pm 0.1\%$.

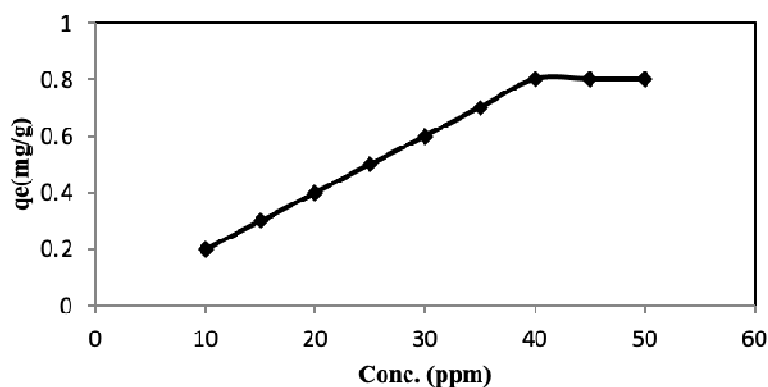
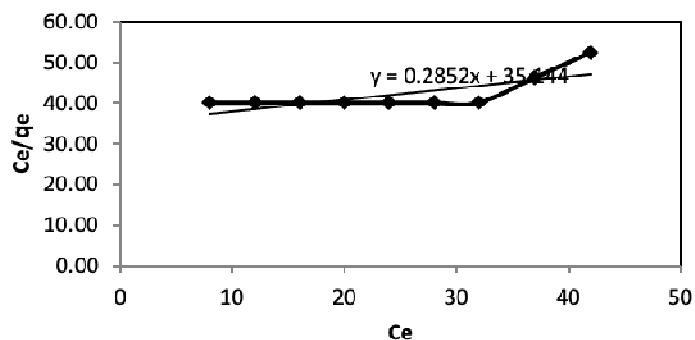


Fig. 1.6 Amount adsorbed q_e as a function of the initial concentrations of dye in solution

The amount of Acid Orange 7 dye adsorbed per unit mass of the polymer (i.e., adsorption capacity) increases with increasing the initial concentration of Acid Orange 7 dye. The maximum adsorption, which represents saturation of active points on the polymer by Acid Orange 7 dye, was 40 mg Acid Orange 7 per g of polymer.

To verify whether system followed by Langmuir-Hinshelwood mechanism, kinetic experiments were carried out with different initial concentrations of the Acid Orange 7 as shown as,



A plot of C_e/q_e versus C_e is linear shows the confirmation of Langmuir adsorption mechanism. The values of K^2 and q_m determined from the slope and the intercept of linear plot are 3.51 L/mg and 35.14 mg of Acid Orange 7 /g of polymer respectively.

Conclusion

Mercury(II), a particularly harmful pollutant that can destroy a person's metabolism, central nervous system, and immune system, poses a particular threat to biological systems. Therefore, it is essential to employ cutting-edge methods for developing efficient, cost-effective, and environmentally acceptable materials for the selective detection and removal of Hg^{2+} . The capacity of polyaminothiophenol to separate Hg^{2+} ions and dye in aqueous solutions has been produced and studied.

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