Applied Clay Science 139 (2017) 72–80

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Synthesis, characterization and optimization of poly(*p*-phenylenediamine)-based organoclay composite for Cr(VI) remediation

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ARTICLE INFO

Article history:
Received 7 September 2016
Received in revised form 10 January 2017
Accepted 11 January 2017
Available online xxxx

Keywords:
Adsorption
Cr(VI) reduction
Composite materials
Poly(phenylenediamines)

ABSTRACT

The contamination of the water supply with high levels of heavy metals from various human and industrial activities continues to present a major environmental problem. Heavy metals such as hexavalent chromium (Cr(VI)) are of particular concern since they pose serious health and environmental risks. Many polymeric materials with remarkable anion adsorbing properties have been developed and reported in the literature. However, there is still need to reduce the cost and/or improve the performance of these materials for environmental remediation. We report here the synthesis, characterization and application of a poly(para-phenylenediamine) (poly-*p*PD) organoclay-based composite for removal of Cr(VI) complexes from wastewater. Adsorption capacity of the composite was evaluated at different sample pH, contact time, adsorbent dose and initial concentration. The poly-*p*PD-based organoclay adsorbent with <55% of the polymer showed similar superior performance to pure polymer over a wide pH range compared to pristine organoclay. Adsorption was better described by the pseudo second-order kinetic model and Langmuir isotherm model, suggesting that chemisorption was the main mechanism of the adsorption process. The Langmuir maximum adsorption capacity for Cr(VI) was 217.4 mg/g and 185.2 mg/g whereas for total Cr it was 193.3 mg/g and 148.8 mg/g for poly-*p*PD and poly-*p*PD-organoclay, respectively. Using XPS, it was proven that the adsorbent also reduces Cr(VI) to Cr (III). The prepared poly-*p*PD-organoclay showed reuse over seven times but still retaining 80% of the recovery for Cr(VI). The composite also performed excellently in batch application to real industrial wastewater containing high levels of Cr(VI) ions and competing anions such as nitrates and sulfates.

1. Introduction

Industrial activities generate large volumes of effluent containing inorganic and organic pollutants, which pose a health hazard to living organisms. Heavy metals are non-biodegradable; hence those released into the environment persist in soil and ground water. These inevitably find their way through the food supply chain. Hexavalent chromium (Cr(VI)), is one of the most toxic industrially produced heavy metals. It ranks among the top 16 toxic pollutants due to its carcinogenic and teratogenic characteristics (Kawasaki et al., 2006). Industrial sources of Cr(VI) include electroplating, metal finishing, iron and steel manufacturing and chemical production industries (Zadaka et al., 2007). Due to its toxicity, the allowable discharge limit for Cr(VI) into surface and potable water are 0.1 mg/L and 0.05 mg/L, respectively (Wojcik et al., 2011).

Many technologies have been developed to remove heavy metal contaminants from wastewater before release into the environment. These techniques have been widely reported and reviewed (Bhatnagar and Minocha, 2006). Adsorption is arguably a promising alternative, and one of the most effective technologies for water treatment due to its simplicity and low capital cost (Bhaumik et al., 2011). Activated carbon has been the water purification industry's standard adsorbent because of its versatility for removal of organic contaminants (Rivera-Utrilla et al., 2011). It is much less efficient against inorganic contaminants (Owlad et al., 2010). There is therefore a need to develop a low cost adsorbent to remove inorganic contaminants like Cr(VI).

The application of conducting polymers like polyaniline (PANI) for the adsorption of Cr(VI) has become an active area of research (Karthik and Meenakshi, 2015). PANI is a low cost, stable conjugated polymer with reversible acid/base doping/de-doping characteristics (Wang et al., 2009). Although it has shown impressive performance

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http://dx.doi.org/10.1016/j.clay.2017.01.015

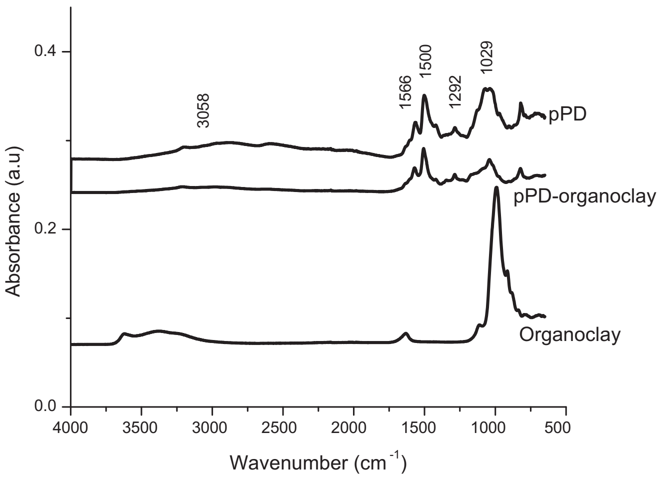

Fig. 1. FT-IR spectra of organoclay, poly-*p*PD and poly-*p*PD-organoclay composite.

for Cr(VI) removal, studies have shown its susceptibility to degradation in highly concentrated Cr(VI) solutions (>100 mg/L) due to oxidation of the polymer by the high oxidative potential of Cr(VI) (Olad and Nabavi, 2007). Additionally the use of composites comprising conducting polymers and inorganic layered materials has gained extensive interest nowadays to improve the polymer bulk properties (Setshedi et al., 2013).

Poly(phenylenediamine) homopolymers with 2,3-diaminophenazine or quinoraline repeat units exhibit high thermostability and have already found many applications (Li et al., 2002). These polymers are less conductive than PANI and are mostly used in biomedical applications where the potential toxicity of aniline and its oligomers is unacceptable (Guimard et al., 2007). Their ability to remove metal ions has been demonstrated (Zhang et al., 2012).

Poly(*o*-phenylenediamine) possesses a strong adsorption ability for Pb(II) and Hg(II) ions in aqueous solutions through chelation reactions (Han et al., 2011; Li et al., 2009). Among the family of poly(phenylenediamines), extensive research has focused on poly(*m*-phenylenediamine). This is due to its properties of Cr(VI) adsorption and reduction (Yu et al., 2013). The third isomer, poly(*p*-phenylenediamine) (poly-*p*PD) has also shown good adsorption of Pb(II) (Huang et al., 2006; Wang et al., 2008).

Pristine polymers show several limitations to practical field applications. They are susceptible to chemical attacks, oxidation and have poor mechanical strengths. They have low densities which can cause a significant pressure drop in adsorption columns (Stejskal, 2015). Recently, composites of layered materials and polymers have been extensively prepared in order to improve polymer bulk properties (Nascimento et al., 2010). As a result, clay materials have received a great level of interests because of their abundant availability, mechanical stability and benign non-toxic nature (Chen et al., 2013). Montmorillonite (Mt) belongs to a smectite group of clay minerals. It has lamellae which are constructed from octahedral silica sheets with a net negative charge on the surface (Li et al., 2014). This polyanionic character stabilizes insertion of positively charged polymer chains. Although Mt. has been used industrially in environmental remediation, it has low adsorption capacity for Cr(VI) (Setshedi et al., 2013). To overcome this, organoclay was functionalized with poly-*p*PD through intercalation. The present work aimed to develop a poly-*p*PD organoclay based composite and describe its properties and application in Cr(VI) remediation.

2. Experimental procedure

2.1. Materials and methods

All reagents were of analytical grade. Ammonium peroxydisulfate and para-phenylenediamine (*p*PD) were purchased from Sigma Aldrich (Johannesburg, South Africa). Potassium dichromate ($K_2Cr_2O_7$) was obtained from Sigma Aldrich (Johannesburg, South Africa). Organically modified (Mt) clay, commercially known as C20A which is an ion exchanged Mt. clay modified with dimethyl dehydrogenated Tallow ammonium salt was supplied by Southern Clay Products, Inc., (Johannesburg, South Africa). Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Merck (Johannesburg, South Africa) and were used without further purification.

2.2. Characterization techniques

Fourier transform infrared (FTIR) spectrometer Perkin–Elmer Spectrum100 (London, UK) spectrometer was used for functional group identification. Thermal stability was measured by thermogravimetric analysis (TGA) on a Perkin Elmer TGA 400 (Massachusetts, USA). XRD patterns were obtained on X-ray diffractometer (Bruker AXS D8 Advance) using Cu-Kα as the radiation source (Karlsruhe, Germany). Surface and fracture morphology was examined with a LEO Zeiss scanning electron microscope with a field emission gun (FE-SEM) (Hillsboro, USA). The specific surface area was measured using Brunauer-Emmett-Teller (BET) instrument (Gemini 2360) by isothermal nitrogen

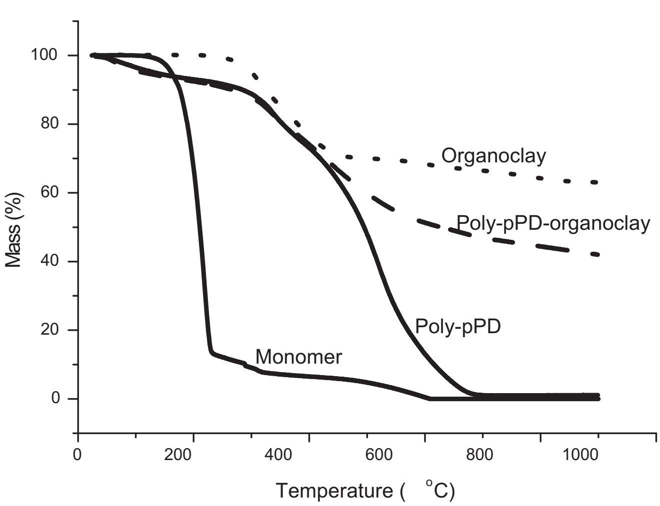

Fig. 2. TGA thermograms of the monomer (*p*PD), poly-*p*PD, organoclay and poly-*p*PD-organoclay.

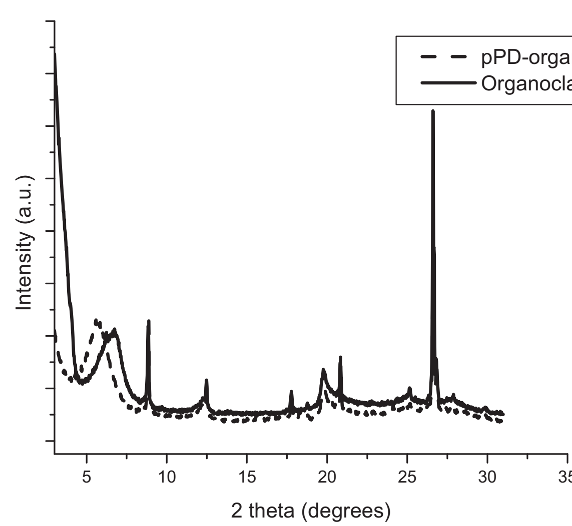

Fig. 3. XRD pattern of (a) organoclay, poly-*p*PD-organoclay composite.