Journal of Environmental Management 214 (2018) 315–324

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Research article

Kinetic and thermodynamic studies on the adsorption of heavy metals from aqueous solution by melanin nanopigment obtained from marine source: *Pseudomonas stutzeri*

Vishnu Manirethan, Keyur Raval*, Reju Rajan, Harsha Thaira, Raj Mohan Balakrishnan

Department of Chemical Engineering, National Institute of Technology Karnataka, Mangalore 575025, India

ARTICLE INFO

Article history:
Received 22 September 2017
Received in revised form
23 February 2018
Accepted 23 February 2018

Keywords:
Adsorption
Heavy metals
Isotherms
Melanin
Pseudomonas stutzeri

ABSTRACT

The difficulty in removal of heavy metals at concentrations below 10 mg/L has led to the exploration of efficient adsorbents for removal of heavy metals. The adsorption capacity of biosynthesized melanin for Mercury (Hg(II)), Chromium (Cr(VI)), Lead (Pb(II)) and Copper (Cu(II)) was investigated at different operating conditions like pH, time, initial concentration and temperature. The heavy metals adsorption process was well illustrated by the Lagergren's pseudo-second-order kinetic model and the equilibrium data fitted excellently to Langmuir isotherm. Maximum adsorption capacity obtained from Langmuir isotherm for Hg(II) was 82.4 mg/g, Cr(VI) was 126.9 mg/g, Pb(II) was 147.5 mg/g and Cu(II) was 167.8 mg/g. The thermodynamic parameters revealed that the adsorption of heavy metals on melanin is favorable, spontaneous and endothermic in nature. Binding of heavy metals on melanin surface was proved by Fourier Transform Infrared Spectroscopy (FT-IR) and X-ray Photoelectron Spectroscopy (XPS). Contemplating the results, biosynthesized melanin can be a potential adsorbent for efficient removal of Hg(II), Cr(VI), Pb(II) and Cu(II) ions from aqueous solution.

1. Introduction

Ground water in different parts of the world is contaminated with several heavy metals, which are either result of industrial anthropogenic activities or due to natural factors like mineral deposits in the earth's crust. Heavy metals such as Cu(II), Pb(II) and Cr(VI) precipitates at pH near to or higher than neutral pH and become inseparable from solutions at lower concentrations. Hg(II) precipitates above 6.5, Cu(II) precipitates above pH 5.6 (Al-Rub et al., 2006), Pb(II) above 5.5 (Bradl, 2004) and Cr(VI) at around 8.5 (Sulaymon et al., 2013). Usually, the heavy metal contaminated ground water has acidic to near neutral pH range and therefore the ground water in this pH range has to be treated to remove the heavy metals (Chapman, 1996). Our investigation aims to remove Hg(II), Cr(VI), Pb(II) and Cu(II) from ground water.

Several industrial sources contribute to the Hg(II) pollution such as petrochemicals, batteries, electronics, etc., (Asuquo et al., 2017). Hg(II) being a neurotoxin can damage the nervous system and can also cause pulmonary and nephron related impairment (Fu and Wang, 2011). Cr(VI) is a priority pollutant and has mutagenic and carcinogenic properties as per the U.S. Environmental Protection Agency (EPA) (Sakulthaew et al., 2017). Pb(II) pollution in the environment is through multiple sources such as service pipes, paints, batteries, photographic materials, explosives, etc. (Bachale et al., 2016). It can cause nerve damage, renal break down, convolutions, behavioral changes, etc. (Boudrahem et al., 2011). Cu(II) being an essential element for vital functions, however in an excess can cause toxicological issues which can even be fatal (Paulino et al., 2006). Researchers have investigated various techniques for the removal of heavy metals from wastewater, such as, reduction (Lakshmipathiraj et al., 2008; Shi, 1999), precipitation (Golder et al., 2011; Kongsricharoern and Polprasert, 1995), membrane separation (Gherasim and Bourceanu, 2013; Ho and Poddar, 2001), ion exchange (Kocaoba and Akcin, 2008), biological methods (Park et al., 2005; Sahinkaya et al., 2012), solvent extraction (Salazar et al., 1992), and adsorption (Gherasim and Bourceanu, 2013). Among them, adsorption process is a potent and adaptable method for the treatment of heavy metals at very low metal concentrations and in combination with desorption process, can help to solve sludge disposal problems (Gherasim and Bourceanu, 2013).

* Corresponding author.
E-mail addresses: keyurnraval@nitk.edu.in (K. Raval), rajmohanbala@gmail.com (R.M. Balakrishnan).

https://doi.org/10.1016/j.jenvman.2018.02.084
0301-4797/

Melanin is a heterogeneous polymer derived from the oxidation of amino acid tyrosine. Melanin is chemically and thermally stable, it can resist concentrated acids and its molecular structure is stable till 106.36 °C (Sawhney, 1994). It can be produced and extracted from various sources such as bacteria, fungus, human hair etc., by enzymatic methods or synthetic methods (Sono et al., 2012). Biological and enzymatic methods are more specific and safer than chemical methods. Melanin being a natural polymer is eco-friendly and does not add up to the contamination level of the aqueous medium (Saini and Melo, 2013). Metal ions can easily bind to the functional groups of melanin due to the charge as well as a high surface area of the melanin. The transfer of metal ions from bulk to the solid phase is hence simplified. Melanin is recently scrutinized for its various biological features like metal ion chelation, antioxidant activity, free radical scavenging behavior and photoprotection (Solano, 2014). Studies had been conducted employing squid melanin for the adsorption of Pb(II) and cadmium (Cd(II)) (Chen et al., 2010) and the melanin pigment synthesized using tyrosinase enzyme exhibited efficient removal of uranium from aqueous solution (Saini and Melo, 2013). Purified melanin extracted from *Klebsiella* sp. GSK was used to adsorb Cu(II) and Pb(II) from the aqueous medium (Sajjan et al., 2013). Synthetic eumelanin synthesized by tyrosinase catalyzed polymerization of L-dopa and eumelanin extracted from human hair were used as adsorbents to remove Pb(II) from the aqueous medium (Sono et al., 2012).

This study makes use of biosynthesized melanin nanoparticles extracted from the bacterium *Pseudomonas stutzeri* for efficient removal of Hg(II), Cr(VI), Pb(II) and Cu(II) from the aqueous system. In order to optimize the conditions for efficient adsorption of heavy metals to melanin, the kinetic and thermodynamic parameters of adsorption process are studied and different experimental models are analyzed to understand the nature and behavior of adsorption.

2. Materials and methods

2.1. Materials

All chemicals were of analytical grade (AR) and were procured from Sigma-Aldrich, India unless otherwise specified. Stock solution of 1000 mg/L of Hg(II) was prepared from mercury nitrate monohydrate (≥98%), Cr(VI) from potassium dichromate (≥99%), Pb(II) from lead nitrate (≥99%) and Cu(II) from anhydrous copper sulphate (≥98%) by dissolving required quantity in distilled water. Standard solutions of heavy metals having a concentration range from 5 to 25 mg/L were prepared by diluting the stock solution. A 0.1 N NaOH and 0.1 N HNO_3 were used for pH adjustments. pH of the solution was adjusted using pH meter (HI98130, Hanna Instruments, Romania). Known concentrations of 25 mL heavy metal solution were taken in 250 mL conical flasks for all the adsorption experiments unless otherwise specified.

2.2. Methodology

2.2.1. Biosynthesis of melanin pigment

Pseudomonas stutzeri was obtained from MTCC culture collection, Chandigarh (India). The Pseudomonas strain was originally isolated by Ganesh Kumar et al. (2013). The bacterial colony was inoculated into the Tryptic Soy Broth (TSB) prepared in seawater. After 48 h of incubation, the extracellular black pigment was released by the organism to the medium. The melanin was dissolved in the broth by adding 1N NaOH until pH reached 10 and further autoclaved at 120 °C and 100 kPa for 20 min. The autoclaved solution was centrifuged (6930 series, Kubota, Japan) at 5000 rpm for 10 min and the supernatant was collected. The alkaline pigmented supernatant was acidified to pH less than 2 using 1N HNO_3 and centrifuged at 12,000 rpm for 20 min to harvest the precipitated melanin. The obtained melanin was washed thrice with distilled water followed by three times washing with ethyl alcohol, dried overnight at room temperature and stored at −20 °C (Ganesh Kumar et al., 2013).

2.2.2. Characterization of biosynthesized melanin

2.2.2.1. Morphological characterization and surface chemistry determination. The size and morphology of the biosynthesized melanin were apprehended using Scanning Electron Microscopy (SEM, JSM-6380, JEOL, Japan) and Transmission Electron Microscopy (TEM, JEM-2100, JEOL, Japan). In the case of SEM imaging, the samples were sputter coated with a thin layer of gold before imaging for charge dissipation. For TEM imaging, the biosynthesized melanin was dispersed in distilled water using an ultrasonic bath and a small drop of dispersed sample was placed on a TEM copper grid coated with a thin layer of amorphous carbon. The surface chemistry of the biosynthesized melanin was determined using Fourier-Transform Infrared Spectroscopy (FT-IR). All spectra were documented in the range of 4000-400 cm^{-1} (silicon carbide source, 16 number of scans and 4 cm^{-1} resolution, model Alpha, Bruker, Germany).

2.2.2.2. Particle size analysis of biosynthesized melanin. Particle size analysis of the biosynthesized melanin was done using Nano particle analyzer ('Nanopartica' SZ−100, Horiba Scientific, Japan). Samples were dispersed in distilled water using an ultrasonic bath before introducing into the instrument.

2.2.3. Batch adsorption studies at different pH

Batch adsorption experiments were conducted by adding 0.2 g/L of dried melanin to 10 mg/L sample solutions of Hg(II), Cr(VI), Pb(II) and Cu(II). The pH was adjusted to the desired value using 0.1N NaOH and 0.1N HNO_3. The 25 mL solution in a 250 mL conical flask was then agitated at 200 rpm in an orbital shaker maintained at 318 K. The samples were collected at specific time intervals and centrifuged at 12,000 rpm for 10 min. The residual concentrations of Hg(II), Cr(VI), Pb(II), and Cu(II) were analyzed using Inductively Coupled Plasma − Optical Emission Spectrometer (ICP-OES, Agilent 5100, USA) and the amount of metal ions adsorbed on to the melanin was calculated by using Equation (1) as follows:

$$q_t = (C_0 - C_t) \cdot \frac{V}{W} \quad (1)$$

Where, q_t (mg/g) is the amount of heavy metal ions adsorbed at a given time per unit mass of the adsorbent, C_0 (mg/L) is the initial heavy metal concentration, C_t (mg/L) is the residual heavy metal concentration in solution at equilibrium, V (L) is the sample volume and W (g) is the amount of adsorbent.

2.2.4. Adsorption kinetic and equilibrium studies

Biosynthesized melanin of 0.2 g/L was mixed in individual heavy metal solutions having concentration 5 mg/L and 15 mg/L at 200 rpm and 318 K. Lagergren's pseudo-first-order and pseudo-second-order equations were used to model the kinetics of Hg(II), Cr(VI), Pb(II) and Cu(II) adsorption on melanin (Gupta and Bhattacharyya, 2008). Isotherm studies were conducted by contacting 0.2 g/L of melanin with heavy metal solutions at different concentrations, ranging from 5 to 25 mg/L. Langmuir and Freundlich adsorption isotherm models were used to evaluate the relationship between adsorbed and aqueous concentrations of metal ions at equilibrium.

2.2.4.1. Intra-particle diffusion model. A mechanistic approach to