

Preparation and characterization of aspartic acid doped polypyrrole for the efficient removal of Cr(VI) from aqueous solution



Augustine Amalraj, M. Kalai Selvi, A. Rajeswari, Anitha Pius*

Department of Chemistry, The Gandhigram Rural Institute-Deemed University, Gandhigram, Dindigul 624 302, Tamil Nadu, India

ARTICLE INFO

Article history:

Received 18 January 2016

Received in revised form 13 April 2016

Accepted 9 May 2016

Available online 26 May 2016

Keywords:

Aspartic acid

Polypyrrole

Hexavalent chromium

Adsorption

Isotherm

ABSTRACT

A new aspartic acid doped polypyrrole (Asp-PPy) was prepared via *in situ* polymerization of pyrrole with aspartic acid for the removal of Cr(VI) from aqueous solutions. The prepared Asp-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 viz., contact time, pH, adsorbent dose, co-ions and temperature that influence the adsorption rate. Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherm models were applied to describe isotherm constants. Equilibrium data agreed well with the Langmuir isotherm model with maximum adsorption capacity of 176.7 mg/g. Thermodynamic studies revealed that the nature of adsorption is spontaneous and endothermic. The kinetic process demonstrates that the adsorption process follows pseudo-second-order and intra-particle diffusion models. The mechanism of Cr(VI) adsorption by Asp-PPy was governed by the ionic interaction between NH_3^+ of Asp and HCrO_4^- ions. Asp-PPy can be reused successfully for the removal of Cr(VI) four times without loss of its removal efficiency. Asp-PPy can be a promising material to remove toxic Cr(VI) from the aqueous environment due to having high Cr(VI) capacity, good ion exchange property, non-toxic, environmental stability and low cost.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

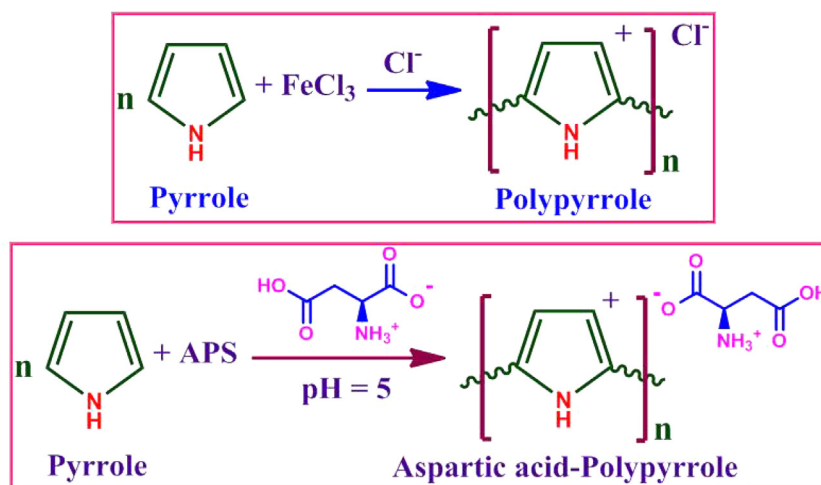
Surface and ground waters have been subjected to severe utilization and damage since the beginning of industrialization by mining, manufacturing, chemical and goods production, electricity production, agriculture and improper sanitation. Heavy metals pose severe problem because of their toxicity towards aquatic life, plants, animals, human beings and to the environment. They are generally used in leather tanning, metal industries, nuclear power plants, cement industries, electro plating, dye, textile, paint, water cooling, photographic materials, fertilizer, pesticide industries and metal salt production. They are not biodegradable and have a tendency to accumulate in living organisms. The consequences of heavy metal ingestion and exposure are adverse, they include damage to the central nervous system, skin dermatitis, pulmonary congestion, vomiting and liver damages etc [1–4].

The presence of high concentration of heavy metals such as Cr, Hg, Pb, Cd, Co, and Ni in both natural water supplies and industrial wastewater streams, is a critical health and environmental issue due to their high toxicity and bioaccumulation through the food

chain and hence in the human body. Amongst the prevalent heavy metals in aqueous environments, chromium is known to be very toxic and hazardous element to living organisms and the environment. It is on the list of priority pollutants due to its high toxicity as mentioned by the United States Environmental Protection Agency (U.S.E.P.A). It is harmless in its elemental state, but in ionic form it can be toxic and mutagenic in large doses [5–10]. Cr(VI) on the other hand is 500 times more toxic than Cr(III) state [6]. Cr(VI) is highly mobile, non-biodegradable and easily accumulated in soil and aquatic systems and can easily be absorbed into the human body through the digestive system, respiratory tract and skin contact [8–10]. Generally, HCrO_4^- , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ are different forms of Cr(VI) found in aqueous solution depending on the pH and concentration of Cr(VI) solution [11,12]. Industries like tannery, electroplating, metal finishing, textile, photography and nuclear power plants are the main sources of Cr(VI) pollution in the environment [11]. The allowable limit for Cr(VI) for discharge to inland surface water is 0.1 mg/L and in potable water, it is 0.05 mg/L as set by the U.S.E.P.A and World Health Organization (WHO) [3,13]. Effluents from certain industries often contain values higher than the prescribed standard and therefore, it is necessary to remove Cr(VI) concentration to an acceptable level before discharging into the environment.

* Corresponding author.

E-mail address: dranithapius@gmail.com (A. Pius).



Scheme 1. Preparation of PPy and Asp-PPy.

Several methods including chemical precipitation, ion-exchange, reverse osmosis, nanofiltration and electrochemical methods have been proposed, and are currently used for heavy metals [14,15]. However, these methods have several drawbacks such as fouling of membranes by metal hydroxides and carbonates, large consumption of reagents, insufficient recovery of treated metals for reuse, low effectiveness in low concentrations of heavy metals, and high costs. Adsorption is renowned as highly effective wastewater treatment technology, in terms of cost and removal efficiency. It is simple, offers flexibility in design and operation and produces high quality treated effluent. Moreover adsorption is reversible, adsorbents can be regenerated by appropriate desorption process [14–21]. In adsorption, selection and crafting smart adsorbent is important and necessary. Heavy metal ion removal has been previously carried out using different adsorbents such as activated carbon, fly ash, zeolites, clay minerals, metal oxides, hybrid materials, ionic liquid based materials and agricultural residues [22–25]. However, most of these adsorbents suffer from low adsorption capacities and slow kinetics, weak mechanical strength, separation after treatment and low surface areas. Thus, the adsorption processes involve multiple usages of the adsorbents, which increase the cost. Polymeric nanocomposites/composites are expected to exhibit new properties and present comparatively high metal ion adsorption capacities due to the synergism between the constituents. Recently, conducting polymers have been established as promising materials for the adsorption of Cr(VI) from aqueous solutions [6,26–29]. Availability, easy preparation and functionalization have made them highly desirable in many applications.

Amongst the conducting polymers, polypyrrole (PPy) is one of the most frequently studied polymer, having high electrical conductivity, ion exchange property, environmental stability, non toxicity and low cost. PPy have a strong tendency to agglomerate via π - π stacking [26]. Modification in the polymer chain during polymerization reactions was effected to overcome the aggregation of PPy as well as to increase the surface area [4,26–29]. Setshedi et al. [6] found 119.3 mg/g adsorption capacity using exfoliated PPy/organically modified montmorillonite clay nanocomposite for the removal of Cr(VI). Bhaumik et al. [26] prepared PPy- Fe_3O_4 nanocomposite and found a maximum adsorption capacity of 169.4 mg/g when investigated for the removal of Cr(VI).

In this study, aspartic acid doped polypyrrole (Asp-PPy) was used to remove Cr(VI) and found to have a well dispersed adsorbent and high capacity for Cr(VI) removal. Moreover, the prepared Asp-PPy having good ion exchange property, environmental sta-

bility without toxicity and low cost. To the best of our knowledge, this is the first attempt to synthesize an Asp-PPy nanocomposite for the adsorption of Cr(VI) from aqueous solutions. The prepared nanocomposite was characterized by FT-IR, SEM with EDS, XRD, XPS and BET. The factors affecting the adsorption process like pH, adsorbent dose, time and temperature were investigated in batch mode. Asp-PPy can be a promising material to remove toxic Cr(VI) from the aqueous system.

2. Materials and methods

2.1. Chemicals

Pyrrole (Py) monomer (98% purity), Ammonium peroxydisulfate [APS] ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) (98% purity), aspartic acid (Asp) (98% purity) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) (99% purity) 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 Asp-PPy

Polypyrrole was prepared by the chemical oxidative polymerization of pyrrole monomer in the presence of FeCl_3 as an oxidant as described by Ballav et al. [4]. Aspartic acid doped polypyrrole (Asp-PPy) was synthesized via *in situ* polymerization method (Scheme 1). In this polymerization process, 1.0 g of Asp was dissolved in 100 mL of Millipore water at ambient temperature in a 250 mL conical flask. pH of the solution was 5 and to this solution, 1.0 mL of pyrrole was syringed. Then the mixture was stirred for 30 min at ambient temperature. 20 mL of 3.3 g of APS solution was added drop wise to the above solution with constant stirring. Then the reaction mixture was kept for 12 h without stirring. The obtained black powder was filtered and washed with Millipore water until the filtrate became colorless and thereafter washed with acetone. The Asp doped PPy was then dried at 60°C for 6 h under vacuum, until the total mass became constant [4].

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 with a resolution of 4 cm^{-1} in transmittance mode with 16 scans. 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 disper-

Download English Version:

<https://daneshyari.com/en/article/232442>

Download Persian Version:

<https://daneshyari.com/article/232442>

[Daneshyari.com](https://daneshyari.com)