



Synthesis of Polyaminothiophenol complex and their application in removal of dye from aqueous solutions

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Abstract

Severe illness and heavy metal ion poisoning of the environment rank as one of the major problems in global public health. 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 to produce efficient, cost-effective, and environmentally friendly materials for the selective removal of dye. The ability of the polyaminothiophenol to function as a separation dye in aqueous conditions has been synthesised and studied.

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 (SO₃) 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 -NH₂ 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 sulfahydryl 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 sulfahydryl 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.

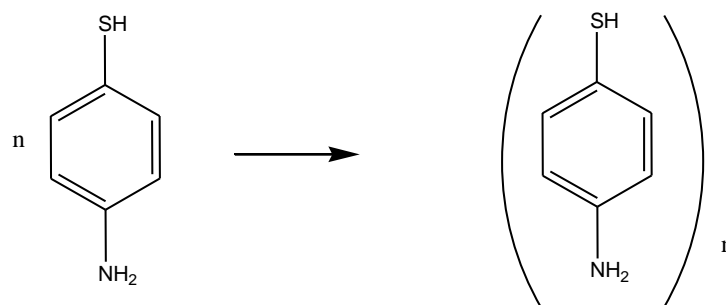


Fig. 1 Structure of Polyaminothiophenol

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 ₆ H ₇ 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 ₄) ₂ S ₂ O ₈	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 Blue 74 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 Blue 74 is purple powder having chemical name 5, 5' Indigodisulfonic acid disodium salt. It is a food additive that is widely used in market. It is also used as a dye for cationic cotton fabrics. It is sensitive to light and very sensitive to oxidizing agents. Its molecular formula and structure is given as below,

Molecular Formula: $C_{16}H_8N_2Na_2O_8S_2$

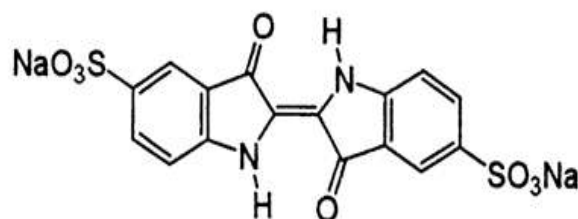


Fig. 3 Chemical structure of Acid blue 74

The pH of dye solution plays an important role in the whole adsorptions process and particularly on the adsorption capacity. The effect of pH on Acid Blue 74 adsorption by the polymer powder is shown in Fig. 4

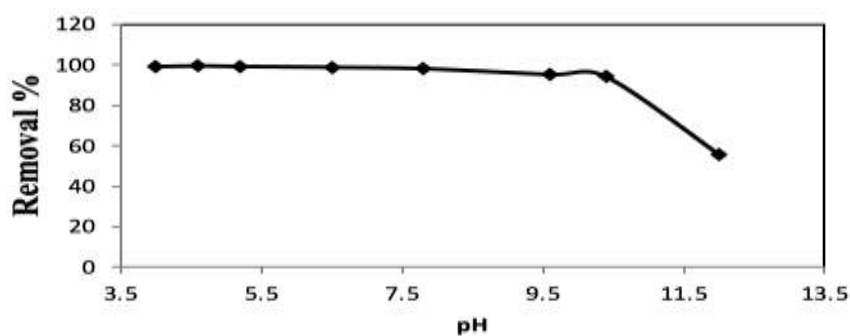
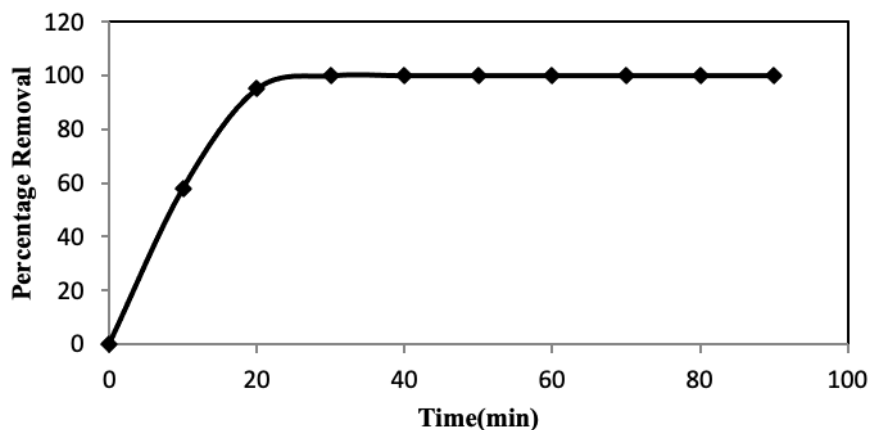


Fig. 4 The effect of pH on Acid Blue 74 adsorption by the polymer powder.

The data shown in fig. 4 shows that the adsorption is higher below pH 8 than it's 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 Blue 74) which is anionic dye is enhanced.

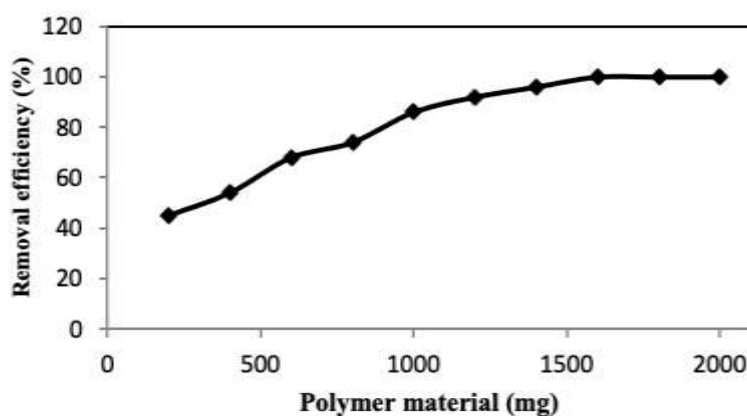


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Figure 5 shows the time dependence of the adsorption capacities of Acid Blue 74 ions on the polymer powder as a function of time. Acid Blue 74 adsorption increases with time during the first 30 min, after which it levels off (Fig. 5), exhibiting fast kinetics for binding the Acid Blue 74 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 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 Blue 74 (40 mg/L) and stirring speed (200 rpm) remained constant.



The percentage of Acid Blue 74 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. 6. This marked the optimum quantity of the polymer powder (1600 mg) needed to bind maximally. The highest removal efficiency (%) of Acid Blue 74 dye achieved was calculated as $100 \pm 0.1\%$.

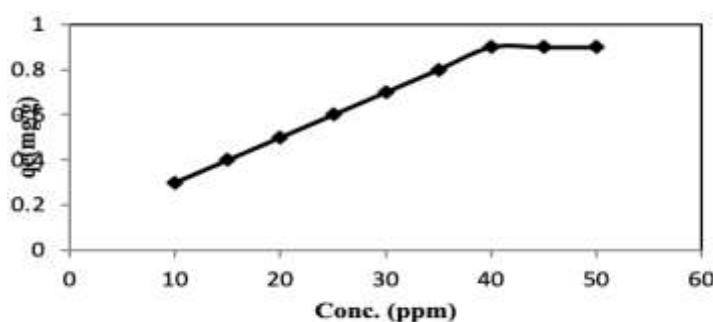
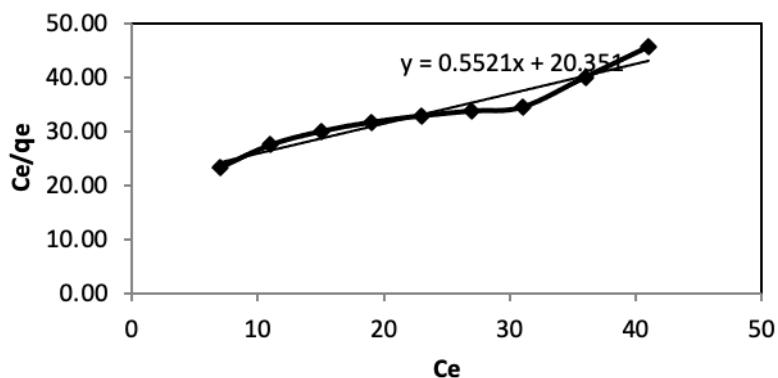


Fig. 7 Amount adsorbed q_e as a function of the initial concentrations of dye in solution

The amount of Acid Blue 74 dye adsorbed per unit mass of the polymer (i.e., adsorption capacity) increases with increasing the initial concentration of Acid Blue 74 dye. The maximum adsorption,



which represents saturation of active points on the polymer by Acid Blue 74 dye, was 40 mg Acid Blue 74 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 Blue 74 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 1.81 L/mg and 20.35 mg of Acid Blue 74/g of polymer respectively.

Conclusion

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. Therefore, it is crucial to use cutting-edge techniques to create effective, economical, and environmentally sound products for colour removal. Polyaminothio-phenol has been created and tested for its ability to remove dye from aqueous solutions.

References

- [1]. J. Yue, A. J. Epstein, J. Am. Chem. Soc., **1990**, 7, 2801.
- [2]. J. Yue, A. J. Epstein, A. G. Mac Diarmid, J. Mol. Cryst. Liq. Cryst., **1990**, 189, 261.
- [3]. J. Yue, Z. H. Wang, K. R. Cromack, A. J. Epstein, A. G. Mac Diarmid, J. Am. Chem. Soc., **1991**, 113, 2671.
- [4]. J. Yue, A. J. Epstein, Z. Zhong, P. K. Gallagher, A. G. Mac diarmid, Synth. Met., **1991**, 41, 768.
- [5]. J. Yue, A. J. Epstein, J. Chem. Soc., Chem. Commun., **1992**, 21, 1542.



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- [6]. T. Nogami, T. Hishida, M. Yamada, H. Mikawa, Y. Shirota, *J. Chem. Soc.*, **1975**, 48, 3714.
- [7]. V. Balogh, M. Fétizon, M. Golfier, *J. Org. Chem.*, **1971**, 36, 1341.
- [8]. R. G. Srivastava, R. L. Pandeyo, P. S. Venkataramani, *Indian J. Chem.*, **1981**, 20, 995.
- [9]. C. Barbero, J. J. Silber, L. Sereno, *J. Electroanal. Chem.*, **1989**, 263, 352.
- [10]. A. Q. Zhang, C. Q. Cui, Y. Z. Chen, J. Y. Lee, *J. Electroanal. Chem.*, **1994**, 373, 121.
- [11]. R. I. Tucceri, C. Barbero, J. J. Silber, L. Sereno, D. Posadas, *Electrochimic. Acta.*, **1997**, 42, 927.
- [12]. R. M. Torresi, S. I. C. de Torresi, C. Gabrielli, M. Keddami, H. Takenouti, *Synth. Met.*, **1993**, 61, 296.