

REMOVAL OF HEAVY METAL IONS USING LOW COST ADSORBENTS

R. SUBITHA (Research Scholar)

(Reg No: 18213162032014)

Dr. G.S. PRABHA LITTIS MALAR* (Assistant professor)

Department of Chemistry & Research Centre, Scott Christian College (Autonomous)

Nagercoil- Tamil Nadu, India. 629003

Affiliated to Manonmaniam Sundaranar University, Abhishekapatti, Tirunelveli-627012

Tamil Nadu, India.

Email ID: rsubitha7@gmail.com

ABSTRACT - Due to increase in the world population and development of industrial applications, environmental pollution problem became important. Communities produce both liquid and solid wastes. The liquid waste-water is essentially the water supply of the community after it has been used in a variety of applications. In recent years, heavy metal concentrations have increased to reach dangerous levels for living environment in many regions. They can be toxic or carcinogenic in nature. Due to its low cost, availability and eco-friendly nature the adsorption process is used for the removal of heavy metal ions. Among various conducting polymers, polythiophene-silica based adsorbent plays a major role for removal of various heavy metal ions due to its ease of synthesis, biocompatibility and redox properties. In the present work, polythiophene-silica nanocomposites have synthesized in the presence of Sodium dodecyl sulfate as surfactants and ferric chloride as oxidant. The synthesized nanocomposites were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) Fourier transform-infrared spectroscopy (FT-IR), X-ray diffraction pattern (XRD), Energy dispersive x-ray spectroscopy (EDX). The synthesized nanocomposite adsorbents were applied as an efficient sorbent for Cr (VI), Zn (II), Cu (II) ion removal from contaminated water.

KEYWORDS: heavymetals· nanocomposites· silica· thiophene· adsorbent

Introduction

Currently, water pollution caused by heavy metal ions is a major cause of environmental problem threatening the creatures. Heavy metals ions are discharged into water system from various industrial activities such as mining, metal plating, tanneries, batteries, fertilizers, pesticides and paper industry [1]. Heavy metals such as arsenic, copper, zinc, nickel, cadmium, chromium, mercury, lead which are usually associated with toxicity. As trace elements, some metals are essential to maintain the metabolism of the human body. However at higher concentration they can lead to poisoning [2]. Ion exchange, electrochemical treatment, reverse osmosis, solvent extraction and adsorption are the many techniques used for removing heavy metal ions from aqueous solutions [3,4]. Plant materials are mainly comprised of cellulose materials that can absorb heavy metal cations in aqueous solution. Rice husk is a waste biomass source. Silica is the key component of rice husk [5]. Silica is an inert support material with a high surface area and amorphous form of silica have largest industrial applications compared to other types of silica [6,7]. In recent years, conducting polymers have become an important areas of research in polymer science and engineering because of their excellent electroactive behaviour [8]. Conducting polymers with large π -conjugated structure have received much attention due to their applications in design flexibility, environmental stability and chemical inertness, tunable conductivity, electrical devices and facile preparation [9]. Polyaniline polythiophene, polyindole, polypyrrole and their substituted derivatives have received a great attention because of their good electrical properties, environmental stability, and ease of synthesis [10]. In recent years, developments of inorganic-organic composite materials on nanometer scale have been receiving significant attention due to a wide range of potential applications and high absorption in the visible part of the spectrum and high mobility of the charge carriers [11]. Synthesis of nanocomposites using conjugated polymers with metals had drawn much the attention nowadays due to their thermal and electrical properties [12]. Polythiophene and its derivatives, have attracted considerable attention because for their easy polymerization and excellent environmental and thermal stability, higher conductivity and photoconduction [13]. Polythiophene are one of the most valuable types of conducting polymers, which may be easily modified to afford a variety of useful electrical and physical properties, such as solubility, electrical conductivity, mobility [14]. Nanosilica has been studied for preparation of polymer-

silica composites due to its low cost, high surface area and easy dispersion[15,16].The chemical oxidative polymerization of polythiophene-silica can be prepared in aqueous media by using ferric chloride as oxidant and sodium dodecyl sulphate as surfactant. Surfactants are used in chemical polymerization to control the size and shape of conducting polymers. Adsorption is the most effective techniques for the removal of heavy metal ions[17,18]. Due to flexibility and simplicity of design, initial cost, ease of operation and insensitivity to toxic pollutants adsorption found to be superior. Adsorption does not result in the formation of harmful substances [19,20]. The pH of the solution, adsorbent dosage, contact time, initial concentration of heavy metal ions are the main factors affecting the adsorption of heavy metal ions[21,22].In the present work, we prepared an organic-inorganic composite material containing polythiophene as the organic component and silica nano powders as the inorganic component. Polythiophene-Silica composites were prepared by the in situ chemical oxidative polymerization method were characterized by Fourier transform infrared (FTIR), scanning electron microscopy (SEM), Energy dispersive x-ray spectroscopy(EDX), X-ray diffraction (XRD) and transmission electron microscopy (TEM).

2 Experimental methods

2.1 Materials

Thiophene monomer, Ferric chloride and sodium dodecyl sulphate, ethanol, sodium hydroxide. All of them were supplied by Sigma Aldrich as well.

2.2 Preparation of silica nanoparticles

The rice husk samples were washed thoroughly with distilled water and dried for nearly 20 hours to ensure that the rice husk is devoid of soil ,dust, and rice grains particles. Then, the cleaned rice husks were burned for 2 hours at 600⁰C to get ash. A sample of 10 g rice husk ash was stirred in NaOH solution. The solution was heated in a covered beaker for 4h by stirring constantly and allowed to settle down for a day and the solution was filtered. To the filtrate dil.hydrochloric acid was added under constant stirring at controlled conditions until it reached pH 2 and then buffer solution was added up to pH 8.5 for ascertaining purity and allowed to stand at room temperature for 3h. The precipitate was washed for several times with deionised water and dried in hot air oven at 100⁰C for 16 hours to obtain pure silica.

2.3 Preparation of Polythiophene-silica nanocomposites

Polythiophene-silica nanocomposites were synthesized by the chemical oxidative polymerization of thiophene in an aqueous solution containing silica nanoparticles using ferric chloride as the oxidising agent. A quantitative amount of silica nanoparticles were mixed with sodium dodecyl sulphate in distilled water and ultrasonicated for 10 minutes followed by dispersion with thiophene (0.1M) and again ultrasonicated for a period of 20 minutes. After that FeCl₃ was gradually added into the stirred polythiophene-silica solution with constant stirring.The polymerization was carried out at room temperature for 5 hours with constant stirring at room temperature.The resulting solution was kept for one day below room temperature, for the completion of polymerization.The product was filtered off and washed with water and ethanol several times and finally dried under vacuum at room temperature for one day to obtain brown powder of Polythiophene-silica nanocomposites.

2.4 Adsorption studies

Polythiophene-silica nanocomposites have been used as a adsorbent for removal of heavy metal ions. The adsorption behaviour of the adsorbent samples was studied by evaluating the percentage removal of the metal ions from the solution using the following equation

$$removal\ efficiency\ (\%) = \frac{C_i - C_e}{C_i} \times 100$$

Where

C_i - initial concentration of the metal ion in the solution

C_e - concentration of the metal ion

3 Characterization techniques

3.1 FT-IR analysis

In FT-IR spectrum of polythiophene-silica nanocomposites, the absorption peaks at 3424.12cm⁻¹ described the OH stretching vibration.The band at 2921.37 cm⁻¹ and 2852.39 cm⁻¹ depict C-H stretching vibration. The IR band at 1635.21cm⁻¹ is due to C=C asymmetric stretching vibration of thiophene ring. Peaks around 1466.67cm⁻¹ confined the presence of C=C symmetric stretching vibration stretching mode of thiophene ring. C-H bending

vibration in 1215.23 cm^{-1} . The absorption band 1101.03 cm^{-1} is due to asymmetric stretching vibration of Si-O-Si molecule. Bend at 970.94 cm^{-1} ascribed due to Si-OH bonds. The absorption bands at 804.96 cm^{-1} is due to Si-O symmetric stretching vibration. The peak at 787.65 cm^{-1} shows C-H out-of-plane of 2,5-substituted thiophene ring created by the polymerization of thiophene monomer. Broad peak at 468.65 cm^{-1} corresponds to symmetric stretching vibration of Si-O.

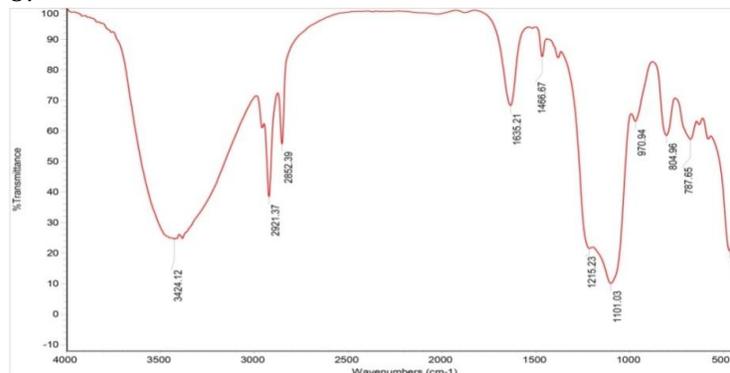


Fig.1 FT-IR spectrum of Polythiophene- silica nanocomposites

3.3 Energy dispersive x-ray spectroscopy (EDX)

Elemental analysis of polythiophene-silica nanocomposites shown in fig: 4. The EDX analysis of polythiophene-silica nanocomposites predict the deposition of the main constituent elements such as C, S, O and Si. EDX graph directly indicate the occurrence of silica and thiophene in the composites. The occurrence of silica and oxygen in polythiophene-silica nanocomposites indicates that silica nanoparticles was integrated in thiophene. Thiophene, silica and oxygen are the main constituent elements of the polythiophene-silica nanocomposites.

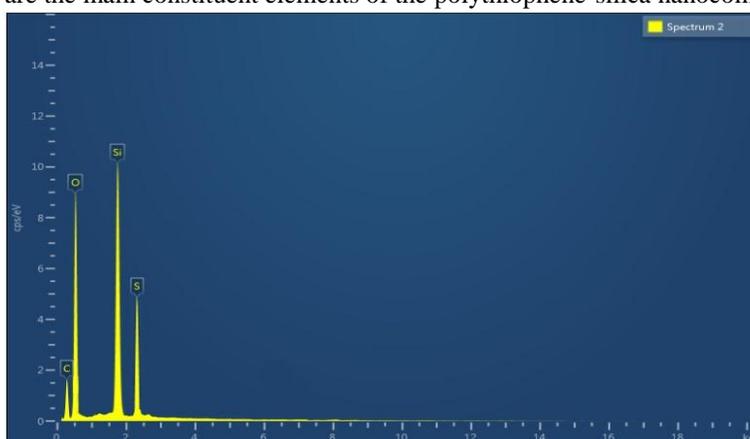


Fig.3 EDX image of Polythiophene-silica nanocomposite

3.4 Scanning electron microscope (SEM)

Morphological character of polythiophene and polythiophene-silica nanocomposites was characterized by SEM. SEM image (fig.4) of polythiophene-silica nanocomposites showed the incorporation of spherical shaped silica particles into the polythiophene polymer matrix. The SEM confirms that the polymer nanoparticles are deposited on the inorganic particles. To improve the strength and functionality, the silica nanoparticles are coated with the polymer.

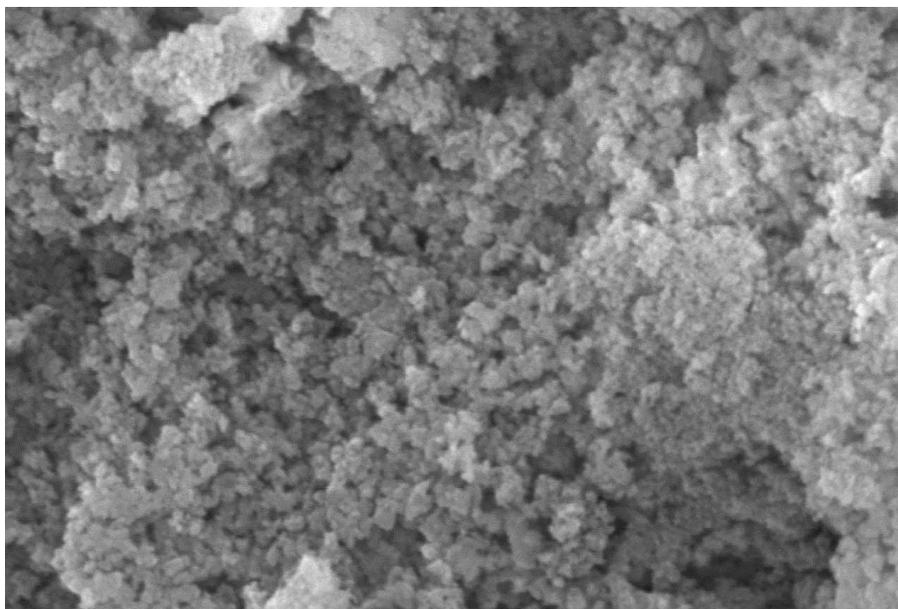


Fig.4 SEM image of Polythiophene- silica nanocomposites

3.5 Transmission electron microscopy(TEM)

TEM images (fig.5) of polythiophene-silica nanocomposites show spherical morphology with an average diameter of about 50nm. There will be a strong intermolecular interaction between the polythiophene and silica nanoparticles. TEM image clearly shows uniform size and homogeneous distribution of polythiophene-silica nanocomposites in(fig.5).

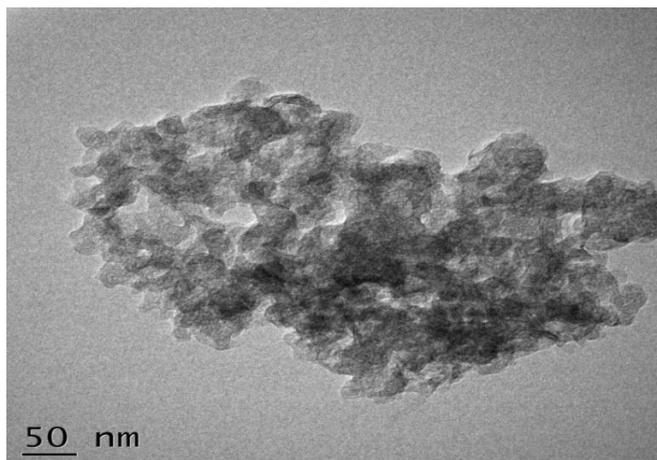


Fig. 5 TEM images of Polythiophene-silica nanocomposites

4 Adsorption studies

When a solid surface is exposed to a gas or a liquid, molecules from the gas or the solution phase accumulate or concentrate at the surface. The phenomenon of concentration of molecules of a gas or liquid at a solid surface is called adsorption. The substance that deposits at the surface is called adsorbate and the solid on whose surface the deposition occurs is called the adsorbent. There are many factors affecting the adsorption of heavy metal ions. These factors include the pH of solution, adsorbent dosage, contact time and concentration of initial heavy metal ions.

4.1Effect of contact time

The effect of contact time on the adsorption process was studied by varying the constant time and keeping the other factors constant.

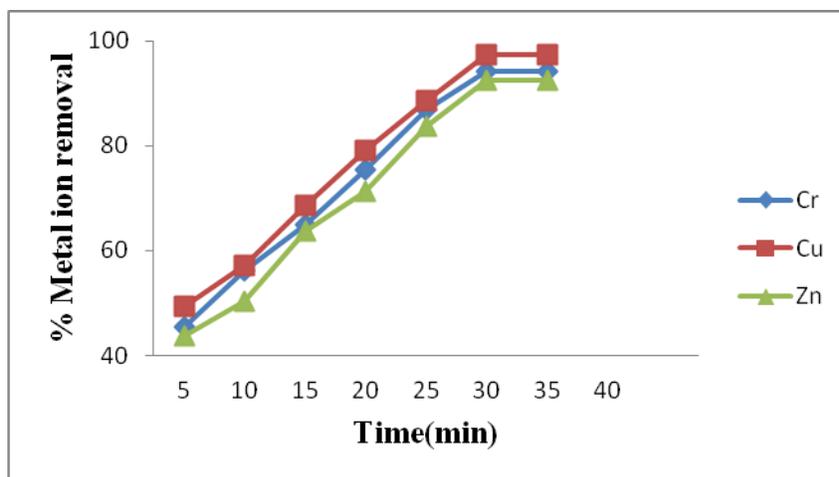


Fig. 6 Effect of contact time

The percentage uptake were increases with certain time and it reaches a constant value after sometime is shown in the fig(6).The amount of metal ions being adsorbed by the adsorbent was in a state of dynamic equilibrium with the amount of metal ions desorbed from the adsorbent.The amount of metal ion adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent capacity of the adsorbent under these particular conditions.The result showed that the adsorption of metal ion increases with time upto 30 minutes and then it becomes almost constant at the end of the experiment.

4.2 Effect of adsorbent dosage variation

Effect of the adsorbent dosage variation on the adsorption process was studied by varying the adsorbent weight.

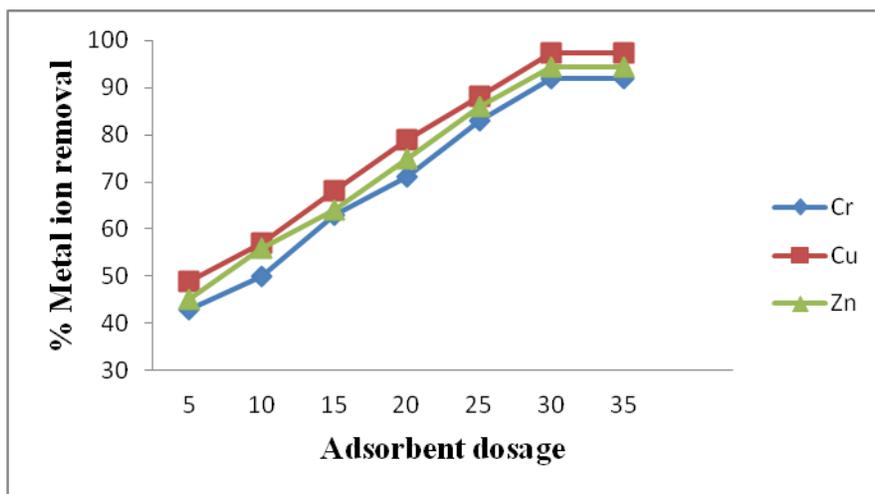


Fig. 7 Effect of adsorbent dosage variation

The effect of adsorbent dosage on metal adsorption is shown in fig(7). The adsorption of metal ions increased with the adsorbent dosage.The percentage of metal removal increased with the increasing amount of biomass.This may be attributed to the availability of more and more binding sites for complexation of metal ions.

4.3 Effect of varying concentration of metal ions

Effect of concentration variation on the percentage removal of heavy metal ions were studied by varying the amount of metal ion concentration and keeping the other factors constant.

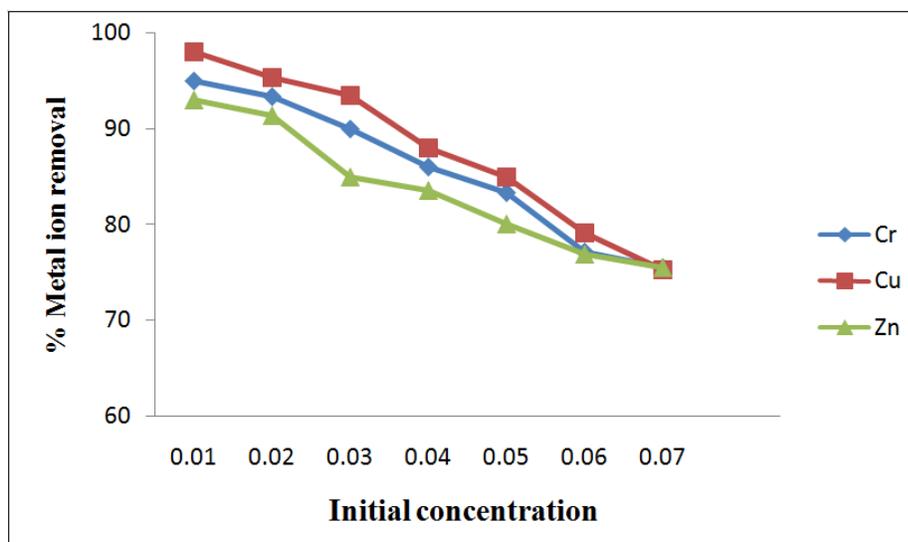


Fig. 8 Effect of varying concentration of metal ions

Effect of concentration variation studied by varies the amount of metal ion concentration. The amount of metal ion concentration were increase with decrease in the amount of adsorption shown in fig(8). In lower metal ion concentration the percentage uptake was higher due to large surface area oof adsorbent being available for adsorption. At higher concentration the percentage removal decreased because the available sites for adsorption became less due to saturation of adsorption sites.

4.4 Effect of pH

The effect of pH can be studied by varying pH of the medium and keeping the other factors constant.

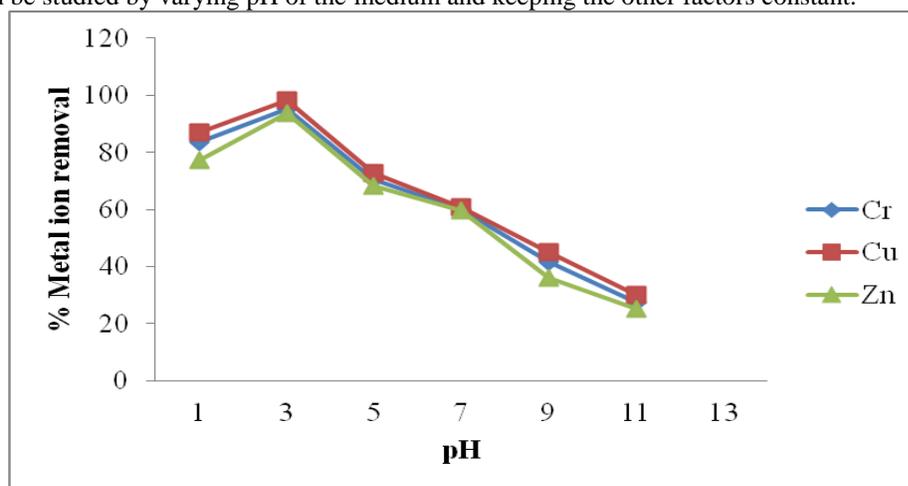


Fig. 9 Effect of pH

The pH of the solution shows increasing with decreasing in fig (9). The pH of the solution affects the charge on the surface of the adsorbents. So the change in pH also affects the adsorption process and the H⁺ ion concentration may react with the functional groups on the active sites on the adsorption surface. The maximum value was reached at an equilibrium pH of around 3.

Conclusion

In this study, the FT-IR spectra of polythiophene-silica nanocomposites signify the occurrence of silica particles in the polymer nanocomposite. From SEM-EDX images and XRD studies confirms a mixed like morphology in the case of silica bring in polymer nanocomposites. Polythiophene-silica nanocomposites prepared using this inexpensive waste substrate can be used as a new type of adsorbent for advance preparation of adsorbent with polymeric matrices. Polythiophene-silica have been widely used for the preparation of effective nanoadsorbents for the removal of heavy metal ions from water. It is inexpensive, highly effective nanoadsorbents based on

conducting polymers. Polythiophene-silica shows better efficiency for the removal of heavy metal ions such as Copper (Cu), Chromium (Cr) and Zinc(Zn).

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Compliance with ethical standards**Conflict of interest**

The authors declare that they have no competing interests

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