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Removal of copper from aqueous solution using polyaniline and polyaniline/ferricyanide composite

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ABSTRACT

In situ oxidative polymerization method was used to synthesize the composite of polyaniline with ferricyanide ion. The polyaniline and its composite were characterized by FTIR, XRD, SEM and EDX. Comparison between the removal of Cu(II) from aqueous solution using polyaniline and polyaniline/potassium ferricyanide composite was investigated by UV–visible spectroscopy. The adsorption of Cu(II) by polyaniline and polyaniline/ferricyanide composite was found to be dose dependent. The adsorption kinetic results of Cu(II) showed that adsorption reached equilibrium within 180 min in case of polyaniline and 60 min for polyaniline/ferricyanide composite and their measured adsorption capacities are 38.265 and 41.625 mg g^{-1}, respectively. The adsorption process can be described by the pseudo-first order for the polyaniline and pseudo-second order for the polyaniline/ferricyanide ion composite. Adsorption of Cu(II) onto polyaniline and its composite agreed well with the Freundlich model, as revealed by the higher values of correlation coefficients. Thermodynamic study revealed that the adsorption process is endothermic and spontaneous in nature. The results indicate that both polyaniline and polyaniline/ferricyanide composite could be used as efficient adsorbents for the removal of Cu(II) from aqueous solution.

Introduction

Industries contaminate the environment with heavy metals like mercury, chromium, lead, copper, barium and cadmium [1–4]. These metals even present in traces are hazardous to biological species and are difficult to remove at low concentration. Most of the remediation technologies are ineffective to remove heavy metal ions from aqueous solution at low concentration (1–20 mg L^{-1}). The removal procedures involve a high cost for their implementation. For this reason, novel effective low cost technologies are desirable [5]. Metal plating, mining operations, tanneries, dying in textile industries etc. are the main sources of contamination. Increasing impact of heavy metals is felt everywhere in the world. Some of the methods that have been developed worldwide for the decontamination of heavy metals and toxic dyes from the aqueous solutions are chemical precipitation, solvent extraction, ion-exchange, reverse osmosis and adsorption [6–9]. Among all these methods, adsorption is one the most and extensively used method owing to its low cost, easy handling, simplicity in design, insensitivity to toxic substances, availability of different adsorbents and especially because of its high efficiency [10]. In the recent years, numerous adsorptive materials have been proved as effective materials for heavy metal removal. Activated charcoal, zeolites, biomaterials, metal oxides like Fe_2O_3, Fe_3O_4 etc. are used for heavy metal removal owing to their interesting features such as magnetic character, large surface area and large number of active sites for the adsorption [11–15]. Adsorption process depends on experimental conditions like particle size, pH, metal ion concentration, ligand concentration and competing ions [16,17]. Particles in small size can augment the adsorption phenomenon due to large specific surface area [18]. In this work, we have chosen Cu(II) for the remedial experiments due to its health hazard problems. Cu(II) has strong chelating tendency with bio-molecules and form very stable complexes. Its ingestion can cause liver and kidney damage, nausea, headaches and gastrointestinal problems [19]. The maximum permissible limit of Cu(II) in drinking water as per the reports of US Environmental Protection Agency (EPA) is 1.3 mg L^{-1}[5].

Polymeric polyaniline and polythiophene are widely used as adsorbents to remove heavy metals as well as dyes and pigments

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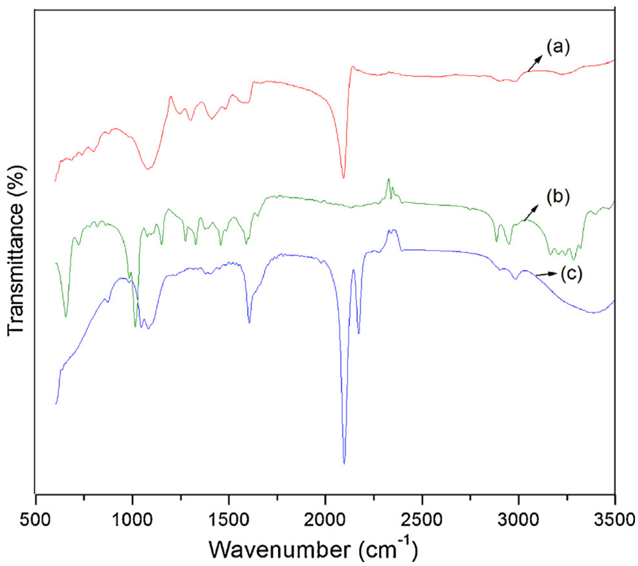

Fig. 1. FTIR of (a) potassium ferricyanide, (b) polyaniline and (c) polyaniline/ferricyanide composite.

from the solution. Polyaniline emeraldine salt was used for the removal of sulphonated dyes [20]. Polyaniline microspheres were also used for the removal of methyl orange from aqueous solution [21]. Polyaniline/chitosan composite was used for fluoride ion adsorption and the same composite was used again for the removal of sulphonated dyes [22]. Polyaniline/silica composite was used for removing Acid green dyes from aqueous solution [23]. Polyaniline composites were used for removal of metal ions such as Hg(II), Pb (II), Cr(III), Ba(II) etc. [1–4]. Polyaniline/lignin composite was used for the elimination of reactive Ag(I) ion from aqueous solution of ammonia [24]. Polyaniline/palygorskite composite was used for the removal of Cu(II), Ni(II), Cd(II) and Cr(VI) from aqueous solution [25]. The properties associated with polymeric materials are because of accessible active sites, large surface area and short diffusion length. Polyaniline is a low cost adsorbent having high adsorption capacity and selectivity towards heavy metal ions and dyes [16]. Polyaniline with nitrogens of amine groups having lone pair of electrons are considered the most functional groups for the removal of heavy metals like Cr, Hg, Pb, Cu etc. and protonic amine

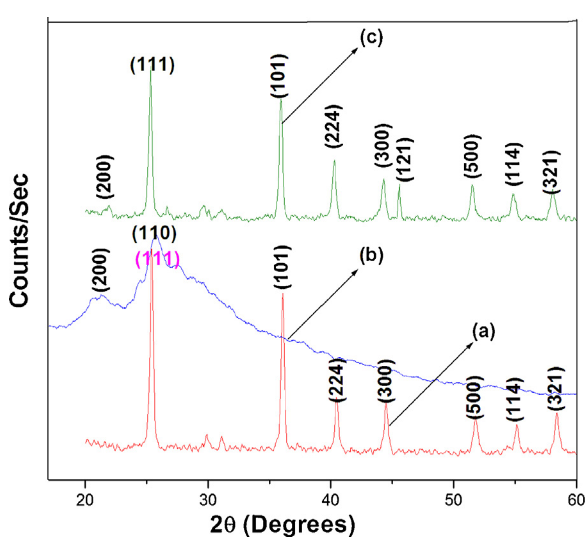

Fig. 2. XRD pattern of (a) potassium ferricyanide, (b) polyaniline and (c) polyaniline/ferricyanide composite.

groups can adsorb anionic contaminants by electrostatic attraction.

The present work involves the synthesis of polyaniline and its composite with ferricyanide ion via in situ oxidative polymerization method. The synthesized composite is one of its kinds that contain both inorganic complex and organic component. The composite takes the synergic benefit of both the components. Ferricyanide ion intensifies the charge density on polyaniline chains, thereby increases the adsorption affinity of composite towards Cu(II) from the aqueous solution. The selection of ferricyanide ion was done on the basis of its low cost, easy availability, thermal stability, inertness towards thermal substitution reactions, non-toxicity unlike to that of toxic chemicals like HCN, KCN or NaCN salts and bridging nature of cyanide ligands. The cyanide ion can take metal ions from the solutions due to its bridging nature through inner sphere coordination mechanism. The equilibrium and thermodynamic aspects of the adsorption of Cu(II) by polyaniline and polyaniline/ferricyanide composite has been discussed and presented in this paper.

Experimental

Materials

Potassium ferricyanide {$K_3[Fe(CN)_6]$}, cupric nitrate {$Cu(NO_3)_2$} were of Merck quality. Aniline was supplied by Loba chemicals and used after distillation. Ammonium persulphate {$(NH_4)_2S_2O_8$} was also supplied by Loba chemicals. Hydrochloric acid (HCl) was of analytical grade. Triply distilled water was used for synthesis.

Instrument and measurements

The FTIR spectra were recorded on a Perkin-Elmer spectrometer using KBr pellets. XRD data was collected from PW 3050 base diffractometer with CuK_{α} radiation of 1.540598 Å. Surface morphology of the samples was done on ZEISS EVO series scanning electron microscope model EVO50. Energy dispersive X-ray (EDX) of Bruker model was used for the investigation of elemental composition. Ultraviolet–visible (UV–vis) spectra were taken on double beam UV–visible spectrophotometer T 80 using a cell of 1 cm optical path length and wavelength range of 200–1000 nm. Surface area was determined by N_2 adsorption–desorption at 75 K with Brunauer–Emmet–Teller (BET) method using an ASAP 2420 System.

Synthesis

Synthesis of pure polyaniline (PANI)

Polyaniline was prepared by known methods of oxidation with ammonium persulphate $(NH_4)_2S_2O_8$ [26]. 10 mL of distilled aniline was mixed with 10 mL concentrated HCl and cooled in a refrigerator for 10 min. Then, it is dissolved in 150 mL of distilled water. 4.5 g of $(NH_4)_2S_2O_8$ dissolved in 30 mL of water was added drop wise to this solution with constant stirring. The solutions were kept stirring for about 2 h and were left for more than 1 h. The greenish black precipitate resulting from this solution was filtered and washed repeatedly with distilled water. The precipitate was collected and dried in an oven at 40 °C.

Synthesis of polyaniline composite (PANI-[Fe(CN)6] composite)

Polyaniline composite was prepared by oxidative polymerization method using ammonium persulphate $(NH_4)_2S_2O_8$ as an oxidant. To precooled solutions of 10 mL of distilled aniline dissolved in 150 mL of distilled water with 10 mL of concentrated HCl, 10 mL of ferricyanide ion was added into the solution with constant stirring. To this solution, 4.5 g of $(NH_4)_2S_2O_8$ dissolved in