



Efficient removal of toxic hexavalent chromium from aqueous solution using threonine doped polypyrrole nanocomposite



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ABSTRACT

A new threonine doped polypyrrole (Thr-PPy) was prepared via *in situ* polymerization of pyrrole with threonine for the removal of Cr (VI) from aqueous solutions. The prepared Thr-PPy was characterized using FT-IR, SEM with EDS, XRD, XPS and BET methods. The adsorption experiments were carried out in batch mode to optimize various parameters like contact time, initial concentration, pH, adsorbent dose, coexisting ions and temperature that influence the adsorption rate. Langmuir, Freundlich, Dubinin-Radushkevich and Temkin adsorption isotherm models were applied to describe isotherm constants. Equilibrium data obeyed well with the Langmuir isotherm model with maximum adsorption capacity of 185.5 mg/g. Thermodynamic studies revealed that the nature of adsorption is spontaneous and endothermic. The results of the kinetic experiments show that Cr (VI) adsorption on Thr-PPy follow pseudo-second-order and intra-particle diffusion models. The mechanism of Cr (VI) adsorption by Thr-PPy was governed by the ionic interaction between NH_3^+ of Thr and HCrO_4^- ions. Thr-PPy can be reused successfully for the removal of Cr (VI) four times without loss of its removal efficiency.

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1. Introduction

Water pollution by heavy metal ions is considered to be one of the major environmental issues due to the adverse effects of heavy metals on ecosystem and on human health. Chromium is one of the dangerous metal pollutants, generally introduced into water bodies from many industrial processes, such as leather tanning, electroplating, textiles and dyeing, ceramic manufacture, metal processing, wood preservation, chromium salt industry, water cooling, film and pigment manufacture, chemical industries, and mining operation. Chromium exists in two main stable oxidation states, namely Cr (III) and Cr (VI), in aqueous systems, in which, Cr (VI) is generally considered to pose great human health risk because it is more toxic, soluble and mobile than Cr (III). Chromium (VI) species are 100 times more toxic than Cr (III) species. Several Cr (VI) compounds act as carcinogens, mutagens and teratogens in biological systems [1–6]. Subsequently, WHO set the maximum permissible limits of Cr (VI) in potable water, inland surface water and industrial wastewater and they are 0.05, 0.1 and 0.25 mg/L, respectively [7]. A sequence of *in vitro* and *in vivo* studies have demonstrated that Cr (VI) brings an oxidative stress through better

production of reactive oxygen species (ROS) leading to genomic DNA damage and oxidative deterioration of lipids and proteins [4,8]. The purification methods have to avoid generation of secondary waste and to evolve materials that can be recycled and easily used on an industrial scale. Various treatment technologies such as ion exchange, reverse osmosis, electrolytic removal, liquid-liquid interaction, adsorption, chemical precipitation, membrane filtration and solvent extraction have been reported for the removal of Cr (VI) from water or waste water [1,9,10]. However, most of these technologies are associated with high operational and maintenance cost, incomplete metal removal, high energy requirement and generation of toxic residual metal sludge that pose a disposal problem. Comparatively, to handle a large volume of wastewater with low concentration of Cr (VI), adsorption is considered as the simplest and the most cost effective method [10–12].

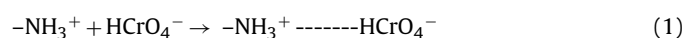
Many kinds of adsorbents for wastewater treatment have been developed, such as activated carbon [13–15], activated alumina [16], coated silica gel [17], biosorbents [18–20], modified resins [21,22] and metal oxides [23,24]. Most of these adsorbents have very low chromium adsorption capacity and slow process dynamics. So there is a necessity to develop novel adsorbents with high capacity and fast kinetics for the removal of Cr (VI) from water.

In recent years, conducting polymer nanocomposites have attracted special attention in the fields of nanoscience and nanotechnology due to their large surface area, low cost, high efficiency

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and regeneration ability. Preparation of conducting polymers is a single step reaction using very few low cost starting materials and definitely cost effectiveness is an advantage. Polypyrrole (PPy), a conducting polymer, is one of the most promising materials for the removal of toxic ions, especially Cr (VI) ions from water/waste water. To enhance maximum adsorption capacity, various functional groups, including amine, carboxylate, hydroxyl, sulfate, phosphate and amide groups have been used to modify the polymeric nanocomposites (NCs) [4,10,25–29]. Among these functional groups, amino- functionalized polymers would be expected to be efficient ones for removing heavy metals. Amino-functionalized polymeric nanocomposites are expected to be efficient ones rather than other functional groups such as carboxylate, hydroxyl, sulfate, phosphate etc., for removing Cr (VI). Threonine is one of the amino acids, easily doped with polypyrrole. There is no study on the removal of Cr (VI) using Thr-PPy. Under acidic conditions, amino groups are easier to be protonated and electrostatic attraction can happen between -NH_3^+ and anions as in Eq. (1) [4,30]. Here, -NH_3^+ and HCrO_4^- are taken as representatives:



To the best of our knowledge, there is no study on the removal of Cr (VI) using Thr doped PPy. In the present study, Thr-PPy was prepared and characterized by using different analytical methods like FT-IR, SEM with EDS, XRD, XPS and BET. Thr-PPy was applied for the removal of Cr (VI) from an aqueous solution. The effects of solution pH, contact time, initial Cr (VI) concentration, competition from coexisting ions, desorption and reusability were tested in batch experiments. The adsorption isotherms and kinetics were also studied.

2. Materials and methods

2.1. Chemicals

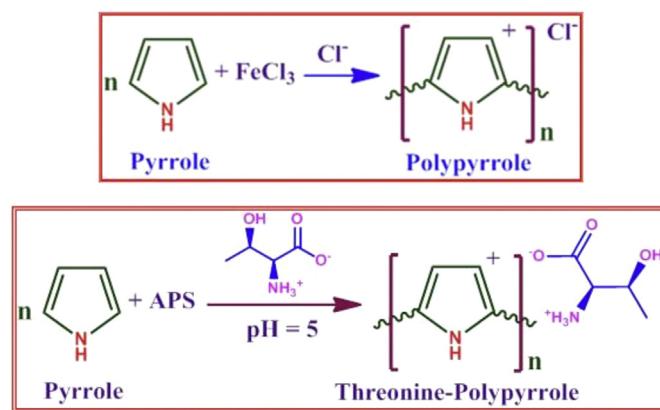
Pyrrole (Py) monomer, Ammonium peroxydisulfate [APS] ($(\text{NH}_4)_2\text{S}_2\text{O}_8$), threonine (Thr) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) were purchased from Sigma-Aldrich, India. All other chemicals used in this study were of analytical grade and were supplied by Sigma-Aldrich, India.

2.2. Preparation of the PPy and Thr-PPy

Polypyrrole (PPy) and threonine doped polypyrrole (Thr-PPy) were prepared by the chemical oxidative, *in situ* polymerization of pyrrole monomer and with threonine respectively in the presence of FeCl_3 as an oxidant as described by Ballav et al. with suitable modifications (Scheme 1) [27].

2.3. Characterization and analysis

Fourier transform infra-red (FT-IR) spectra were recorded before and after adsorption on the adsorbents by JASCO FT/IR-460 plus instrument. The surface morphology of the adsorbent, before and after adsorption was determined using scanning electron microscope (SEM). Elemental analysis was carried out by using energy dispersive analyzer unit (EDS) attached with SEM (Vega3Tescan, Bruker). The crystalline natures of the adsorbents were determined using X-ray diffraction (XRD) (Xpert-Pro). Chromium concentrations in solutions were determined by using Atomic Absorption Spectrometer (AAS) (Perkin – Elmer A Analyst 100)



Scheme 1. Preparation of PPy and Thr-PPy.

2.4. Adsorption experiments

Batch technique was selected to attain the equilibrium and kinetic data. About 0.1 g of adsorbent was added to 50 mL of solution containing 50 mg/L as initial chromium concentration. The mixture was shaken in a thermostated shaker at a speed of 200 rpm at room temperature. The solution was then filtered and the residual chromium concentration was measured using AAS. The adsorption capacity of the adsorbent was studied at different conditions like contact time, initial concentration, adsorbent dose, pH and the effect of other common ions present in the water.

3. Results and discussion

3.1. Structural characterization of Thr-PPy

FT-IR spectra were used to characterize the chemical structure of PPy (Fig. 1 (a)), Thr-PPy before (Fig. 1 (b)) and after adsorption of Cr (VI) (Fig. 1 (c)). The peak at 1459 cm^{-1} is due to stretching mode of C–N in the pyrrole ring [27,31]. The bands around 1180 and 1038 cm^{-1} are attributed for C–H in plane vibration and C–H in plane bending mode vibrations respectively [32,33]. The peaks at 3124 , 1679 and 1050 cm^{-1} are C=O symmetric, asymmetric stretching vibrations and vibration of C–N in NH_3 group of zwitter ionic threonine respectively [27,34]. The N–H bending vibration peak at 1548 cm^{-1} was intensified and shifted to 1560 cm^{-1} after Cr (VI) adsorption on Thr-PPy [27]. The peaks at 790 and 927 cm^{-1}

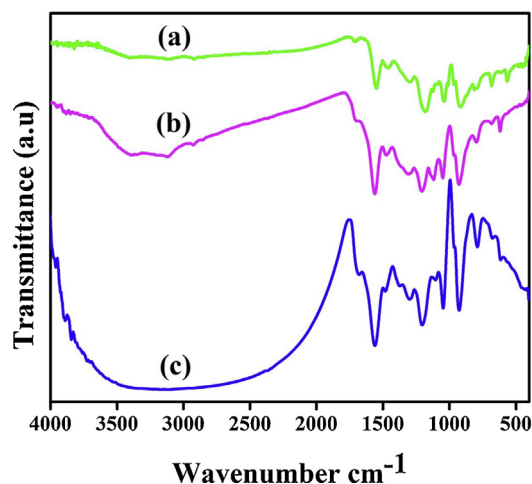


Fig. 1. FT-IR spectra of (a) PPy (b) Thr-PPy before and (c) Thr-PPy after adsorption with Cr (VI).

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