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## Synthesis of Polyaminothiophenol Mercury(II) complex and their application in removal of dye from aqueous solutions

Dr. Mangala R. Pal ( Dr. Prachi R. Bonde)

10, Arti apartment Chakradhar Nagar, Nagpur

### Abstract

One of the main issues in worldwide public health is the contamination of the environment by heavy metal ions and severe sickness. Biological systems are particularly at risk from mercury (II), a particularly toxic contaminant that can damage a person's metabolism, central nervous system, and immune system. In order to provide effective, economical, and ecologically acceptable products for the selective removal of dye, it is crucial to use cutting-edge techniques. It has been synthesised and investigated if polyaminothiophenol can serve as a separation dye in aqueous settings.

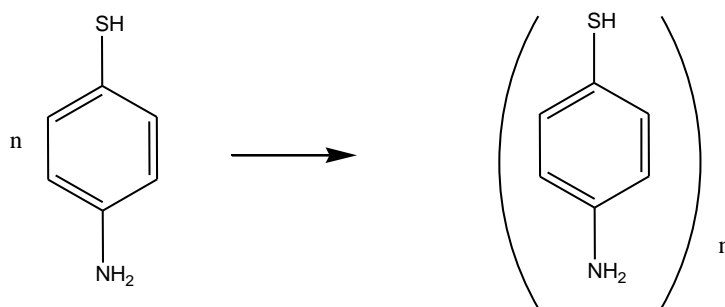
### Introduction

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<sub>3</sub>) present in fuming sulfuric acid [1-5].

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<sub>2</sub> group of OAP, yielding two types of heteroaminic structures. While chemical oxidation of OAP yields the formation of 2-aminophenoxazine (APZ) [6-8], redox reactions involving the structure (phenoxazine units) have been proposed for electrochemically prepared POAP films [9-12].

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 sulfahydril 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 °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 sulfahydril H<sup>+</sup> 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 Structure of Polyaminothiophenol**

## Material and Methods

### Synthesis

For the synthesis of polyaminothiophenol, the chemicals with their source, molecular weight and purity are listed in Table 2. The monomer aminothiophenol and other chemicals have been used as received (AR) grade. The detail of chemical used as

**Table 2 shows chemicals, molecular weight and chemical formula**

Chemicals	Molecular weight	Source	Chemical formula	Purity %
Aminothiophenol	125.19	EMerck, India	C <sub>6</sub> H <sub>7</sub> NS	97.0%
Hydrochloric acid	36.5	S.D.fine Chem. Ltd.	HCl	98.0%
Ammonium per sulfate	228.2	S. D. fine Chem. Ltd.	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	99.0%

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 °C. After complete addition of the oxidizing agent, the reaction mixture was kept under constant stirring for 24 hours at 0-4 °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°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°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°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**

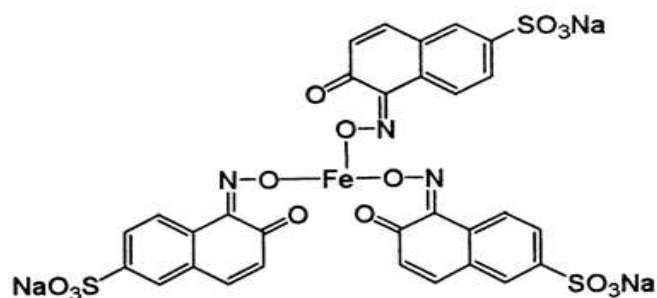
The material prepared and characterized by the various methods are used for the environmental applications.

### **Dye Removal**

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 Green 1 onto polymer from their aqueous solutions have been investigated. 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.

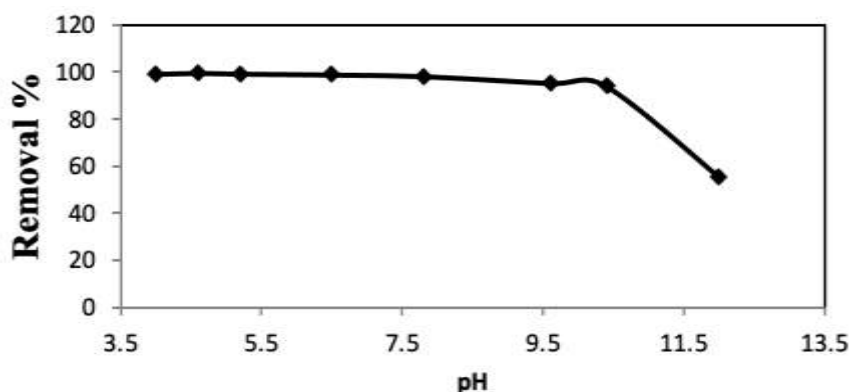
Acid Green 1 is manufactured by nitrosation of 6-hydroxy-naphthalene-2-sulfonic acid and transferred to iron sodium salt. It has excellent absorption and excellent light fastness in a saturated salt solution. It has good solubility and stability. It is used mainly in solar salt industry wool, silk, and nylon fabric dyeing, printing and in leather dyeing. It is used in

histology to stain collagen. For industry purpose, Naphthol green B, used for staining wool, nylon, paper, anoxidised aluminium and soap. Its molecular formula is  $C_{30}H_{15}FeN_3Na_3O_{15}S_3$  and its chemical structure is given below,



**Fig. 1 The chemical structure of Acid green 1**

The pH of dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity.



**Fig. 2 The effect of pH on Acid Green 1 adsorption by the polymer powder**

The data shown in fig. 2 shows that the adsorption is higher below pH 8 than its above where the adsorption is dropped. In acidic conditions the surface of the adsorbent is positively charged due to the high concentration of  $H^+$ , so the electrostatic attraction between the adsorbent and adsorbate (Acid Green 1) which is anionic dye is enhanced.

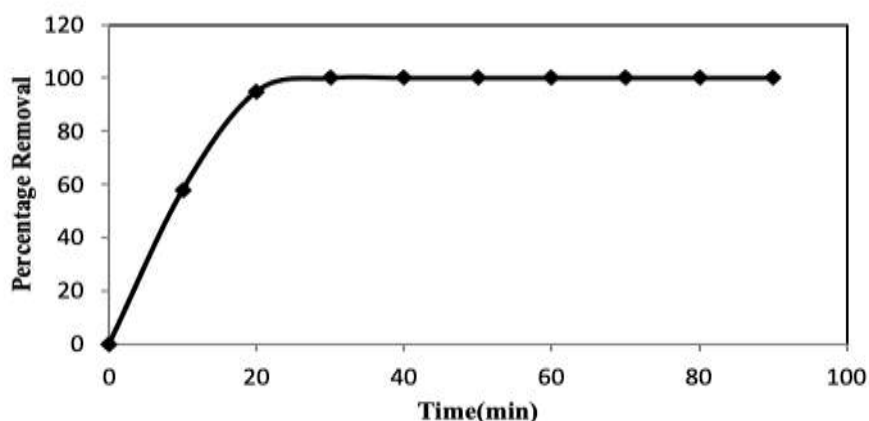
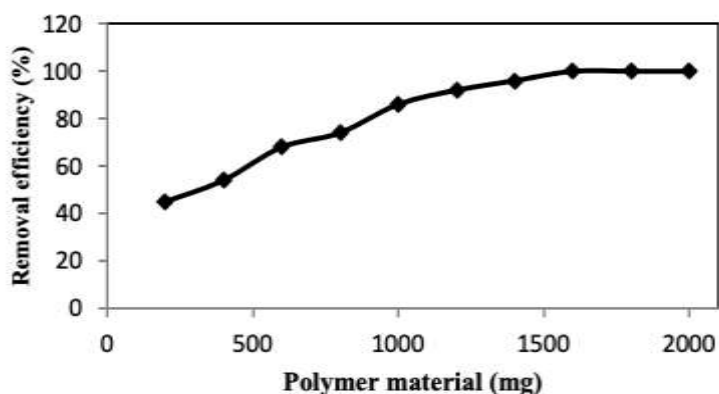


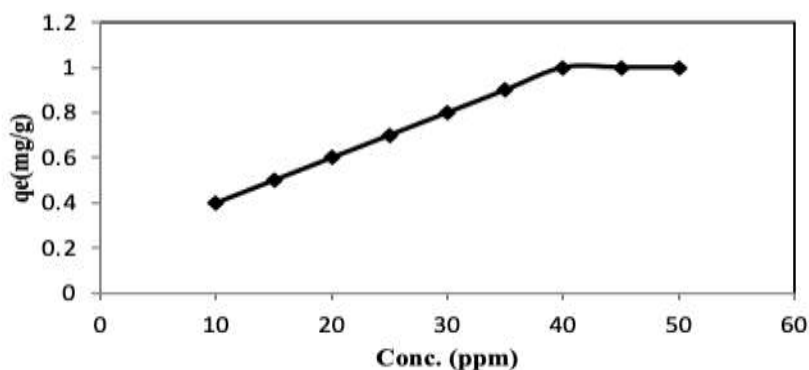
Figure 3 shows the time dependence of the adsorption capacities of Acid Green 1 on the polymer powder as a function of time. Acid Green 1 adsorption increases with time during the first 30 min, after which it levels off (Fig. 3), exhibiting fast kinetics for binding the Acid Green 1 dye. Good removal 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 dye. The dependence of dye sorption on polymer material 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 (40 mg/L) and stirring speed (200 rpm) remained constant.



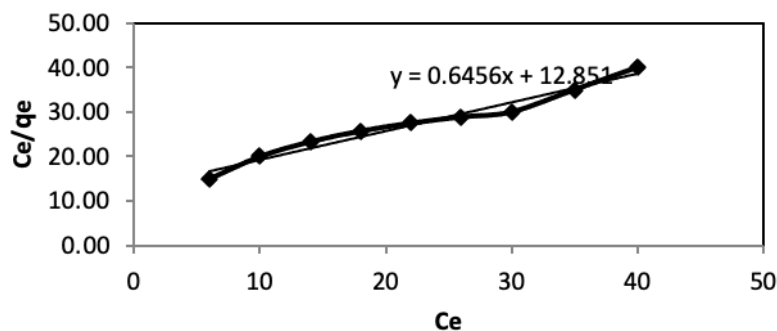
**Fig. 4** Polymer material (mg) dosages

The percentage of Acid Green 1 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. 4. This marked the optimum quantity of the polymer powder (1600 mg) needed to bind maximally. The highest removal efficiency (%) of Acid Green 1 dye achieved was calculated as  $100 \pm 0.1\%$ .



**Fig. 5** Amount adsorbed  $q_e$  as a function of the initial concentrations of dye in solution

The amount of Acid Green 1 dye adsorbed per unit mass of the polymer (i.e., adsorption capacity) increases with increasing the initial concentration of Acid Green 1 dye. The maximum adsorption, which represents saturation of active points on the polymer by Acid Green 1 dye, was 40 mg Acid Green 1 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 Green 1 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 1.55 L/mg and 12.85 mg of Acid Green 1 /g of polymer respectively.

## Conclusion

We can draw the conclusion that polyamionthiophenol can be made chemically and will be an excellent material for removing dye from aqueous solutions. More research is needed to fully understand the chemistry of the substance developed for this study because of its amazing capabilities. More prospectuses for the polyamionthiophenol's use in catalysis, photocatalysis, and metal ion removal processes are available.

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