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Sequestration of heavy metal ions by Methionine modified bentonite/Alginate (Meth-bent/Alg): A bionanocomposite

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article info

ABSTRACT

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The present work critically evaluated the role of (Meth-bent/Alg) nanocomposite as an adsorbent for the removal of Pb(II) and Cd(II). The synthesized adsorbent was characterized by SEM, TEM, EDX, XRD, TGA– DTA and FTIR. The equilibrium was attained in 120 min and the optimum pH for adsorption was found 5 and 4 for Pb(II) and Cd(II) respectively. The experimental data is better fitted to pseudo second order kinetics and Freundlich isotherm model with lower value of root mean square error. The adsorption capacities for Pb(II) and Cd(II) obtained from Langmuir isotherm was 30.86 and 217.39 mg g^{-1} at 303 K. The thermodynamic parameter shows the process to be exothermic, spontaneous with increased randomness of the adsorbent. The desorption study shows that 99% of the adsorbed Pb(II) and Cd(II) can be desorbed by using 0.1 M oxalic acid as eluting agent with regeneration capability upto fifth cycle successfully.

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1. Introduction

Due to human non-adherence to environmental laws in their quest for rapid industrialization, veneration of our pristine environment is geometrically diminishing [\(Auta and Hameed, 2013\)](#page--1-0). Water contamination due to toxic heavy metals such as Pb(II), Cd (II), Hg(II), Cu(II) and Ni(II) is hazardous due to its selective toxicity even at low concentration. As per the present scenario, the resources become increasingly limited with the exponentially increasing population; therefore, the need for controlling heavy metal contamination has become wide area of investigation ([Un](#page--1-0)[uabonah et al., 2008](#page--1-0)). Acute exposure to lead can cause brain dysfunction, nausea, vomiting, and chronic exposure can cause anemia, encephalopathy, nephropathy, palsy etc. [Ahmad and Ha](#page--1-0)[seeb \(2013\)](#page--1-0). The permissible limit for Pb(II) in drinking water as set by the EU, USEPA and WHO is 0.010, 0.015 and 0.010 mg L^{-1} , respectively [\(Ahmad and Haseeb, 2013](#page--1-0)). Acute exposure of Cd(II) can cause lung inflammation, and chronic exposure can cause lung cancer, osteomalacia, proteinuria ([Kulkarni and Kaware, 2013\)](#page--1-0). The maximum permissible limit for Cd(II) concentration in drinking water in India is 0.01 mg L^{-1} ([Kulkarni and Kaware, 2013\)](#page--1-0).

A great deal of effort has been devoted for the effective remediation of environmental contaminants and now it is a great challenge for the modern world. Various techniques/methods potentially used for the treatment of heavy metal ions includes precipitation, floatation, oxidation, evaporation, electro-chemical removal, reduction, ion-exchange, filtration, reverse osmosis and adsorption [\(Badruddoza et al., 2013\)](#page--1-0). But due to high efficiency, ease of handling, availability of raw materials, cost effectiveness and low energy consumption; adsorption is generally preferred for the removal of low concentrations of heavy metal ions [\(Yu et al.,](#page--1-0) [2013\)](#page--1-0).

Bentonite, have several advantages used as a support, including its lack of toxicity, chemical reactivity and hydrophilicity. It is a 2:1 type of a clay. Bentonite was modified by the biologically-based ligand, L-methionine, through a simple sorption technique. L-methionine is an interesting non-toxic biomolecule in the heavy metal trapping field because of its amino, carboxylic and thiol ligand side chain ([Faghihian and Nejati-Yazdinejad, 2009](#page--1-0); [Ozturk](#page--1-0) [et al., 2008\)](#page--1-0). The polysaccharide, Sodium alginate, a water-soluble salt of alginic acid, is a natural binary heteropolymer containing varying proportions of 1, 4-linked α -*L*-glutamic acid and β-*D*mannuronic acid units in a pyranose form, arranged in linear blocks ([Kim et al., 2013\)](#page--1-0). Because of its biocompatibility, abundance, environment friendly and relatively low cost compared to other biopolymers, it has been widely used for removal of metal ions from waste water [\(Alboofetileh et al., 2014\)](#page--1-0).

Recently, mentha piperita carbon ([Ahmad and Haseeb, 2013\)](#page--1-0), Fe3O4/CD polymer nanocomposites [\(Badruddoza et al., 2013](#page--1-0)), cysteine modified bentonite [\(Faghihian and Nejati-Yazdinejad,](#page--1-0) [2009\)](#page--1-0), alginate–alumina collagen fibers [\(Kim et al., 2013\)](#page--1-0), natural phosphate as a adsorbent ([Yaacoubi et al., 2014](#page--1-0)), alginate-immobilized bentonite clay ([Tan and Ting, 2014](#page--1-0)), aminated

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polyacrylonitrile nanofiber mats [\(Kampalanonwat and Supaphol,](#page--1-0) [2014\)](#page--1-0), silica aerogel activated carbon nanocomposite [\(Ofomaja](#page--1-0) [et al., 2005\)](#page--1-0), carbon-iron oxide nanocomposite [\(Bajda et al., 2015\)](#page--1-0) have been reported for the removal of heavy metal ions.

The work presented in this paper critically evaluated the role of L-methionine modified bentonite/alginate nanocomposite for the removal of Pb(II) and Cd(II) from aqueous solution. The influence of various factors such as pH, contact time and concentration with respect to temperature of metal ions were also studied. The experimental data were elucidated by using various isotherms model such as Langmuir, Freundlich, Tempkin and D-R model. The data was further applied for pseudo–first and pseudo second kinetics. Thermodynamic parameters such as ΔH° , ΔG° and ΔS° were also calculated. The desorption studies were also carried out to check the regenerative and reusability tendency of the adsorbent. The synthesized nanocomposite was characterized by FTIR, XRD, SEM, EDX, TEM, TGA–DTA techniques.

2. Materials and methods

2.1. Materials

The nitrate salts of lead, cadmium, copper, nickel (99% pure) A. R. Grade were purchased from Merk, India. Sodium alginate and Lmethionine were purchased from CDH, New Delhi. Bentonite was obtained from Sigma-Aldrich (USA). HCl and NaOH (A.R. Grade) were used as received without further purification. The stock solution (1000 mg L^{-1}) were prepared by dissolving the requisite amount of metal nitrate in double distilled water.

2.2. Preparation of adsorbent

Bentonite (10 g) was left for dispersion in 250 ml water at 60 °C for 4 h and then 0.1 M solution of L -methionine prepared in 100 ml was added slowly to bentonite solution and left for stirring for 3 h at 60 °C at 600 rpm for interaction between bentonite and L-methionine. Sodium alginate solution was prepared by dissolving 5 g of sodium alginate in 100 ml of double distilled water with subsequent stirring at 60° C for 2 h until a homogeneous gelly like solution was obtained. The sodium alginate solution prepared in the previous step was gradually added to the modified bentonite solution and this solution was vigorously stirred for approximately 42 h at room temperature. After that, composite was precipitated by addition of acetone (250 mL) and was filtered with subsequent washing with double distilled water. The composite was dried at 100 °C and powdered in mortar for subsequent study.

2.3. Adsorbent characterization

The surface morphology of nanocomposite before and after metal adsorption was examined by scanning electron microscope (model JSM 6510 LV, JEOL, Japan) at 3000 magnification. The SEM analysis was performed after gold-plating of the sample to ensure conductivity. The functional groups present in precursors, nanocomposite and metals adsorbed nanocomposite was analysed in the wave number range of 400–4000 cm^{-1} by Fourier Transform Infrared Spectrophotometer (Perkin Elmer, USA model, Spectrum-BX) using KBr pellets. The elemental analysis or chemical characterization of the nanocomposite was examined using Energy Dispersive X-Ray Spectroscopy (JSM-6510LV). The changes in physical and chemical properties of sample were measured as a function of increasing temperature using Thermo Gravimetric Analysis by Perkin Elmer, STA 6000. The temperature difference between reference and sample was recorded using Differential Thermal Analysis and the differential temperature is plotted against temperature. The area under the DTA peak shows the enthalpy change. The TG/DTA was analysed by Perkin Elmer, STA 6000. The size of the nanocomposite was examined by using Transmission Electron Microscopy (TEM, JEM 2100, JEOL, Japan). The crystallinity of the sample, the XRD patterns of sample was analysed through X-Ray Diffractometer (Siemens D 5005) with Cu kα radiation over a 2θ collection range of 10–80 $^{\circ}$ scanning angle. The concentration of metal ions were analysed using Atomic Absorption Spectrophotometer (GBC 902, Australia). The pH measurements during the experimental work was conducted on pH meter (Perkin Elmer, USA).

2.4. Batch adsorption studies

The studies was conducted in a 250 mL Erlenmeyer flasks containing 20 ml of 50 ppm of metal ion concentration and 0.2 g of adsorbent and the pH was adjusted using 0.5 M NaOH and 0.5 M HCl solution.

2.4.1. Effect of pH and contact time

The effect of solution pH was carried out to find the optimum pH for adsorption of nanocomposite for both Pb(II) and Cd(II) metal ions. The study was conducted in the pH range 1–6. In order to find the equilibrium time for maximum adsorption the effect of contact time was done by varying the time from 5 to 360 min.

2.4.2. Effect of concentration with respect to temperature

The solutions of different concentration (20, 30, 40, 50, 60, 80, and 100 mg L^{-1}) were left on a rotary shaker at 110 rpm at temperature at 30, 40 and 50 °C for 2 h. The capacity of the adsorbent i.e. the amount of the adsorbate adsorbed at equilibrium q_e $(mg g^{-1})$ was evaluated using equation:

$$
q_e = \frac{(C_o - C_e)}{W} \times V
$$

and the adsorption efficiency (%) was calculated using formula:

$$
\% = \frac{(C_o - C_e)}{C_o} \times 100
$$

where;

 C_o and C_e are the initial and equilibrium metal ion concentration in (mg L^{-1}).

 q_e = adsorption capacity (mg g⁻¹).

 $W =$ mass of the dried adsorbent in (g).

V = volume of the metal ion solution (L).

2.5. Point of zero charge

For the investigation of the surface charge, acidic and basic character of the adsorbent, the determination of point of zero charge was also carried out. For this investigation, 0.1 M KCl solution was prepared and its initial pH was adjusted between 2 and 12 then 20 ml of 0.1 M KCl solution was taken in 100 ml conical flask and 0.2 g of adsorbent was added to each flasks and was left for 24 h. The final pH of the solution was measured using pH meter. The graph was plotted between initial pH and Δ pH and the point of zero charge was determined.

2.6. Desorption studies

In order to make the process more feasible and economical, desorption and regeneration studies were also carried out. The desorption was done by using 0.1 M oxalic acid solution.

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