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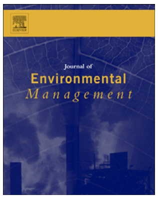

Research article

Removal of Pb(II) from water using a bio-composite adsorbent-A systematic approach of optimizing synthesis and process parameters by response surface methodology

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The synthesis parameters for preparing a novel bio-composite adsorbent by integrating a copolymer of 2-hydroxyethyl methacrylate (HEMA), acrylamide (AM) and crosslinker *N*, *N*′-methylene bis acrylamide (MBA), polyethylene glycol (PEG) and *Azadirachta Indica* or Neem leaf (NL) and the process parameters for its subsequent use for adsorption of Pb(II) ion from water were optimized with central composite design (CCD) of response surface methodology (RSM). The structure of the bio-composite was characterized by FTIR, XRD, TGA, DMA, FESEM-EDX and PZC analysis. The optimized adsorbent prepared with a AM: HEMA molar ratio of 5:1, MBA, PEG and NL wt% of 0.75, 4 and 2.5, respectively showed 182.85 mg/g (92.5%) adsorption of Pb(II) from water containing low concentration of 50 mg/L of Pb(II) ion and 911 mg/L (57%) adsorption of the same metal ion for a high feed concentration of 400 mg/L in a solution pH of 6, adsorbent dose of 0.25 g/L and a feed temperature of 30 °C. This functional bio-composite may also be suitably used for separation of other metal ions and polar molecules from water.

1. Introduction

In mechanical, chemical and electroplating industries various metals are used (Warshawsky, 1988) but the presence of these heavy metal ions in the environment cause serious pollution because of its toxic and carcinogenic natures. Lead (Pb) is one of the heavy metal ions extensively used in various industries for making different products. However, it is a metabolic poison, enzyme inhibitor and also damages DNA resulting in chromosomal and nuclear aberrations (Iqbal, 2016). Lead is carcinogenic and causes allergic reaction, mental retardation and brain damage (ASTDR, 2012). The maximum toleration limit for Pb(II) in the environment without any harmful effect is only 0.5 mg/L (Aziz et al., 2008). Thus, the removal of toxic and non-biodegradable heavy metals including lead from water is very important to save animals, plants and other form of lives. Several techniques such as precipitation (Parmar et al., 2009), coagulation (Zeng and Park, 2009), co-precipitation (Bakar et al., 2009), reverse osmosis (Greenlee et al., 2009), ion exchanges (Ostroski et al., 2009) and adsorption (Kursunlu et al., 2009; Vivek Narayanan and Ganesan, 2009) have been employed for the treatment of wastewater containing heavy metal ions. Recently, polymeric adsorbents having numerous functional groups, high surface area and porosity (Azanova and Hradil, 1999) have been employed to remove heavy metal ions from aqueous solutions. Several researchers combined both natural and synthetic polymers in the form of hydrogels (Skardal et al., 2010; Ward et al., 2010) to use it as adsorbent for removing these metal ions. In recent years, bio-materials has also taken much attention for the removal of synthetic dyes or heavy metal ions from the waste water because it contains numerous functional groups such as alcohol, ketone and carboxylic groups which involve in the ion exchange or complexation reactions with metal ions or dye molecules (Sharma and Bhattacharyya, 2005a; Tahir et al., 2017). Further, these biodegradable biomaterials are abundant in nature and thus of low cost. Several biomaterials such as eriobotrya japonica seed, mangifera indica and citrus peel waste have been reported for removal of Cu(II), Pb(II) and Zr(IV), respectively from water (Mushtaq et al., 2016; Nadeem et al., 2016; Bhatti et al., 2016). Bio-waste materials such as peanut waste or rice bran were integrated with several synthetic polymers to form bio-composite based adsorbents (Tahir et al., 2017; Bhatti et al., 2017). Neem leaf (NL) is a biomaterial having numerous functional groups such as —OH, —NH$_2$ ≡CH, >C=N<, ≡C—C≡, ≡C—N<, ≡C—O—, >C=O, >C=C<

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and >C=S.

Neem trees (*Azadirachta Indica*), the source of neem leaves (NL) are abundant throughout the world including India with as many as 14 million trees growing in India (Ahmaruzzaman and Gayatri, 2011). Accordingly, NL powder alone has been reported as an adsorbent for removal of low concentration of synthetic dyes, phenols and heavy metal ions like cadmium, nickel and lead from water (Ahmaruzzaman and Gayatri, 2011; Sharma and Bhattacharyya, 2005b; Febriana et al., 2010; Bhattacharyya and Sharma, 2004a). However, for better mechanical stability and regeneration ability it needs chemical modification like its entrapment in the matrix of a mechanically stable functional polymer such as acrylic copolymers.

Among the various acrylic polymers, polyacrylamide and poly (hydroxyl ethyl methacrylate) or poly (HEMA) is biocompatible, nontoxic and the copolymer (CP) of poly (acrylamide-*co*-HEMA) has also been reported as an adsorbent material (Bhattacharyya and Ray, 2014). Similarly, another bio compatible non-toxic functional polymer PEG has also been used to prepare adsorbent (Bhattacharyya and Ray, 2015). The objective of the present work was to synthesize a low cost biocompatible and non-toxic bio-adsorbent for removal of low concentration of Pb(II) ion from water. Accordingly, in the present work several biocomposite type hydrogels were prepared by copolymerizing acrylamide (AM) and hydroxyl ethyl methacrylate (HEMA) of varied molar ratios in water containing varied wt% of MBA (crosslinker), PEG and NL. The novelty of the work lies on in-situ entrapment of PEG and NL in the copolymer (CP) matrix during its polymerization which resulted in uniform integration of these three different adsorbents, viz., the CP, NL and PEG into a single functional bio-adsorbent. Further, the various synthesis parameters such as comonomer molar ratios (AM: HEMA) and wt% of MBA, PEG and NL were optimized with respect to adsorption capacity of the resulting adsorbents containing varied amounts of the above ingredients using central composite design (CCD) of response surface methodology (RSM). The adsorbent prepared with optimized synthesis parameters were further used at varied process conditions, i.e., initial feed metal ion concentration, solution pH, dose of gel and contact time. The process parameters were also optimized with similar RSM.

2. Materials and methods

2.1. Materials

Polyethylene glycol (PEG) was purchased from Sigma, USA. Monomers, i.e. acrylamide (AM) and 2-hydroxyethyl methacrylate (HEMA) were purchased from Merck, Darmstadt, Germany. The redox pair of initiators, i.e., Potassium persulfate (KPS) and Sodium metabisulfite (SBS) and crosslinker *N*, *N*-methylenebisacrylamide (MBA), were purchased from Fluka (Buchs, Switzerland). Lead nitrate, $Pb(NO_3)_2$ was of analytical grade and used without any further purification. All other chemicals were also of analytical grade.

2.2. Methods

2.2.1. Treatment of neem leaves (NL)

The mature neem leaves collected from Neem tree were first washed carefully with running water to remove dust and other unwanted particles followed by its drying at ambient condition for few days and then in an air oven at around 80 °C until it became completely dry and crisp. The dry leaves were then crushed and converted to NL powder in a blender. The NL powder was then sieved to obtain fine biomass of around 50–70 μm size and stored for polymerization.

2.2.2. Synthesis of bio-composite adsorbent

A pre-weighed amount of PEG (1–4 g) was added to 50 ml deionized water in a 500 ml glass reactor equipped with a mechanical stirrer and stirred for 20 min at 250 rpm till a clear solution is obtained. The weighed amount (0.5–2 g) of NL powder was then dispersed in the aqueous PEG solution for around 1 h. The reactor was placed in a thermostated water bath to control the reaction temperature at 30 °C. The monomers HEMA, AM and the crosslinker, MBA were simultaneously added and the reaction mixture was stirred for another 15 min. Then the redox pair of initiators, viz., KPS and SBS was added and the polymerization reaction was continued for around 30–40 min till the gel point. The reaction product was then allowed to cool to ambient temperature. The bio-composite gel as synthesized above were poured in to excess ethanol-water mixture for a week with occasional shaking to remove the water soluble uncrosslink and low molecular weight substances from the gel. Finally, the filtered hydrogel was dried in a vacuum oven at 60 °C for 10 h. After grinding by a mortar, the hydrogels were stored in a closed container to protect it from moisture, heat and light.

2.2.3. Characterization of the bio-composite adsorbent

The structure of the bio-composite gels was characterized in terms of detection of functional groups by FTIR spectra in the range 400–4000 cm^{-1} on a FTIR spectrometer (Perkin Elmer, model-Spectrum-2, Singapore) using KBr pellets. The change in crystallinity of PEG after entrapment in the copolymer matrix was characterized by wide angle X-ray diffraction profile (XRD) of the hydrogel samples at 25 °C with a diffractometer (model: X'Pert PRO, made by PANalytical B.V., The Netherlands) using Ni-filtered Cu K_α radiation ($\lambda = 1.542$ Å) and a scanning rate of 0.005 deg (2θ)/s). The angle of diffraction was varied from 5 to 72°. The structure of the adsorbent samples was also evaluated by thermogravimetric analysis (TGA). The samples were heated from 30 to 600 °C at a heating rate of 10 °C per minute. The morphology of this bio-composite adsorbent was evaluated by field emission scanning electron microscopy (FESEM) with the accelerating voltage set to 15 kV. The energy dispersive X-rays analysis (EDX), consisting of a SEM coupled with X-ray was undertaken in order to confirm the presence of Pb(II) ions in the adsorbent after the adsorption experiment. The mechanical strength of the adsorbent sample under dynamic conditions was characterized by a dynamic mechanical analysis (DMA, Perkin Elmer, USA). Point zero charge (PZC) analysis was carried out for the adsorbent samples to analyze the change in ionic charges of its surface functionality in water of a constant pH. Around 50 mg of sample was immersed in 0.1N potassium nitrate solution in a 100 mL conical flask. The initial pH of the solution (pH_i) was adjusted from 2 to 12 by adding 0.1N nitric acid or sodium hydroxide. The sample was kept in this constant pH solution for 48 h to reach equilibrium with occasional shaking. The pH (pH_f) of the supernatant liquid was measured. The difference between these two pH values ($\Delta pH = pH_i - pH_f$) was plotted against initial solution pH (pH_i) and the point of intersection of the curve at $\Delta pH = 0$ gives the value of pH at PZC for the hydrogel.

2.2.4. Adsorption study

Varied concentrations (25–400 mg/L) of Pb(II) ions in deionized water were prepared from $Pb(NO_3)_2$. Around 50 mg adsorbent sample was taken in 50 ml of the above metal ion solutions in a stoppered conical flask and it was mechanically stirred till equilibrium was reached. The sample was then separated by decantation from the solution. The concentration of Pb(II) ion in water before and after addition of the adsorbent sample was determined by flame atomic absorption spectrophotometry (AAS, Double Beam Optics, Thermo Fisher Scientific ICE 3300) with air-acetylene flame