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Research paper

Chitosan based nano composite adsorbent—Synthesis, characterization and application for adsorption of binary mixtures of Pb(II) and Cd(II) from water

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ABSTRACT

Composite type adsorbent was prepared by integrating chitosan (Cs) with crosslinked polymethacrylic acid (PMA) and nano sized halloysite nanotube (HNT). The structure of the resulting Cs-PMA/HNT adsorbents was characterized by FTIR, NMR, XRD, TGA, SEM/EDX and rheological properties. These functional adsorbents were used for removal of Pb(II) and Cd(II) as single and binary competitive mixtures from water. There was a significant improvement in adsorption properties of crosslinked PMA in the presence of Cs and HNT. The effect of synthesis parameters such as wt.% of Cs and HNT on swelling and process parameters such as solution pH, adsorbent dosage, contact time and feed concentration on adsorption of metal ions from water were studied in batch experiments. For a feed concentration of 100 mg/L of metal ion, an adsorbent dose of 0.25 g/L and a solution pH of 6, the Cs-PMA/HNT composite adsorbent containing 4 wt% Cs and 3 wt% HNT showed an adsorption capacity (mg/g)/removal% of 357.4/89.4 and 341.6/85.4 for single Pb(II) and Cd(II), respectively which reduced to 313.7/78.4 and 303.6/77.3 for the same metal ions in their binary mixtures in water.

1. Introduction

Adsorption is a major industrial separation technique for effluent treatment (Chen, Zhu, Zhao, & Zheng, 2012; Karmakar et al., 2017). Recent studies have focused on relatively low cost organic adsorbents such as sawdust (Bulut & Tez, 2007), bark (Al-Asheh et al., 2000), biomass (Ahluwalia & Goyal, 2007), lignin (Parajuli, Inoue, & Ohto, 2005), chitosan (Crini, 2005), and other naturally occurring polymers (Bekiari & Lianos, 2006) as well as inorganic adsorbents like various clays including zeolite, montmorillonite, kaolinitic, mineral silicates, sepiolite, etc. (Brigatti, Lugli, & Poppi, 2000; Liu & Wang, 2007; Guerra, Viana, & Airoldi, 2009). However, the adsorption capacity and adsorption rate of these adsorbents for heavy metal ions is poor (Bhattacharyya & Gupta, 2008). Adsorbents with high adsorption capacity may be prepared by integrating a natural polymer with a synthetic polymer and clay to produce a unique organic (polymer)/inorganic (clay) composite type adsorbent containing numerous functional groups. In order to prepare adsorbent from such materials, different types of natural, modified natural and synthetic polymers have been used (Gil & Hudson, 2004; Ranjha, Mudassir, & Akhtar, 2008; Singha et al., 2017). Among the various natural polymers, chitosan (poly-β-(1,4)-2-amino-2-deoxy-glucopyranose noted as Cs), obtained by deacetylation of chitin is the second most abundant natural biopolymer on earth after cellulose (Septhum, Rattanaphani, Bremner, & Rattanaphai, 2007).

Cs is an excellent natural adsorbent in that its amine ($-NH_2$) and hydroxyl ($-OH$) groups may serve as coordination sites to form complexes with various heavy metal ions. This low- cost bio-polymer is self-degradative, non-toxic and environmentally benign. However, use of Cs as a single adsorbent is not feasible because of its small surface area, low porosity and poor selectivity (Ahmaruzzaman, 2008). Thus, Cs has been chemically modified by allowing interaction of its amine ($-NH_2$) functionality with carboxylic ($-COOH$) group of an acidic polymer.

Poly (amic acid) modified chitosan was used for biosorption of methylene blue from water (Xing & Sujan, 2014). Similar to poly (amic) acid, poly(methacrylic acid)(PMA) is another classic acidic polymer. It can also form polyelectrolyte complexes by electrostatic interactions with an oppositely charged polymer such as Cs in aqueous solution. This would break the hydrogen bonding between amino groups and hydroxyl groups in Cs, resulting in an amorphous structure of the polyelectrolyte complex (Lee, Kim, Kim, Lee, & Lee, 1999). Chitosan-PMA IPN type gel was reported as adsorbent for removal of methyl violet dye from water (Maity & Ray, 2014) while chitosan-polyacrylic acid/polymethacrylic acid composite (Jing, Chen, Huang, & Jiang, 1994) was studied for catalytic hydrogenation of palladium complex. Apart from a synthetic polymer, chitosan has also been modified with inorganic filler. Chitosan-bentonite clay composite was reported for the removal of Cu(II) from water (Azzam et al., 2016). Among other clay

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Table 1
Synthesis parameters and equilibrium swelling ratio (ESR) of the polymer composites.

SL No.	Composites	Cs (%,w/v)	MAA (%, w/v)	Cs (wt%) + MA (wt%)	HNT (wt% w. r. to monomer)	MBA (wt% w. r. to monomer)	Initiator (wt% w. r. to monomer)	ESR
1	Cs-PMA	0.5	25	1.96 + 98.04	–	1	0.5	45.342
2	**Cs-PMA**	**1**	**25**	**3.85 + 96.15**	**–**	**1**	**0.5**	**48.419**
3	Cs-PMA	1.5	25	5.66 + 94.34	–	1	0.5	43.231
4	Cs-PMA	2	25	7.40 + 92.60	–	1	0.5	35.734
5	Cs-PMA/HNT1	1	25	3.85 + 96.15	1	1	0.5	49.636
6	Cs-PMA/HNT2	1	25	3.85 + 96.15	2	1	0.5	50.365
7	**Cs-PMA/HNT3**	**1**	**25**	**3.85 + 96.15**	**3**	**1**	**0.5**	**51.453**
8	Cs-PMA/HNT4	1	25	3.85 + 96.15	4	1	0.5	47.786

Bold value corresponds optimum composition.

materials, halloysite nanotube ($Al_2Si_2O_5(OH)_4{\cdot}nH_2O$, noted as HNT), a clay mineral of the kaolin group forms nanotubes with tubular structures having inner diameters of 10–30 nm and outer diameters of 50–70 nm (Zhang & Yang, 2012).

As a natural aluminosilicate clay mineral, halloysite consists of one alumina octahedron sheet and one silica tetrahedron sheet in a 1:1 stoichiometric ratio (He et al., 2013). In comparison to other synthesized nano-scale materials, HNT is a natural nanomaterial with a unique combination of a hollow tubular nanostructure and a large aspect ratio. It has excellent mechanical strength, numerous functionality, biocompatibility, and it is also available in large amounts at low cost. It is even cheaper than carbon nanotube (CNT). HNT consists of multilayer walls with negatively charged Si—OH on the outer surface and positively charged Al—OH on the inner surface at a pH between 4–9. It does not require exfoliation and this unique bivalent morphology with spatially negative and positive surfaces makes HNT a promising candidate for use as an efficient adsorbent for dyes and metal ions (Zhao, Repo, Yin & Sillanpa, 2013). Further, large specific surface area as well as hollow and layered structure also makes HNT an efficient adsorbent (Liu et al., 2012). Dong, Wang, Wang, and Rena (2012) used natural HNT for removal of zinc ions from water. However, HNT has limited use as adsorbent since in contact with water HNT swells and forms a colloidal suspension from which separation of HNT is very difficult. Further, in column mode of separation halloysite bed is very compact with low permeability (Liu et al., 2012). Thus, HNT needs chemical modification for improving its adsorption properties. HNT may be easily modified by chemical treatment (Yuan et al., 2008; Xie, Qian, Wu, & Ma, 2011). Jinhua et al. (2010) modified HNT with a surfactant, viz., hexadecyltrimethyl ammonium bromide (HDTMA) for rapid adsorption of chromium ions. HNT may also be modified by its incorporation in a polymer matrix since with a rod like morphology, HNT never intertwines each other and thus unlike CNT it is easily dispersed in a polymer matrix in solution (Xie, Qian, Wu, & Ma, 2011). Liu et al. (2012) and De Silva et al. (2013) prepared nano-composite membrane consisting of Cs and HNT and studied the characteristics of this composite. Chitosan-HNT composite adsorbent was also reported for removal of methylene blue and malachite green from water (Peng, Liu, Zheng & Zhou, 2016). Alginate/HNT beads reported for the removal of dyes showed a high adsorption capacity of about 250 mg/g (Chooa et al., 2016).

Based on the above discussion, in the present work, HNT incorporated Cs-PMA nanocomposite type adsorbent was synthesized and used for the removal of single and binary mixture of Pb(II) and Cd(II) ions from aqueous solutions.

2. Materials and methods

2.1. Materials

Chitosan (Cs, 85% deacetylation) was purchased from Sigma, USA. Methacrylic acid (MA) was purchased from Merck, Darmstadt, Germany. Potassium persulfate (KPS), Sodium metabisulfite (SMBS) and *N*, *N*'–methylenebisacrylamide (MBA), were purchased from Fluka (Buchs, Switzerland). Lead nitrate and cadmium nitrate were of analytical grade and used without any further purification. Halloysite nanotube (HNT, specific gravity 2.53 g/cm^3, pore volume 1.3 mL/g, diameter 30–70 nm and length: 1–3 μ) was purchased from Sigma, USA.

2.2. Methods

2.2.1. Synthesis of composite polymer adsorbent

HNT was oven dried at 60 °C for 2 h. It was then dispersed in 50 mL deionized water for around 4 h. A pre-weighed amount of Cs was then added to this 50 mL water in a 100 mL reactor equipped with a mechanical stirrer and stirred at 250 rpm for 20 min. The reactor was placed in a thermo-stated water bath to control the reaction temperature at 30 °C. After dissolving Cs in water in the presence of acetic acid, the monomer MA and the crosslinker MBA were simultaneously added and the reaction mixture was stirred for 15 min. Then the redox pair of initiator KPS and SMBS was added and the polymerization reaction was continued for around 30–40 min till the gel point was reached. The reaction product was then allowed to cool at ambient temperature. The composite polymer (noted as Cs-PMA/HNT) synthesized above was then poured in to water, washed for several times followed by an additional wash with excess water–ethanol mixture for a week with occasional shaking to remove the water soluble uncrosslink and low molecular weight substances from the composite. Finally, the filtered polymer composite was dried in a vacuum oven at 60 °C for 10 h. After grinding by a mortar, the polymers were stored by protecting from moisture, heat and light. Similar polymerization method was employed for preparing composite Cs-PMA without any HNT. The detailed synthesis parameters showing the amount of monomer, crosslinker, initiator, Cs and HNT used for preparing different polymer composites by the above method along with their equilibrium swelling ratio (ESR) is shown below in Table 1.

2.2.2. Characterization of the composite polymers

The Fourier transform infrared (FTIR) spectra of the polymer samples were carried out on a FTIR spectrometer (Perkin Elmer, model: Spectrum-2, Singapore) in the range 400–4000 cm^{-1} using KBr pellets made by mixing KBr with fine powder of the polymer samples (10:1 mass ratio of KBr to polymer). The crystallinity of the polymer samples was determined by the wide-angle X-ray diffraction profile (XRD) of these samples on a diffractometer (model: X'Pert PRO, made by PANalytical B.V., Netherlands) using Ni-filtered Cu K_α radiation ($\lambda = 1.5418$ Å) at the angle of diffraction of 5–70 ° with a scanning rate (2θ/s) of 0.005 deg/s. The thermo-gravimetric analysis (TGA) data of the samples were recorded at a heating rate of 10 °C per min in the temperature range of 30–600 °C on a Perkin Elmer instrument. The morphology of the composite was observed by scanning electron microscopy (SEM, model no. S3400N, VP SEM, Type-II, Hitachi, Japan) with the accelerating voltage set to 15 kV. The energy dispersive X-ray