Environmental Technology & Innovation 6 (2016) 11–26

Contents lists available at ScienceDirect

Environmental Technology & Innovation

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

Removal of lead by adsorption with the renewable biopolymer composite of feather (*Dromaius novaehollandiae*) and chitosan (*Agaricus bisporus*)

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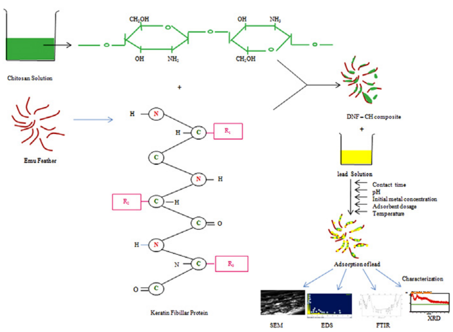
HIGHLIGHTS

- Adsorption equilibrium was achieved within 70 minutes of contact time and followed pseudo second order kinetics.
- The best fit isothermal model is the Langmuir and thermodynamic analysis revealed the process as spontaneous, irreversible and endothermic in nature.
- The maximum adsorption capacity (q_{max}) of the composite found to be 70.42 mg g^{-1}.
- Adsorption mechanism involves one or more of the three types of reactions viz. surface adsorption, complexation and chemisorption.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 November 2015
Received in revised form 20 April 2016
Accepted 27 April 2016
Available online 6 May 2016

Keywords:
Emu
Dromaius novaehollandiae feather (DNF)–chitosan (CH) composite
Adsorption
Lead removal
Aqueous solution

ABSTRACT

Heavy metal pollution of water bodies is an environmental problem of global concern and efforts are being made for their efficient removal using various natural and synthetic materials. Lead is one of the highly toxic metals reaching the water bodies from industries and discarded domestic wastes. Decontamination of the polluted water containing low (<100 ppm) but significantly higher concentrations than the permissible limits, still remains a challenging task. Sensitized with the issue, the present study was undertaken to explore the efficiency of the biopolymer composite synthesized with the feathers of *Dromaius novaehollandiae* (DNF) — a poultry waste and the chitosan (prepared from *Agaricus bisporus*) as constituents, for an economic and eco-friendly removal of lead present in the concentration range of 20–100 mg L^{-1}. With the results of preliminary experiments done by 'one variable at a time method', further experiments have been carried out by a three level full factorial design of Response Surface Methodology (RSM) and consequently

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http://dx.doi.org/10.1016/j.eti.2016.04.004

the optimum conditions for the biosorption of lead have been identified as 6.96 g L^{-1} of adsorbent dosage, 19.77 mg L^{-1} of initial adsorbate concentration and 4.4 pH. The adsorption equilibrium data followed Langmuir isotherm model and pseudo second order kinetics. Analysis of thermodynamic parameters demonstrated the process of adsorption as spontaneous, irreversible and endothermic. Characterization of the adsorbent by SEM–EDS, FTIR and XRD, before and after adsorption, revealed that the adsorption of lead is possibly due to the mechanisms of complexation (between metal and 'N' and 'O' in the composite), chemisorption and ion exchange.

1. Introduction

Human activities such as industrial and mining operations, population increase and urbanization, in addition to unplanned, unscientific disposal methods, are the major contributing factors for rapid increase in the concentrations of heavy metal ions such as lead, copper, zinc, chromium, cobalt, cadmium etc. in the aquifers. Although many heavy metals are necessary in minute quantities for normal metabolism, most of them become toxic at high concentrations. The multitude of activities like mining, smelting, printing, metal plating, explosive manufacturing, dying, and consumer products such as paints, plastics, alloys, batteries, ceramic glass etc. release lead into the environment (Li et al., 2008). All compounds/chemicals containing lead are considered as cumulative poisons (Nadeem et al., 2006). The World Health Organization (2008) pronounced that the concentration of lead should be 10 $\mu g\ L^{-1}$ in drinking water based on the allocation of 50% of the weekly tolerable intake (PTWI) to water. In addition, when present in concentrations beyond the limit of 6 mg L^{-1} in solid food and 1 mg L^{-1} in liquid food (WHO, 1984), the metal enters in to the food chain and gets enhanced at every trophic level, finally affecting the humans (Metcheva et al., 2010; Prasuna Solomon et al., 2012; Chandran et al., 2012; Nazir et al., 2015). Physiological damage to kidney, nervous system, reproductive system, liver and brain are reported in acute exposures, while chronic exposures lead to sterility, abortions, stillbirths and neonatal deaths (Tunali et al., 2006). Therefore, removal of lead prior to discharge by appropriate treatment processes is essential for safeguarding the environment.

Removal of heavy metals from the effluents could be done by conventional/traditional techniques such as ion exchange, filtration and membrane processes, and methods like electro-dialysis and chemical precipitation. But these procedures are inefficient due to high capital investment and operational costs, high sensitivity to operational conditions, significant energy consumption and production of large quantities of wastes. These technical and economical barriers should be evaded through the development of eco-friendly, efficient and low-cost processes. In this regard, sorption is considered as a sustainable technology with the advantages of utilizing naturally available waste products as adsorbents, efficient selectivity for adsorbing metals in low concentrations, easy desorption of metals, recycling of adsorbents etc.

Selection of suitable adsorbents should be based on their sorption capability, abundant local availability, low cost and eco-friendly nature. Avian exo-skeletal elements, the feathers comprising of about 91% keratin, 1.3% fat and 7.9% water, were chosen as the adsorbent material in the present study. Keratin is a self organized heterogeneous protein, consisting of 41% α-helix, 38% β-sheet and 21% disordered structures with a large number of reactive functional groups viz. free carboxyl, hydroxyl and amino groups (Barone and Schmidt, 2006; Gao et al., 2014). Worldwide 8.5 billion tons of feathers are generated annually by poultry processing industries (Agrahari and Wadhwal, 2010). Currently the feathers are disposed off either as landfill or burnt/processed by means which are unfriendly to the environment. In general, the feather fibers are nanoporous and semi-crystalline in nature. The crucial intrinsic properties of the feathers, useful in binding the metal ions, are their stability over a wide range of pH, structural toughness and a high surface area (Kar and Misra, 2004). Chitosan and chitin are carbohydrate derived natural, non-toxic, biocompatible polymers with regeneration capacity and are abundantly available in the exoskeletons of crabs, shrimps and marine zooplankton species. In addition, chitosan is also present in insects' wings and fungal cell walls (Tharanathan and Kittur, 2003). To conserve the biota of aquatic bodies, it is necessary to find agricultural byproducts rich in these biopolymers for commercial utilization. *Agaricus bisporous*, commonly known as button mushroom, is an edible basidiomycete widely used worldwide with an approximate production of about 13.6 million tons per year (Williams et al., 2001; Uzun, 2004). It is estimated that for every kilogram of mushrooms produced, approximately 5 kg of byproducts containing chitosan are generated with no reported commercial value and hence impose an environmental burden of decay and contamination (Cao et al., 2010). These facts prompted the authors to utilize chitosan which could be obtained as a byproduct in mushroom processing for the preparation of the composite material containing free amino, carboxylic and alcohol groups that aid in the removal of heavy metals. Of late, a wide range of natural, synthetic and nano-adsorbents are investigated for the removal of lead, and a few to be mentioned are activated carbon and dried anaerobic sludge (Sulaymon et al., 2013), fungi (Iram and Abrar, 2015), green algae (Jeyakumar and Chandrasekaran, 2014), lentil husk (Basu et al., 2015), leaves of sesame (Liu et al., 2012), *Ficus carica* (Farhan et al., 2013), and *Melia azedarach* L. (Khokhar and Siddique, 2015), core–nanoshell magnetic composites (He et al., 2015), Mg–Al layered double hydroxides/MnO_2 (Bo et al., 2015), 1-alkyl-3-methylimidazolium bromide, ionic liquid mediated mesoporous silica (Ekka et al., 2015), and magnetic chrysotile nanotubes (Yu et al., 2015). Chick, duck and ostrich feathers