



Removal of cadmium ions from wastewater by dithiocarbamate functionalized pyrrole based terpolymers



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ABSTRACT

This study reports the synthesis of a new series of polydithiocarbamates via polycondensation of pyrrole, alkyldiamines and paraformaldehyde followed by functionalization with carbon disulfide. The polymers were characterized by elemental analyzer, ^{13}C NMR, FTIR, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and powder X-ray diffraction (XRD). The polymers were tested for the removal of cadmium ions from aqueous solutions and spiked wastewater samples. The adsorption experiments revealed the superior efficiency of the synthesized polymers in the removal of cadmium ions from aqueous solutions ($Q_m = 14.18$ mg/L). Experimental results showed that the data fits Ho second-order kinetic model with $R^2 > 0.99$, which assumes chemical adsorption. The data showed fitness to Freundlich and Langmuir isotherm models with $R^2 \sim 0.999$. PYEDCS2 cross-linked polymer showed superiority among the synthesized polymers and showed high efficiency with a removal of $\sim 99.7\%$ of Cd^{2+} ions and proven to be a potential adsorbent for treatment of wastewater.

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1. Introduction

It is common knowledge that water is essential to living organisms. Hence, any kind of contamination of water resources would rise health risks to humans and other living systems. One of the main contaminants to water resources is heavy metals [1,2]. Heavy metals are persistent contaminants which are well-known for their non-biodegradable behaviour, bioaccumulation even at trace levels [3–5]. For that reason it is crucial to remove these types of pollutants prior to the release of wastewater from industrial process [6].

Cadmium is a heavy metal which is frequently used in industrial processes, including: nickel-cadmium batteries, anticorrosive agents and pigments. Albeit cadmium containing products can be recycled for industrial applications, and most cadmium pollution incidents arise from incineration and dumping of cadmium waste [7]. In the recent years, cadmium has attracted high attention due to its toxicity behaviour which may lead into various diseases such as bone damage, acute respiratory distress syndromes (ARDS) and kidney damage [8,9].

Various methods have been implemented in heavy metal removal from wastewater; these methods include precipitation, flocculation, separation using membranes and ion exchange

[10,11]. Among the conventional methods of wastewater treatment is adsorption; till now it is considered to be the best method for heavy metal removal due to the efficiency of this method and being cost-friendly [12,13].

The designing process of an efficient adsorbent material is an important criteria for heavy metal removal from wastewater. Hence, many types of materials have been studied for their efficacy in wastewater treatment such as zeolites, biomaterials and activated carbon [14–16]. On the other hand, polymeric materials have shown good performance and remain as one most relevant method for designing adsorbent materials [17]. The adsorption performance is directly proportional to the functionality of the adsorbent. It has been shown that sulfides [18,19] and other adsorbents containing sulfur moieties such as mercaptobenzothiazoles [20], dithiocarbamates, thiols [21], benzoylthiourea [22], show an excellent performance in the wastewater treatment due to the strong covalent bond which is formed between sulfur and the heavy metal.

For the past few decades, many organic polymers containing sulfur moieties, dithiocarbamate (DTC) moiety are one example of such polymers. Recently, surface modification with DTCs on natural or synthetic composites along with nanoparticles got the attention of researchers for the application in wastewater treatment [23–25]. Several research groups reported the modification of organic polymers with dithiocarbamate functionality. Usually, these polymers are modified through the conversion of a present

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primary or secondary amine functionality of the polymer to dithiocarbamate functionality using carbon disulfide [26,27]. A typical example of the synthesis of dithiocarbamate-modified polymers (DTCP) was reported by production of DTCP by Liu et al. In the reported work, triethylenetetramine was grafted on a co-polymer of dimethyldiallylammonium chloride and acrylamide where the amine moieties were changed into DTC groups [23]. In most cases, the DTCP's could be separated from the reaction mixture of such conversions through precipitation step using acetone [28].

This study reports the synthesis and characterization of a new series of pyrrole based dithiocarbamate functionalized polymers, the synthesis of a new polymeric series was prepared by the polycondensation reaction between pyrrole, various alkyldiamines and paraformaldehyde which is used as a linker in the Mannich-type protocol [29]. The amine functionalities are then converted into dithiocarbamate by carbon disulfide. The new and efficient modified DTCP's were tested for their efficacy in the removal of cadmium ions from aqueous solutions and wastewater samples.

2. Experimental

2.1. Materials and methods

Pyrrole (PY), 1,2-Diaminoethane (ED), 1,4-Diaminobutane (BD), 1,8-Diamineoctane (OD), 1,10-Diaminododecane (DD), paraformaldehyde, heptane, carbon disulfide (CS₂), potassium hydroxide, acetone, dimethylformamide (DMF) were used as received without purification. Solvents and other chemicals used were of analytical grade. Elemental analysis was done using a Perkin-Elmer Elemental Analyzer series II Model 2400. FT-IR spectra recorded on a Perkin Elmer 16F PC FTIR spectrometer. Solid-state ¹³C NMR spectra were taken using Bruker WB-400 spectrometer with a spinning rate of 10 kHz. Thermogravimetric analysis (TGA) was performed using a thermal analyzer (STA 429) by Netzsch (Germany). Powder X-ray Diffraction pattern for crystal nature was recorded using Rigaku Miniflex II Desktop X-ray Diffractometer from Theta = 5–50. Concentration of metal ions before and after adsorption were measured by inductively coupled plasma (ICP-MS).

2.2. Synthesis of pyrrole based cross-linked polyamines

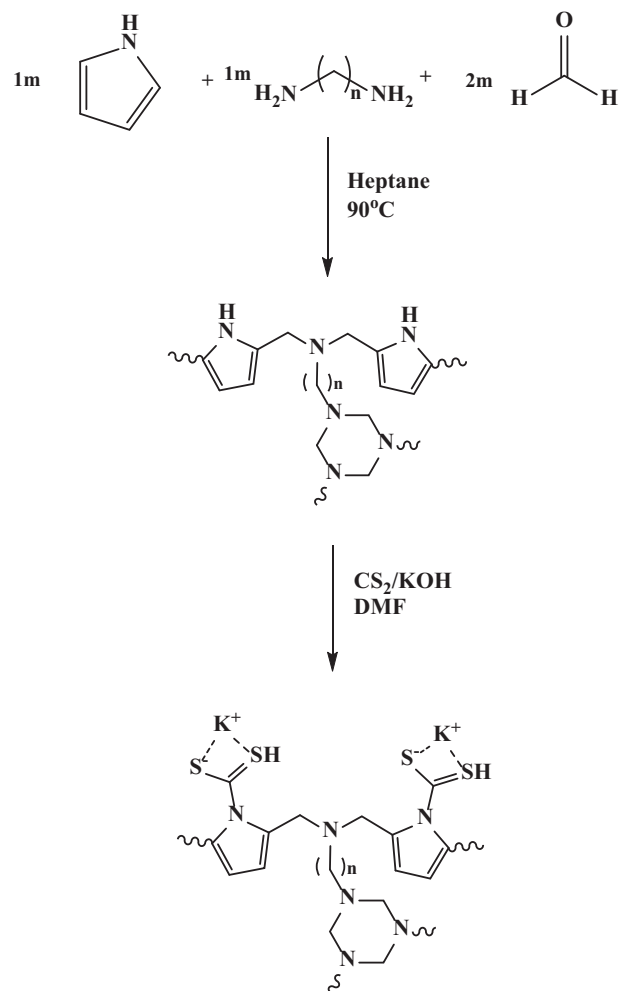
A mixture of pyrrole (0.01 mol), an alkyldiamine (0.01 mol) and paraformaldehyde (0.02 mol) in heptane (20 ml) was stirred at 90 °C for 24 h in a closed round bottom flask (50 ml). The resinous materials were washed with water and acetone several times in order to remove any unreacted material and dried under vacuum at 60 °C until a constant weight is achieved (Scheme 1) (Table 1).

2.3. Dithiocarbamate modified cross-linked polymers

The cross-linked polyamine (0.01 mol), carbon disulfide (0.06 mol) and potassium hydroxide (0.06 mol) in 8 ml of DMF were mixed at room temperature for 72 h. The orange resinous cross-linked dithiocarbamate polymers (DTCP's) were precipitated from the reaction mixture using acetone, and washed with acetone and ethanol several times then dried under vacuum at 60 °C to obtain a solid orange powder. Scheme 1 shows the modification process on the cross-linked polyamines.

2.4. Adsorption experiments

An adsorption set of experiments was conducted using the technique of batch equilibrium in polyethylene vials (50 ml capacity). A mixture of 30 mg of the modified dithiocarbamate polymers immersed in an aqueous solution (20 ml) of Cd²⁺ ions with concen-



Scheme 1. Synthesis of dithiocarbamate pyrrole based cross-linked polymers.

Table 1
Synthesis results of pyrrole based cross-linked polyamines.

Polymer ^a	Yield ^b (%)	Elemental analysis (%)		
		C	H	N
PY-ED	64	58.21	8.15	24.49
PY-BD	67	60.94	9.11	20.15
PY-OD	82	69.11	10.72	16.07
PY-DD	68	76.47	12.35	15.29

^a Pyrrole:formaldehyde:diamine = 1:2:1.

^b Yield = mass of products/mass of reactants * 100%.

tration of 1–5 mg L⁻¹ to test the effect of the chain length. Once the first adsorption experiment was completed, the best polymer of the series was chosen for further adsorption studies at different concentrations (1–5 mg/L), times (0–3 h), temperatures (25, 35 and 50 °C) and pH's (3, 4, 5, 6 and 7). The pH of the solutions was adjusted by preparing acetate buffers. The terpolymers were filtered and the concentration of the metal ions in the filtrate was analysed. The adsorption capacity of terpolymers was calculated using Eq. (1):

$$q_{\text{Cd}^{2+}} = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 is the initial metal ion concentration (mg L⁻¹), C_e is the metal ion concentration at equilibrium (mg L⁻¹), V is the volume

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