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Research article

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

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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).

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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 0.1N NaOH and 0.1N 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

explain the sorption kinetics is the intra-particle diffusion model. Generally, adsorption is governed by either external diffusion, pore diffusion, surface diffusion and adsorption on the surface of pores or in combination of these. Intra-particle diffusion of heavy metals to melanin was explored by modelling the intra particle diffusion model. It is a function of adsorption capacity and time as described by Weber and Morris, which is calculated by Equation (2).

$$q_t = k_{id} \cdot t^{0.5} + C \quad (2)$$

where, k_{id} is the intra-particle diffusion rate constant (mg/g $min^{0.5}$), q_t (mg/g) is the amount of metal ions adsorbed at time t, C (mg/g) is the intercept which represents the thickness of the boundary layer.

2.2.4.2. Lagergren's pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order kinetic model is based on the assumption that the adsorption process depends only on the number of metal ions present in the aqueous solution and the available binding sites on the adsorbent at any particular time period (Ho and McKay, 1999). The integrated form of Lagergren's pseudo-first-order kinetic model can be expressed as Equation (3) (Gupta and Bhattacharyya, 2008):

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right) \cdot t \quad (3)$$

Where, q_t and q_e are the amount of metal ions adsorbed (mg) per unit dry weight of adsorbent (g) at any particular time (t) and at equilibrium, respectively, and k_1 is the pseudo-first-order rate constant (min^{-1}). The corresponding values of the k_1 and q_e were calculated from the intercept and slope of the linear plot of log ($q_e - q_t$) versus t.

The pseudo-second-order kinetic model is based on the assumption that the rate controlling step of an adsorption process is chemical adsorption (Acharya et al., 2009; Hadi et al., 2015; Saini and Melo, 2013). The integrated form of Lagergren's pseudo-second-order kinetic model can be expressed as Equation (4) (Ho and McKay, 1999; Gupta and Bhattacharyya, 2008):

$$\frac{t}{q} = \frac{1}{(k_2 \cdot q_e^2)} + \frac{1}{q_e} \cdot t \quad (4)$$

where, k_2 (g/mg/min) is the pseudo-second-order rate constant. k_2 and q_e values were calculated from the intercept and slope of the linear plot of t/q versus t.

2.2.5. Thermodynamic studies

Batch experiments were conducted with 10 mg/L metal ion solutions and mixed with 0.2 g/L of biosynthesized melanin at different temperatures (288 K, 298 K, 308 K, 318 K and 328 K) to evaluate thermodynamics of the adsorption process.

2.2.5.1. Evaluation of thermodynamic parameters. Thermodynamic parameters such as standard Gibb's free energy change (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) change help to identify if the adsorption process is favorable or not. A negative Gibbs free energy change indicates that the adsorption is favorable. These thermodynamic parameters were determined using Equations (5)–(7) as follows:

$$\Delta G^0 = -R \cdot T \cdot lnK_c \quad (5)$$

$$K_c = \frac{C_{Ae}}{C_e} \quad (6)$$

$$lnK_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R \cdot T} \quad (7)$$

where, K_c is the equilibrium constant, C_{Ae} and C_e are the concentration (mg/L) of heavy metals in adsorbent and in solution, respectively, R is the universal gas constant (8.314 J/mol/K) and T is the temperature in Kelvin.

2.2.5.2. Determination of activation energy. The value of activation energy E_a for the sorption process determines tendency of physisorption or chemisorption. The activation energy was determined using Arrhenius equation as follows:

$$\ln k_2 = lnA - \left(\frac{E_a}{R \cdot T}\right) \quad (8)$$

Where, k_2 is pseudo-second-order rate constant, E_a is the activation energy (kJ/mol), T is the temperature in Kelvin and R is the universal gas constant (8.314 J/mol/K).

2.2.6. Adsorption isotherm studies

2.2.6.1. Effect of initial metal ion concentration on adsorption. Batch adsorption studies were conducted by contacting 0.2 g/L melanin with heavy metal solution ranging from concentrations of 5–25 mg/L.

2.2.6.2. Equilibrium modelling. Isotherm helps to describe the interaction between the adsorbent and adsorbate. Several factors such as concentration of metal ions in the solution, their relative adsorbing abilities and the degree of competition among the metal ions to bind to the active sites of adsorbent determine the shape of isotherms. Langmuir isotherm is based on the assumption of adsorption homogeneity such as uniform energy of adsorption with no transmigration of metal ions in the plane of the adsorbent surface, non-interaction between the adsorbed metal ions and availability of all identical binding sites for monolayer adsorption. The linear form of Langmuir isotherm can be expressed as Equation (9) as follows (Dutta et al., 2015):

$$\frac{C_e}{q_e} = \left(\frac{1}{q_{max}}\right) \cdot \left(\frac{1}{b}\right) + \frac{C_e}{q_{max}} \quad (9)$$

Where, C_e (mg/L) is the equilibrium concentration of metal ions, q_e (mg/g) is the amount of metal ions adsorbed per specific amount of adsorbent at equilibrium, q_{max} is the maximum loading capacity, which is the amount of adsorbate required to form monolayer and b is a constant, which represent the affinity of adsorbent to adsorbate.

From the affinity constant b given in Equation (9), a dimensionless constant called separation factor, R_L which helps to define whether the adsorption process is favorable or not was calculated using Equation (10) as follows (Saini and Melo, 2013; Wang et al., 2015b):

$$R_L = \frac{1}{1 + b \cdot C_i} \quad (10)$$

Where, C_i (mg/L) is the initial metal ion concentration. The value of $R_L > 1$ implies unfavorable adsorption process, $R_L = 1$ is linear, $0 < R_L < 1$ represents favorable adsorption process and $R_L = 0$ implies that the adsorption process is irreversible.

Freundlich adsorption isotherm model is based on the assumption that the metal uptake occurs on a heterogeneous surface by multilayer adsorption with the lateral interaction between adsorbed species on the surface of the adsorbent. The linear form of Freundlich isotherm can be expressed using Equation (11) as

follows (Hall et al., 2009; Saini and Melo, 2013):

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \cdot \ln C_e \quad (11)$$

where q_e (mg/g) is the equilibrium metal uptake capacity, C_e (mg/L) is the residual metal ion concentration, $1/n$ and K_F refer to the intensity of adsorption and Freundlich constant, respectively.

2.2.7. FTIR and XPS analysis of heavy metal adsorption on melanin

For FTIR analysis, 25 mL of 10 mg/L of Hg(II), Cr(VI), Pb(II) and Cu(II) solutions were mixed with 0.2 g/L of dry melanin at 318 K. After 24 h of incubation at 200 rpm, melanin was separated from the solutions by centrifugation and the melanin pellet was washed with ethanol and air dried. Melanin powder in distilled water under same conditions was used as a control for analysis. The spectra were analyzed by ATR (Attenuated Total Reflection) method and documented in the range of 4000-400 cm^{-1}. XPS analysis was conducted with melanin equilibrated with individual heavy metal solutions and then dried overnight in vacuum drier at 50 °C. XPS was done with aluminum kα monochrome X-ray source, Axis Ultra model, Kratos Analytics UK.

2.2.8. Statistical analysis

The data obtained from the experimental study was subjected to one way ANOVA to evaluate the effects of pH, temperature and concentration of heavy metals on adsorption with all means and standard deviations expressed in triplicates. All the analysis were done using Minitab 18.1. The statistical significance of difference between the means was determined by comparing the *P*-value with the significance value using null hypothesis. The significance level (α) was taken as 0.05. Further, Tukey's pairwise comparison was conducted to analyze the significant mean and thereby the optimum value of each parameter.

3. Results and discussion

3.1. Characterization of biosynthesized melanin

Figs. 1 and 2 in Data in Brief (Manirethan et al., 2018), shows particle size distribution, zeta potential analysis and TEM image of biosynthesized melanin respectively. Biosynthesized melanin showed a mean particle size of 32 ± 0.98 nm giving a very low polydispersity index. The zeta potential of biosynthesized melanin at pH 5.6 was −83.5 mV. The melanin appeared as spherical particles in the SEM images (Fig. 3 in Data in Brief, Manirethan et al., 2018) and TEM spherical nature of melanin nanoparticle.

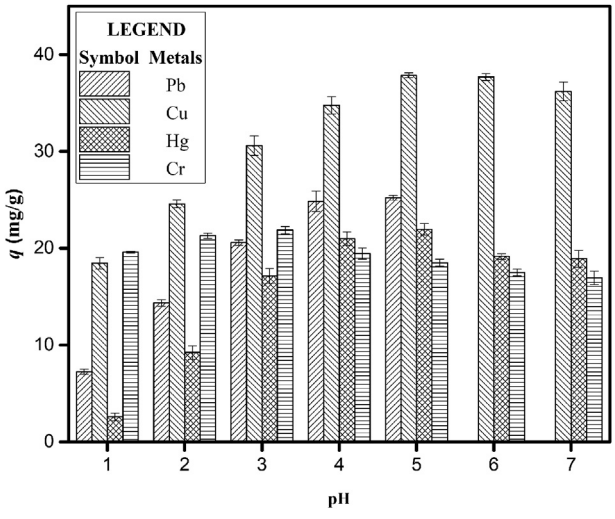

Fig. 1. Effect of pH on heavy metal uptake (C_i = 10 mg/L, W = 0.2 g/L, rpm = 200, shaking diameter = 25 mm).

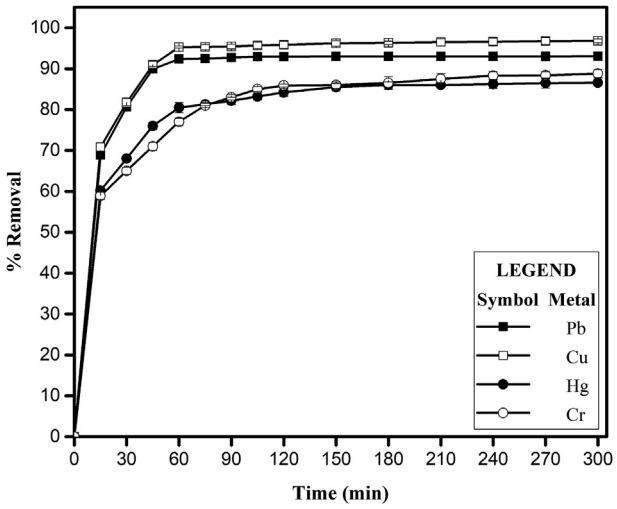

Fig. 2. Effect of contact time on heavy metal uptake (C_i = 10 mg/L, W = 0.2 g/L, rpm = 200, shaking diameter = 25 mm).

3.2. Adsorption studies

3.2.1. Effect of pH

The effect of pH on heavy metal uptake was scrutinized in the range of 1.0–7.0 and the adsorption capacities were calculated using Equation (1). The study was limited to pH 7 since melanin starts to dissolve at alkaline pH. The surface of melanin contains functional groups such as −COOH, −CO, −OH and NH. The mechanism of adsorption is the chelation of metal ions to the functional groups at certain pH. The surface charge of adsorbent, the degree of ionization and speciation of the metal ions are affected by the pH of the solution. The functional groups develop charges based on the solution pH, which makes a physical or chemical interaction with the heavy metals and thereby forms a physical or chemical bond with it (Abdel-Raouf and Abdul-Raheim, 2017). Fig. 1 shows adsorption of different heavy metals onto melanin. Adsorption of heavy metals using melanin depends mainly on the ionic state, the type of functional groups and the metal ion chemistry in solution. The ionization of functional groups depends on the solution acidity (Zhang et al., 2015). The hydronium (H_3O^+) ions present at acidic pH protonate the functional groups in melanin. At pH above 4, the concentration of hydronium ions decreases, resulting in negatively charged functional groups of melanin, to which the Pb(II), Hg(II) and Cu(II) can bind. As the pH increases further, the negative charge decrease leading to the decrease of metal ion binding (Hadi et al., 2015). Effect of pH on Pb(II) adsorption was limited to pH 5 because Pb(II) precipitates to form sparingly stable or highly stable compounds such as $Pb(OH)^+$ above pH 5.5 (Bradl, 2004) (Fig. 12 in Data in Brief, Manirethan et al., 2018).

Hg(II) ions exist as $HgOH^+$ above pH 4 and bind to the negatively charged functional groups of melanin. The dominant form of Hg in solution is Hg(II) at pH value lower than 4 and the functional groups in melanin develop a positive charge at that pH range and hence adsorption of mercuric ions to melanin does not occur. Hence, efficient adsorption of Hg(II) occurred between pH 4 to 6. Considerable binding of Hg(II) to melanin is seen till neutral pH (Arias

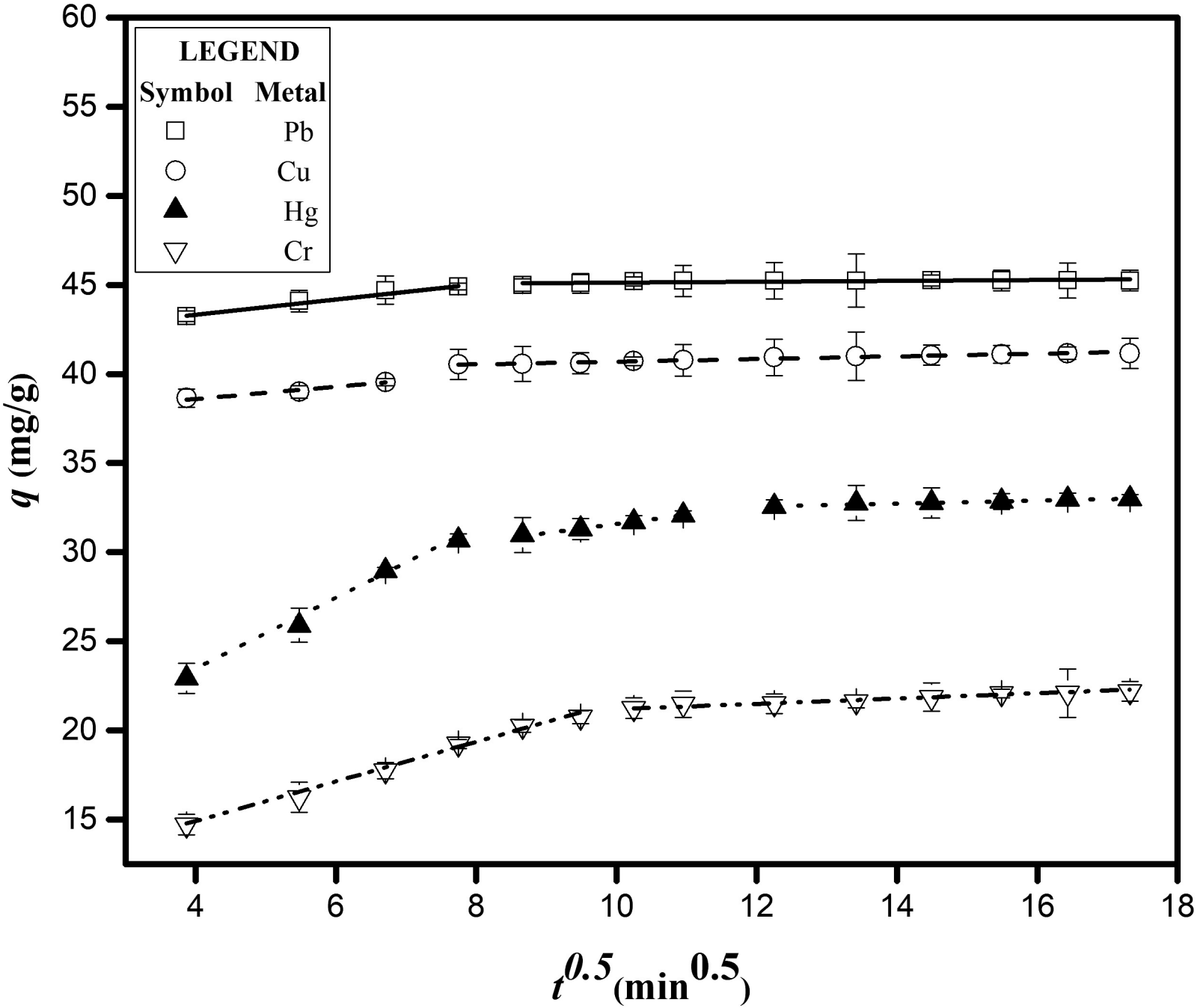

Fig. 3. Intra-particle diffusion model (Ci = 10 mg/L, W = 0.2 g/L, rpm = 200, shaking diameter = 25 mm).

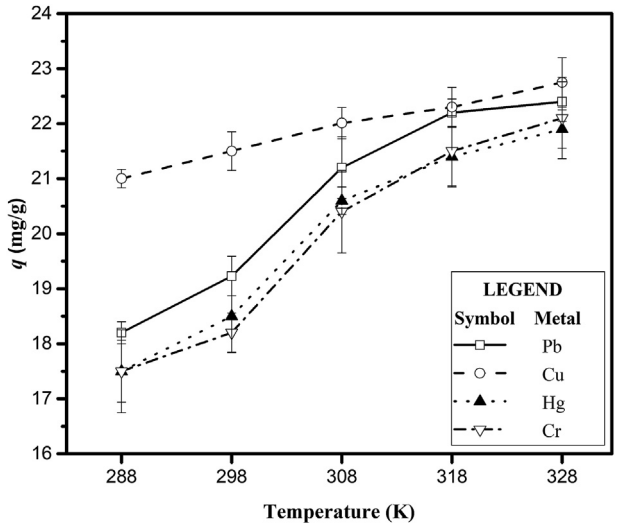

Fig. 4. Effect of temperature on heavy metals uptake ($C_i = 10$ mg/L, W = 0.2 g/L, rpm = 200, shaking diameter = 25 mm).

et al., 2017; Li et al., 2017; Zhang et al., 2018).

Cr(VI) exists as CrO_4^{2-}, $HCrO_4^{1-}$ or $Cr_2O_7^{2-}$ in aqueous solutions and stability of these forms depends on the pH of the solution. Between 2.0 and 6.0 pH, $HCrO_4^{1-}$ and $Cr_2O_7^{2-}$ are predominant ions and as pH increases, the predominant form shift to chromate ion (CrO_4^{2-}) (Baral et al., 2006; Gupta et al., 2010; Yang et al., 2015). From Fig. 1, it is clear that the uptake of Cr(VI) was more at pH 3.0. Lowering of pH lead to the protonation of melanin functional groups to a higher extent and thus the negatively charged (chromate/dichromate) ions in the solution bound to the positively charged functional groups on the surface of melanin. Further, increase in the pH above 3.0 decreased Cr(VI) adsorption due to decreasing net positive surface potential of the melanin. This incited the repulsion of negatively charged Cr(VI) group and COO^- group of melanin. However, a decreasing trend in adsorption was observed at pH less than 2.0 because below pH 2, Cr(VI) predominantly exists as H_2CrO_4 (Karthikeyan et al., 2005). For a low pH value, the amino group in solution get protonated to which the negatively charged chromate group can develop an electrostatic interaction (Vold et al., 2003). As the pH increases, the positive charge of amino group decreases. The lone pair of electrons on the nitrogen of the amino group chelates with the metal ions such as Cu(II), Pb(II) and Hg(II) forming a chelate complex bond between them (Mende et al., 2016).

Above pH 6.0, the decrease in metal uptake was due to the competition between the hydroxyl ions and Cr(VI) ions (Yang et al., 2015; Zhang et al., 2015). However, other mechanisms like physical adsorption also help in the uptake of Cr(VI) above pH 3 (Acharya et al., 2009).

Adsorption of any metal ion on adsorbent depends on its atomic radius, electronegativity and ionization energy. Pb(II) and Cu(II) have higher electronegativity and lower ionization energies to form ions (Table 1 in Data in Brief, Manirethan et al., 2018), thus readily binding to the functional groups in melanin. Higher the electronegativity, stronger will be the attraction to the active sites (Allen and Brown, 1995). Even though Hg(II) has high electronegativity compared to Cr(VI) and Cu(II), its high ionization energy might be the reason for less adsorption on to melanin.

As discussed above, metal adsorption is dependent on pH because different metals exhibit different ionization equilibria at different pH. This affects the adsorption of each heavy metal on any given adsorbent. All adsorbents are adsorbing metals with different efficiency at different pH. Therefore, the adsorbent dose requirement varies to compensate for reduced efficiency. The physisorption is very much sensitive to pH of the solution and therefore, adsorbents based on physical adsorption are required in large quantities. Melanin selectively adsorbs cations because of ionic charge interaction. Therefore, it is able to adsorb the metal ions at lower concentrations. Melanin requirement is also less since it adsorbs heavy metals by chemical adsorption. Melanin adsorbs metal ions at neutral pH with good efficiency, however, at a longer contact time (Saini and Melo, 2013). We observed that melanin was able to adsorb all heavy metals in this study at natural pH but it required 24 h for adsorption. Mass transfer limitations could be the reason behind longer time requirements because we performed experiments at very low initial concentrations par with the ground water heavy metal concentration.

The analysis of variance results showed that the *P*-value for pH was higher than the significance level indicating that the mean adsorption capacities at different pH are not equal and hence the null hypothesis was rejected concluding that the mean value of adsorption capacities are different at different pH. Tukey's test with 95% confidence interval revealed pH 5 for Pb(II), Hg(II) and Cu(II) and pH 3 for Cr(VI) with highest significant mean value.

3.2.2. Effect of contact time on adsorption

Adsorbent - adsorbate contact time required for adsorption process is a crucial factor in the case of adsorption experiments and the results are shown in Fig. 2. Equilibrium state was attained within 3 h of contact time for all metals.

As the figure depicts, the entire adsorption process can be defined by two phases. The first phase corresponds to an initial fast uptake phase, which is due to high concentration gradient and availability of more binding sites on adsorbent. This subsequently reached equilibrium due to decline of the concentration gradient and active metal binding sites deficit (Saini and Melo, 2013). Maximum binding of heavy metals happened within the first 15 min and next 180 min showed a fairly uniform adsorption. Higher initial metal uptake capacity of melanin suggests its potential for efficient heavy metal removal. In order to understand the kinetic mechanism of adsorption, pseudo-first order, pseudo-second order and intra-particle diffusion models were analyzed.

3.2.3. Kinetic modelling of adsorption on melanin

We investigated the controlling mechanism of an adsorption process using intra-particle diffusion model, Lagergren's pseudo-first-order and Lagergren's pseudo-second-order kinetic model.

3.2.3.1. Intra-particle diffusion model. The kinetic data were further analyzed to understand the diffusion mechanism by intra particle diffusion model. According to the Weber and Morris model, the adsorption process is restrained by intra-particle diffusion if the plot of q_t versus $t^{0.5}$ (Equation (2)) is a straight line. They concluded that the adsorption process is controlled by two or more steps if there are multiple linear plots (Doke and Khan, 2017).

Table 1
Isotherm parameters of heavy metal adsorption on Melanin.

Heavy metals	Langmuir isotherm model			Freundlich isotherm model		
	q_m (mg/g)	b (L/mg)	R^2	K_F (mg/g)	1/n	R^2
Hg	82.37	0.57	0.99	26.21	0.49	0.97
Pb	147.49	0.38	0.99	39.36	0.58	0.96
Cr	126.90	0.30	0.99	28.93	0.59	0.97
Cu	167.78	0.41	0.97	43.59	0.48	0.96

The plot of q_t versus $t^{0.5}$ (Fig. 3) for Hg(II), Pb(II), Cu(II) and Cr(VI) adsorption on biosynthesized melanin demonstrated multi-linear plots suggesting that the intra-particle diffusion was not the only rate-limiting step. As seen in Fig. 3, the adsorption of all heavy metals comprised of two phases. The first, phase indicated that mass transfer resistance was limited to the initial stages of adsorption. The initial stages of adsorption process are through the boundary layer diffusion of metal ions from the bulk solution onto the external surface of melanin, whereas the later stages of adsorption are due to the intra-particle diffusion of the metals ions (Fierro et al., 2008). Since the straight line of the second phase of adsorption was not passing through the origin, intra-particle diffusion was not the only rate-limiting step. Therefore, the adsorption data were further analyzed using Lagergren's pseudo-first-order and pseudo-second order kinetic models to evaluate the rate-limiting step (Aly et al., 2014).

3.2.3.2. Lagergren's pseudo-first-order and pseudo-second-order kinetic models. To examine the mechanism of sorption and the rate-limiting steps, the kinetic data of metal ion removal were modelled. The coefficient of determination was evaluated from the experimental data fitted by nonlinear regression analysis in Equations (3) and (4) (Matouq et al., 2015). The parameters of pseudo-first-order and second-order kinetic models are listed in Table 2 in Data in Brief, (Manirethan et al., 2018). The validity of each kinetic model was predicted by comparing the results and it is evident that the experimental data of heavy metal adsorption on the biosynthesized melanin fit well with the pseudo-second-order kinetic model (Fig. 5 in Data in Brief, Manirethan et al., 2018). The coefficient of correlation was higher for pseudo-second order kinetic model than pseudo-first order kinetic model and the predicted q_e values of pseudo-second order model were comparable to the experimental data. Thus validating chemisorption of Hg(II), Pb(II), Cr(VI) and Cu(II) on melanin by exchange or sharing of valence electrons between adsorbent and adsorbate.

3.2.4. Effect of temperature on adsorption

Temperature changes kinetic energy of a molecule and hence it affects chemical adsorption. We investigated the effect of temperature on adsorption of heavy metals on melanin at different temperatures 288, 298, 308, 318 and 328 K and the result are shown in Fig. 4. The study was limited to 328 K since the adsorbent was unstable above 333 K (DSC analysis, data not shown). It is noticeable that, higher temperatures favored adsorption process in case of all studied metal ions, suggesting an endothermic process. The increase in uptake capacity at higher temperature may be due to the increase in collision frequency between the adsorbent and the metal ions (Acharya et al., 2009; Saini and Melo, 2013). With an increase in system temperature, the metals ions attain more kinetic energy to diffuse from the bulk phase of solution to the solid phase of the adsorbent. At higher temperatures, some of the surface components attached with the melanin can get dissociated leading to the generation of more active sites to which the heavy metal can bind (Akpomie et al., 2015).

ANOVA statistics for temperature study have rejected the null hypothesis with the *P*-value less than significance level. Tukey's pairwise comparison test with 95% confidence interval suggested the highest significant mean at 328 K for Hg(II), Pb(II), Cr(VI) and Cu(II) adsorption.

Table 2
One way ANOVA variables and corresponding *P*-values.

Variable	*P*-value			
	Pb	Cu	Hg	Cr
pH	0.001	0.001	0.000	0.000
Temperature	0.000	0.001	0.002	0.001
Concentration of heavy metals	0.000	0.000	0.001	0.000

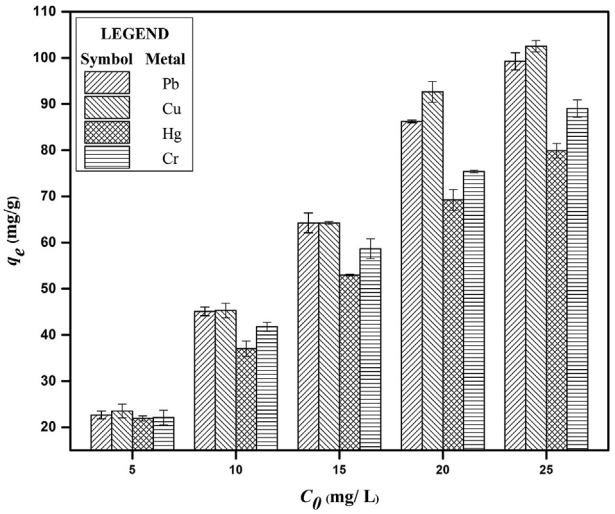

Fig. 5. Effect of initial heavy metal concentration on uptake capacity (C_0 = 5–25 mg/L, W = 0.2 g/L, rpm = 200, shaking diameter = 25 mm).

3.2.4.1. Evaluation of thermodynamic parameters. The change in enthalpy and entropy were calculated from the slope and intercept of the linear plot ln K_c versus *1/T* (Fig. 6 in Data in Brief, Manirethan et al., 2018). From the Van't Hoff equation, the thermodynamic parameters like enthalpy, entropy and Gibbs free energy were calculated using Equations (5)–(7). The obtained thermodynamic parameters are given in Table 3 in Data in Brief, Manirethan et al., 2018.

The negative value of ΔG° at all studied temperatures indicated the thermodynamic feasibility and spontaneous nature of adsorption process. Furthermore, a decrease in the value of ΔG° with the increase in temperature confirmed that at temperatures near 328 K, adsorption was more spontaneous and favorable (Acharya et al., 2009). The positive values of ΔH° suggested that the present adsorption study was endothermic in nature and also positive value of ΔS° indicates increase in randomness at the solid/solution

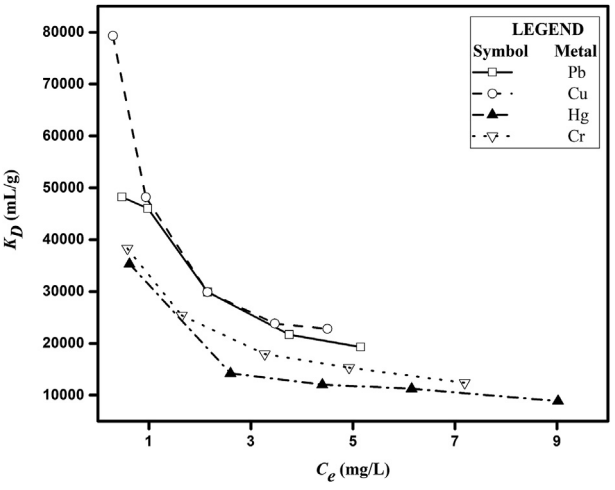

Fig. 6. Distribution coefficient of heavy metals uptake.

interface during the adsorption process (Schneider et al., 2007).

3.2.4.2. Determination of activation energy. The activation energy of heavy metal adsorption on melanin was calculated using Equation (8) and values were 16.3, 19.3, 18.3 and 14.8 kJ/mol for Hg(II), Pb(II), Cr(VI) and Cu(II), respectively (Fig. 7 in Data in Brief, Manirethan et al., 2018). Physical and chemical adsorption are the two types of adsorption process based on the energy requirement for the heavy metals to bind to the adsorbent. The type of adsorption is categorized by the magnitude of activation energy. Physical adsorption involving weak forces of attraction and reversible in nature does not require more than 4.2 kJ/mol of activation energy. Specificity and involvement of strong forces are the characteristic of chemical adsorption and requires more than 4.2 kJ/mol of activation energy. In the adsorption of Hg(II), Cr(VI), Pb(II) and Cu(II), the activation energies were much higher than 4.2 kJ/mol and suggesting a chemical adsorption, which suggests that the adsorption rate increase with the increase in temperature (Kara and Demirbel, 2012).

3.2.5. Adsorption isotherm studies

3.2.5.1. Effect of initial metal ion concentration on adsorption. The adsorption capacity obtained at different initial metal ion concentration for biosynthesized melanin is shown in Fig. 5. Due to increase in the collision frequency between adsorbate and adsorbent, an increase in uptake capacity was observed with the increase of initial metal ion concentration (Saini and Melo, 2013).

The increase in adsorption capacity at higher initial metal ion concentration was due to the higher concentration gradient, which is a driving force to overcome the mass transfer resistance between the bulk aqueous phases to the solid adsorbent phase. The percentage efficiency of adsorption did not increase after a certain concentration of metal ions in the solution because the active sites in melanin is fixed in number and after a certain concentration of metal ions, the active sites get saturated (Akpomie et al., 2015).

From the above experimental data, distribution coefficient, K_D (mL/g) one of the important parameter influencing adsorption was calculated. K_D can be described as the ratio of the equilibrium metal ion concentration in solid and in the aqueous phase (Bhainsa and D'Souza, 2009; Saini and Melo, 2013). K_D value obtained for biosynthesized melanin was plotted against residual metal ion concentration (Fig. 6). Very high values of K_D at a low equilibrium concentration of heavy metals indicate that melanin can adsorb even at very low concentrations.

The statistical analysis of effect of varying metal concentrations on adsorption efficiency using one way ANOVA showed significant difference between the means exists. Interpreting the Tukey pairwise comparison have inferred that 25 mg/L of heavy metals in solution showed maximum adsorption on to melanin. The *P*-values corresponding to ANOVA studies of pH, temperature and concentration are shown in Table 2.

3.2.5.2. Equilibrium modelling. Langmuir isotherm parameters were calculated from Equation (9) by plotting C_e/q_e versus C_e (Fig. 8 in Data in Brief, Manirethan et al., 2018) and are listed in Table 1. The values of R_L calculated from Equation (10) for biosynthesized melanin at different initial metal ion concentrations ranging from 5 to 25 mg/L are in the range of 0–1, suggesting favorable adsorption process.

The parameters of Freundlich isotherm were calculated from Equation (11) by plotting ln q_e versus ln C_e (Fig. 9 in Data in Brief, Manirethan et al., 2018) and are listed in Table 1.

The applicability of Langmuir and Freundlich isotherm models for all metal ions on biosynthesized melanin were assessed from the corresponding isotherm parameters obtained from the respective plots. The experimental data fitted well with higher correlation coefficient for Langmuir isotherm and was compared to Freundlich isotherm. The maximum adsorption capacities obtained for biosynthesized melanin from Langmuir isotherm plot were 82.4, 147.5, 126.9 and 167.8 mg/g for Hg(II), Pb(II) Cr(VI) and Cu(II), respectively. The value of *1/n* for biosynthesized melanin obtained was between 0 and 1 infers that the heavy metal adsorption on melanin is favorable in studied conditions and low *b* value indicates high affinity of heavy metal ions towards melanin (Table 1).

Hence, the biosynthesized melanin having high adsorption capacity and high affinity for Hg(II), Cr(VI), Pb(II) and Cu(II) metal ions at very low concentration can be considered as a promising adsorbent for heavy metal removal. The increase in adsorption capacity with increase in temperature infers that the control mechanism of adsorption is chemisorption. Langmuir isotherm infers that the adsorption of heavy metal ions to melanin is limited to monolayer. The adsorption energy required for binding adsorbate to functional groups in melanin is same for all sites. The adjoining adsorbed metal ions do not interfere with each other and also the occupancy condition of an active site is not affected by another site (Can et al., 2016). The adsorption capacity and the operating parameters of reported adsorbents are compared with the current study (Table 4 in Data in Brief, Manirethan et al., 2018). The maximum adsorption capacity obtained in this study is one of the highest reported so far for all heavy metals except Cu(II).

3.2.6. FT-IR analysis of pure and heavy metal loaded melanin

Fourier-Transform Infrared Spectroscopy was used to detect the vibrational characteristics of functional groups present on the surface of melanin (Fig. 10 in Data in Brief, Manirethan et al., 2018). In the FTIR spectrum of melanin the characteristic absorption band of C–N was identified at wave number 1246.89 cm^{-1}, N–H of the amino group at 1609.52 cm^{-1}, C=O stretching at 1708.09 cm^{-1}, –OH group at 3224.62 and 3330.25 cm^{-1}. Heavy metals have adsorbed by binding to these functional groups. The spectrum of heavy metal bound melanin shown a change in % transmittance indicating that the heavy metals are bound to these functional groups. Increased intensity of C–N stretching peak at wavenumber 1245.60 cm^{-1} indicated binding of Pb(II) to C–N group of melanin. Cu(II), Hg(II) and Cr(VI) binding to C–N group were indicated by an increase in % transmittance of the peak at 1245.90 cm^{-1}, 1238.36 cm^{-1} and 1228.68 cm^{-1} respectively. The transmittance intensity of N–H group at 1609.52 cm^{-1} increased after Pb(II), Hg(II), Cu(II) and Cr(VI) binding, but have shifted to 1601.23, 1617.39, 1611.17 and 1614.84 cm^{-1} respectively. The shifting of peak to higher wavenumber indicates chemisorption of heavy metals to the functional groups. The functional group C=O corresponding to wave number 1708.09 cm^{-1} also shown an increase in % transmittance and a shift to lower frequency of 1703.59, 1702.82, 1701.94 and 1704.88 cm^{-1} after Pb(II), Cu(II), Hg(II) and Cr(VI) binding, respectively. Shifting of peaks to lower wavenumbers can likely be caused by the high electron density induced by the heavy metals bound adjacent functional groups. Increase in intensity of transmittance was observed for –OH bonds corresponding to wavenumbers 3224.62 and 3330.25 cm^{-1} after heavy metal adsorption and the peak at 3330.25 cm^{-1} shifted to 3242.12, 3362.77, 3245.10 and 3213.76 cm^{-1} in case of Pb(II), Cu(II), Hg(II) and Cr(VI) respectively. Shifting of peaks to lower from higher wavenumbers is attributed to the binding of heavy metals to the –OH and –NH functional groups (Sajjan et al., 2013).

The spectra of Cr(VI) and Hg(II) bound melanin showed an increase in % transmittance as compared to the spectra of Pb(II) and Cu(II) bound melanin. Cr(VI) predominantly binds to melanin as negatively charged $HCrO_4^{-1}$ and $Cr_2O_4^{-2}$ groups to positively charged melanin. Hg binds to negatively charged melanin as $HgOH^+$ group.

Meanwhile Cu(II) and Pb(II) bind to negatively charged melanin. Presence of oxygen and hydrogen atoms in the adsorbed complexes of Cr(VI) and Hg(II) may be the reason for increased % transmittance observed (Liao et al., 2002).

3.2.7. X-ray Photoelectron Spectroscopy (XPS)

XPS spectra high resolution scans were studied for Hg(II), Cr(VI), Pb(II) and Cu(II) on biosynthesized before and after adsorption. The spectra studies confirmed the adsorption of Hg 4f, Pb 4f, Cr 2p and Cu 2p on melanin after it was equilibrated with individual solutions of heavy metals (Fig. 11 in Data in Brief, Manirethan et al., 2018).

In case of Hg, binding energy corresponding to $4f_{7/2}$ peak reference is only in the range of 99.9–101.4 eV (Hutson et al., 2007). The reference point of Hg^0 is 99.9 eV. The peaks in XPS data shows a shift from 99.9 eV to 101.34 eV. The Hg 4f lines centered around 101.34 eV indicates that the Hg is in oxidized form (Wang et al., 2015a). It must be inferred that there isn't any Hg^0 since the $4f_{7/2}$ peak at 99.9 eV have shifted and it can be Hg(II) or $HgOH^+$ adsorbed on to melanin. The spectrum analysis of Pb(II) bound melanin has led to the identification of Pb $4f_{7/2}$ at 138.57 eV, which is the characteristic binding energy for Pb(II) ions. The $4f_{5/2}$ peak at 139.75 eV represents the binding energy of Pb, which represents the chemisorbed Pb(II) to the functional groups in melanin (Bertrand and Fleischauer, 1980). The spectrum analysis of Cr(VI) bound melanin has identified a peak Cr $2p_{3/2}$ at 577.56 eV, which was decomposed to three peaks located at 576.35, 577.52 and 579.21 eV. First one corresponds to Cr_2O_3, the second corresponds to $Cr(OH)_3$ and the last corresponds to $Cr_2O_7^{2-}$ (Ithurbide et al., 2007). The XPS results shed light onto the mechanism of Cr(VI) adsorption. Some of the Cr(VI) ions on binding are reduced to Cr(III) ions (Duranoglu et al., 2012). Both, Cr(VI) and Cr(III) are adsorbed to the functional groups of melanin. On analysis of the XPS spectra of Cu(II) bound melanin, two peaks Cu $2p_{3/2}$ and Cu $2p_{1/2}$ with binding energies 934.08 and 954.03 eV were observed, which are characteristic peaks of Cu(II). Cu 2p satellite peak at 942.02 eV is also an indication of Cu(II). The peaks corresponding binding energies at 931.83 and 952.4 eV can be inferred to Cu^0/Cu^+. The binding energies of Cu^0 and Cu^+ are very close, hence the difference cannot be inferred from XPS. From XPS data, it can be confirmed that the Cu(II) on adsorption to functional groups in melanin reduce to Cu^0/Cu^+ (Li et al., 2018).

These results indicate that the melanin nanoparticles from bacterial source are an excellent adsorbent with high adsorption efficiency. Melanin is a natural product with no level of toxicity or hazard. The future scope of the research would include studies on desorption characteristics of heavy metals from melanin. The reusability of melanin will be investigated. Simultaneously, a promising scope would be development of small filter bags using melanin powder. In practical terms, melanin filter bags can be suspended in water to adsorb the heavy metals to make the water potable. Other scope of the research would be development of melanin coated carriers, such as, activated carbon, membranes, alumina etc. These melanin coated carriers will be characterized in terms of important engineering parameters such as, maximum heavy metal binding capacity, desorption characteristics, breakthrough capacity etc. Later, a batch and continuous filter system will be designed for heavy metal remediation as per WHO standard for drinking water.

4. Conclusion

The present investigation sheds light on the promising melanin pigment extracted from gram-negative bacteria *Pseudomonas stutzeri* for adsorption of heavy metals from aqueous solutions. About 32 nm sized melanin particles were obtained from the biosynthesis with very low polydispersity index. Binding of heavy metals on melanin surface was confirmed by FT-IR and results showed that possible functional group responsible for heavy metal adsorption are carboxyl (COOH), amine groups (NH) and phenolic hydroxyl (OH). XPS analysis confirmed the presence and the state of heavy metals adsorbed to the functional groups. Different parameters were studied and the optimum value of pH, time, temperature and mass loading for efficient removal of Hg(II), Cr(VI), Pb(II) and Cu(II) were found. The study revealed that melanin is an excellent adsorbent, which could remove heavy metals within a short time span of 3 h. Melanin efficiently works in the pH range of neutral and mildly acidic which is a desirable quality for an adsorbent for the treatment of ground water. Melanin exhibited excellent adsorption ability even at lower concentrations of heavy metals in solution (10 mg/L) and very low quantity of melanin, in milligrams, is required for the dissolved metal removal. The thermodynamic parameters revealed that the adsorption of heavy metals on melanin was favorable, spontaneous and endothermic in nature.

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References

Abdel-Raouf, M.S., Abdul-Raheim, A.R.M., 2017. Removal of heavy metals from industrial waste water by biomass-based materials: a review. J. Pollut. Eff. Cont. 5, 180.

Acharya, J., Sahu, J.N., Sahoo, B.K., Mohanty, C.R., Meikap, B.C., 2009. Removal of chromium(VI) from wastewater by activated carbon developed from tamarind wood activated with zinc chloride. Chem. Eng. J. 150, 25–39.

Akpomie, K.G., Dawodu, F.A., Adebowale, K.O., 2015. Mechanism on the sorption of heavy metals from binary-solution by a low cost montmorillonite and its desorption potential. Alex. Eng. J. 54, 757–767.

Allen, S.J., Brown, P.A., 1995. Isotherm analyses for single component and multi-component metal sorption onto lignite. J. Chem. Technol. Biotechnol. 62, 17–24.

Aly, Z., Graulet, A., Scales, N., Hanley, T., 2014. Removal of aluminium from aqueous solutions using PAN-based adsorbents: characterisation, kinetics, equilibrium and thermodynamic studies. Environ. Sci. Pollut. Res. 21, 3972–3986.

Al-Rub, F.A., El-Naas, M.H., Ashour, I., Al-Marzouqi, M., 2006. Biosorption of copper on *Chlorella vulgaris* from single, binary and ternary metal aqueous solutions. Process Biochem. 41, 457–464.

Arias, F.E.A., Beneduci, A., Chidichimo, F., Furia, E., Straface, S., 2017. Study of the adsorption of mercury (II) on lignocellulosic materials under static and dynamic conditions. Chemosphere 180, 11–23.

Asuquo, E., Martin, A., Nzerem, P., Siperstein, F., Fan, X., 2017. Adsorption of Cd(II) and Pb(II) ions from aqueous solutions using mesoporous activated carbon adsorbent: equilibrium, kinetics and characterisation studies. J. Environ. Chem. Eng. 5, 679–698.

Bachale, S., Sharma, S., Sharma, A., Verma, S., 2016. Removal of lead (II) from aqueous solution using low cost adsorbent: a review. Int. J. Appl. Res. 2, 523–527.

Baral, S.S., Das, S.N., Rath, P., 2006. Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust. Biochem. Eng. J. 31, 216–222.

Bertrand, P.A., Fleischauer, P.D., 1980. X-ray photoelectron spectroscopy study of the surface adsorption of lead naphthenate. J. Vac. Sci. Technol. 17, 1309–1314.

Bhainsa, K.C., D'Souza, S.F., 2009. Thorium biosorption by *Aspergillus fumigatus*, a filamentous fungal biomass. J. Hazard. Mater 165, 670–676.

Boudrahem, F., Aissani-Benissad, F., Soualah, A., 2011. Adsorption of lead (II) from aqueous solution by using leaves of date trees as an adsorbent. J. Chem. Eng. Data 56, 1804–1812.

Bradl, H.B., 2004. Adsorption of heavy metal ions on soils and soils constituents. J. Colloid Interface Sci. 277, 1–18.

Can, N., Ömür, B.C., Altındal, A., 2016. Modeling of heavy metal ion adsorption isotherms onto metallophthalocyanine film. Sensor. Actuators B Chem. 237,

953–961.
Chapman, D., 1992. Water Quality Assessments. A Guide to the Use of Biota, Sediments and Water in Environmental Monitoring. Chapman & Hall, London, p. 585.
Chen, S., Xue, C., Wang, J., Feng, H., Wang, Y., Ma, Q., Wang, D., 2010. Adsorption of Pb (II) and Cd (II) by squid *Ommastrephes bartrami* melanin. Bioinorg. Chem. Appl. 2009.
Doke, K.M., Khan, E.M., 2017. Equilibrium, kinetic and diffusion mechanism of Cr(VI) adsorption onto activated carbon derived from wood apple shell. Arab. J. Chem. 10, S252–S260.
Duranoglu, D., Trochimczuk, A.W., Beker, U., 2012. Kinetics and thermodynamics of hexavalent chromium adsorption onto activated carbon derived from acrylonitrile-divinylbenzene copolymer. Chem. Eng. J. 187, 193–202.
Dutta, A., Diao, Y., Jain, R., Rene, E.R., Dutta, S., 2015. Adsorption of cadmium from aqueous solutions onto coffee grounds and wheat straw: equilibrium and kinetic study. J. Environ. Eng. 142, C4015014.
Fierro, V., Torné-Fernández, V., Montané, D., Celzard, A., 2008. Adsorption of phenol onto activated carbons having different textural and surface properties. Microporous Mesoporous Mater 111, 276–284.
Fu, F., Wang, Q., 2011. Removal of heavy metal ions from wastewaters: a review. J. Environ. Manag. 92, 407–418.
Ganesh Kumar, C., Sahu, N., Narender Reddy, G., Prasad, R.B.N., Nagesh, N., Kamal, A., 2013. Production of melanin pigment from *Pseudomonas stutzeri* isolated from red seaweed *Hypnea musciformis*. Lett. Appl. Microbiol. 57, 295–302.
Gherasim, C.V., Bourceanu, G., 2013. Removal of chromium (VI) from aqueous solutions using a polyvinyl-chloride inclusion membrane: experimental study and modelling. Chem. Eng. J. 220, 24–34.
Golder, A.K., Chanda, A.K., Samanta, A.N., Ray, S., 2011. Removal of hexavalent chromium by electrochemical reduction-precipitation: investigation of process performance and reaction stoichiometry. Sep. Purif. Technol. 76, 345–350.
Gupta, S.S., Bhattacharyya, K.G., 2008. Immobilization of Pb (II), Cd (II) and Ni (II) ions on kaolinite and montmorillonite surfaces from aqueous medium. J. Environ. Manag. 87, 46–58.
Gupta, V.K., Rastogi, A., Nayak, A., 2010. Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material. J. Colloid Interface Sci. 342, 135–141.
Hadi, P., To, M.H., Hui, C.W., Lin, C.S.K., McKay, G., 2015. Aqueous mercury adsorption by activated carbons. Water Res. 73, 37–55.
Hall, S., Tang, R., Baeyens, J., Dewil, R., 2009. Removing polycyclic aromatic hydrocarbons from water by adsorption on silicagel. Polycycl. Aromat. Compd. 29, 160–183.
Ho, W.S., Poddar, T.K., 2001. New membrane technology for removal and recovery of chromium from waste waters. Environ. Prog. Sustain. Energy 20, 44–52.
Ho, Y.S., McKay, G., 1999. Pseudo-second order model for sorption processes. Process Biochem. 34, 451–465.
Hutson, N.D., Attwood, B.C., Scheckel, K.G., 2007. XAS and XPS characterization of mercury binding on brominated activated carbon. Environ. Sci. Technol. 41, 1747–1752.
Ithurbide, A., Frateur, I., Galtayries, A., Marcus, P., 2007. XPS and flow-cell EQCM study of albumin adsorption on passivated chromium surfaces: influence of potential and pH. Electrochim. Acta 53, 1336–1345.
Kara, A., Demirbel, E., 2012. Kinetic, isotherm and thermodynamic analysis on adsorption of Cr (VI) ions from aqueous solutions by synthesis and characterization of magnetic-poly (divinylbenzene-vinylimidazole) microbeads. Water, Air, Soil Pollut. 223, 2387–2403.
Karthikeyan, T., Rajgopal, S., Miranda, L.R., 2005. Chromium (VI) adsorption from aqueous solution by *Hevea brasilinesis* sawdust activated carbon. J. Hazard. Mater 124, 192–199.
Kocaoba, S., Akcin, G., 2008. A kinetic investigation of removal of chromium from aqueous solutions with a strong cation exchange resin. Monatsh. fur Chem. Mon. 139, 873–879.
Kongsricharoern, N., Polprasert, C., 1995. Electrochemical precipitation of chromium (Cr^{6+}) from an electroplating wastewater. Water Sci. Technol. 31, 109–117.
Lakshmipathiraj, P., Raju, G.B., Basariya, M.R., Parvathy, S., Prabhakar, S., 2008. Removal of Cr (VI) by electrochemical reduction. Sep. Purif. Technol. 60, 96–102.
Li, J., Xing, X., Li, J., Shi, M., Lin, A., Xu, C., Zheng, J., Li, R., 2018. Preparation of thiol-functionalized activated carbon from sewage sludge with coal blending for heavy metal removal from contaminated water. Environ. Pollut. 234, 677–683.
Li, Y., Li, W., Liu, Q., Meng, H., Lu, Y., Li, C., 2017. Alkynyl carbon materials as novel and efficient sorbents for the adsorption of mercury (II) from wastewater. J. Environ. Sci. https://doi.org/10.1016/j.jes.2016.12.016 (in press).
Liao, L.F., Lien, C.F., Shieh, D.L., Chen, M.T., Lin, J.L., 2002. FTIR study of adsorption and photoassisted oxygen isotopic exchange of carbon monoxide, carbon dioxide, carbonate, and formate on TiO_2. J. Phys. Chem. B 106, 11240–11245.
Manirethan, V., Raval, K., Rajan, R., Thaira, H., Balakrishnan, R.M., 2018. Data supporting the adsorption studies of heavy metals from aqueous solution by melanin nanopigment obtained from marine source: Pseudomonas stutzeri. Data in Brief submitted. (In press).
Matouq, M., Jildeh, N., Qtaishat, M., Hindiyeh, M., Al Syouf, M.Q., 2015. The adsorption kinetics and modeling for heavy metals removal from wastewater by moringa pods. J. Environ. Chem. Eng. 3, 775–784.
Mende, M., Schwarz, D., Steinbach, C., Boldt, R., Schwarz, S., 2016. Simultaneous adsorption of heavy metal ions and anions from aqueous solutions on chitosan-investigated by spectrophotometry and SEM-EDX analysis. Colloids Surf. A Physicochem. Eng. Asp. 510, 275–282.
Park, D., Yun, Y.-S., Jo, J.H., Park, J.M., 2005. Mechanism of hexavalent chromium removal by dead fungal biomass of *Aspergillus Niger*. Water Res. 39, 533–540.
Paulino, A.T., Minasse, F.A.S., Guilherme, M.R., Reis, A.V., Muniz, E.C., Nozaki, J., 2006. Novel adsorbent based on silkworm chrysalides for removal of heavy metals from wastewaters. J. Colloid Interface Sci. 301, 479–487.
Sahinkaya, E., Altun, M., Bektas, S., Komnitsas, K., 2012. Bioreduction of Cr (VI) from acidic wastewaters in a sulfidogenic ABR. Min. Eng. 32, 38–44.
Saini, A.S., Melo, J.S., 2013. Biosorption of uranium by melanin: kinetic, equilibrium and thermodynamic studies. Bioresour. Technol. 149, 155–162.
Sajjan, S.S., Anjaneya, O., Kulkarni, G.B., Nayak, A.S., Mashetty, S.B., Karegoudar, T.B., 2013. Properties and functions of melanin pigment from Klebsiella sp. GSK. Korean J. Microbiol. Biotechnol. 41, 60–69.
Sakulthaew, C., Chokejaroenrat, C., Poapolathep, A., Satapanajaru, T., Poapolathep, S., 2017. Hexavalent chromium adsorption from aqueous solution using carbon nano-onions (CNOs). Chemosphere 184, 1168–1174.
Salazar, E., Ortiz, M.I., Urtiaga, A.M., Irabien, J.A., 1992. Equilibrium and kinetics of chromium (VI) extraction with Aliquat 336. Ind. Eng. Chem. Res. 31, 1516–1522.
Sawhney, S.S., 1994. Thermal stability of melanin. Thermochim. Acta 247, 377–380.
Schneider, R.M., Cavalin, C.F., Barros, M.A.S.D., Tavares, C.R.G., 2007. Adsorption of chromium ions in activated carbon. Chem. Eng. J. 132, 355–362.
Shi, X., 1999. Reduction of chromium (VI) and its relationship to carcinogenesis. J. Toxicol. Environ. Heal. Part B Crit. Rev. 2, 87–104.
Solano, F., 2014. Melanins: skin pigments and much more-types, structural models, biological functions, and formation routes. New J. Sci. 2014.
Sono, K., Lye, D., Moore, C.A., Boyd, W.C., Gorlin, T.A., Belitsky, J.M., 2012. Melanin-based coatings as lead-binding agents. Bioinorg. Chem. Appl. 2012.
Sulaymon, A.H., Mohammed, A.A., Al-Musawi, T.J., 2013. Competitive biosorption of lead, cadmium, copper, and arsenic ions using algae. Environ. Sci. Pollut. Res. Int. 20, 3011–3023.
Vold, I.M.N., Varum, K.M., Guibal, E., Smidsrod, O., 2003. Binding of ions to chitosan-selectivity studies. Carbohydr. Polym. 54, 471–477.
Wang, X.Q., Wang, P., Ning, P., Ma, Y.X., Wang, F., Guo, X.L., Lan, Y., 2015a. Adsorption of gaseous elemental mercury with activated carbon impregnated with ferric chloride. RSC Adv. 5, 24899–24907.
Wang, Y., Liu, D., Lu, J., Huang, J., 2015b. Enhanced adsorption of hexavalent chromium from aqueous solutions on facilely synthesized mesoporous iron-zirconium bimetal oxide. Colloids Surf. A Physicochem. Eng. Asp. 481, 133–142.
Yang, J., Yu, M., Chen, W., 2015. Adsorption of hexavalent chromium from aqueous solution by activated carbon prepared from longan seed: kinetics, equilibrium and thermodynamics. J. Ind. Eng. Chem. 21, 414–422.
Zhang, Q., Liu, N., Cao, Y., Zhang, W., Wei, Y., Feng, L., Jiang, L., 2018. A facile method to prepare dual-functional membrane for efficient oil removal and in situ reversible mercury ions adsorption from wastewater. Appl. Surf. Sci. 434, 57–62.
Zhang, Y.J., Ou, J.L., Duan, Z.K., Xing, Z.J., Wang, Y., 2015. Adsorption of Cr (VI) on bamboo bark-based activated carbon in the absence and presence of humic acid. Colloids Surf. A Physicochem. Eng. Asp. 481, 108–116.