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## Potential of *Melaleuca diosmifolia* leaf as a low-cost adsorbent for hexavalent chromium removal from contaminated water bodies

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## ABSTRACT

The present study describes for the first time the utilization of dried twigs of *Melaleuca diosmifolia*, fallen off from the plant, to detoxify and remove hexavalent chromium or Cr(VI) from aqueous systems. Initial characterization by gas chromatography revealed that the selected biomaterial is one of the natural sources of eucalyptol. It constituted high concentrations of reducing compounds (iron, phenols and flavonoids). Batch studies revealed that the biosorbent (5 g L<sup>-1</sup>) was able to remove 97–99.9% of 250 mg L<sup>-1</sup> Cr(VI) at wide-ranging pH (2–10) and temperature (24–48 °C). Adsorption kinetics was well described using the pseudo-second-order kinetic model, while the equilibrium adsorption data were interpreted in terms of the Langmuir isotherm model. The monolayer adsorption capacity was 62.5 mg g<sup>-1</sup>. Both inductively coupled plasma optical emission spectrometry and liquid chromatography analyses of the aqueous and solid phases revealed that the mechanism of Cr(VI) removal was ‘adsorption-coupled reduction’. Scanning electron microscope, infrared spectroscopy and X-ray diffraction analyses of the biosorbent before and after adsorption also confirmed that both adsorption and reduction of Cr(VI) to Cr(III) followed by complexation onto functional groups of the active surface contributed to the removal of Cr(VI) from aqueous solution. The selected biomaterial effectively (99.9%) removed Cr(VI) in lake and sea water samples, highlighting its potential for remediating Cr(VI) in real environmental conditions.

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## 1. Introduction

Hexavalent chromium or Cr(VI) is the most dominant heavy metal in the natural environment, and is highly toxic even when present at negligible concentrations ( $50 \mu\text{g L}^{-1}$ ) in water bodies (Sarkar et al., 2010). Being an anion, Cr(VI) is highly mobile and enters the soil environment easily posing a tremendous risk for groundwater contamination. Cr(VI) has catastrophic health effects on the human body which include respiratory diseases, skin ulceration, nasal irritation and lung cancer. Genotoxicity and carcinogenicity of Cr(VI) has become a serious issue leading to a classification of Cr(VI) as a Group A inhalation carcinogen by US EPA (United States Environmental Protection Agency), and Group I human carcinogen by IARC (International Agency for Research on Cancer) (Sreenivas et al., 2014). Due to its serious impact on the environment and people's health, industrial effluents containing Cr(VI) must be treated as a rule. The maximum permissible limit for Cr(VI) in inland water is  $0.1 \text{ mg L}^{-1}$  and  $0.05 \text{ mg L}^{-1}$  for potable water (Saha et al., 2011; Sreenivas et al., 2014).

Several physical, chemical and biological technologies have been developed and implemented for Cr(VI) remediation. However, high chemical and energy requirement, generation of toxic by-products and incomplete removal limits the wide applicability of these treatment techniques (Saha and Orvig, 2010; Kuppusamy et al., 2016a). Thus, in recent years, sorption has been considered one of the most popular methods where a natural or engineered sorbent material acts as a sink for the contaminant and immobilizes it (Wang and Chen, 2009; Atar et al., 2012; Çolak et al., 2013; Kuppusamy et al., 2016b).

Natural biomaterials such as agricultural or plant wastes are cost-effective for immobilizing toxic environmental contaminants because they are highly accessible, cheap, ecofriendly, and have high adsorptive properties due to their diverse chemical and physical characteristics (Kuppusamy et al., 2015). Also, biomaterials can be modified using a variety of physico-chemical treatments to enhance their sorptive potential by changing surface properties. Recently, many investigators have studied the feasibility of using low-cost and easily available adsorbents such as banana peel (Memon et al., 2009), pomegranate husk carbon (Nemr, 2009), spent activated clay (Weng et al., 2008), rice straw (Gao et al., 2008), sunflower stem (Jain et al., 2009), sugarcane bagasse (Garg et al., 2009), dried water hyacinth roots (Mohanty et al., 2006), activated carbon from tamarind wood (Acharya et al., 2009), ash gourd peel (Sreenivas et al., 2014), activated neem leaves (Babu and Gupta, 2008), etc., for removing Cr(VI) from synthetic wastewater. There are four mechanisms for removing Cr(VI) by biomaterials viz., anionic adsorption, adsorption-coupled reduction, anionic and cationic adsorption, and cationic adsorption (Saha and Orvig, 2010). The search for alternative new, low-cost, efficient biosorbents to replace the commercially available adsorbents is ongoing.

*Melaleuca diosmifolia*, commonly known as green honey myrtle, is a plentiful, cheap and easily available shrub in Australia, and is regarded as an environmental weed in Victoria. It is used as an excellent wind break in South Australian regions and is known to be non-toxic. Since the dried twigs of this plant are thrown away as garbage, this biomaterial can be put to good use as a sorbent for removing toxic metals from industrial effluents. To our knowledge, the use of *M. diosmifolia* as low-cost sorbent for the removal of Cr(VI) from water has not been investigated. With a 'waste to resource' approach, for the first time we used biomaterial from *M. diosmifolia* without

any pretreatment through either physical or chemical means. Biosorption studies were carried out under various parameters such as pH, temperature, adsorbent dosage, contact time and initial Cr(VI) concentration. Kinetic data and sorption equilibrium isotherms were done in batch process, and were analyzed using different models. We also tested the applicability of the selected biomaterial for Cr(VI) removal in real environmental water samples and evaluated its reusability.

## 2. Materials and methods

### 2.1. Materials

Twigs that had fallen off from fully-grown *M. diosmifolia* plants were collected from the road-sides in Mawson Lakes, South Australia during March 2014, washed with Milli-Q water ( $18 \Omega \text{ cm}^{-1}$ , Milli-Q, ELGA labwater, UK) to remove the adhering soil particles, air-dried, ground and sieved to a particle size of nearly 0.5 mm. The powdered material was stored in a desiccator with polythene sealing and used for experiments as needed. Stock solution of the model Cr(VI) compound, potassium dichromate, was prepared in Milli-Q water. NaOH ( $0.1 \text{ mol L}^{-1}$ ) and HCl ( $0.1 \text{ mol L}^{-1}$ ) were employed to adjust the pH. All the chemicals used were of analytical grade purchased from Sigma-Aldrich.

### 2.2. Characterization of biomaterial

#### 2.2.1. Surface area and zeta potential

Specific surface area of the material was measured on a Gemini V surface analyser (Micrometrics Instrument Corp., USA). Zeta potential was measured at different pH by a Malvern Zetasizer Nano instrument (Malvern Instruments, USA).

#### 2.2.2. ICP-MS and GC-MS analyses

The biomaterial was analyzed for total carbon (C) and nitrogen (N) by dry combustion with a Trumac CN analyzer (Leco<sup>®</sup> Corporation, US). Subsequently, portions (0.5 g) of the biomaterial was digested in triplicates with 5 mL *aqua regia* in a Teflon digestion vessel using a microwave accelerated reaction system (CEM-MARS X<sup>®</sup>) as outlined in US EPA method SW 3051. The total elemental (mineral) contents in diluted suspensions of the extracts were determined using a standard reference material (Montana soil SRM 271, certified by National Institute of Standards and Technology) and a blank in an Agilent 7500c (Agilent Technologies, Japan) inductively coupled plasma mass spectrometer (ICP-MS).

Predominant chemical constituents of the biomaterial were estimated by gas chromatography (GC). Briefly, hot water extract of the material was acidified with few drops of conc. HCl, extracted by ultrasonication for 15 min (12 kHz sweep bandwidth, Soniclean pulse swept<sup>®</sup> power ultrasonicator, Soniclean Pty. Ltd., Australia) with ethyl acetate, filtered ( $0.4 \mu\text{m}$  filter) and injected in a GC 5975 VL mass selection detector equipped with triple axis detector (Agilent Technologies, USA). The GC injection port was configured for  $1 \mu\text{L}$  on-column injections, with an initial temperature of  $50^\circ\text{C}$ , held for 5 min, and ramped up to  $260^\circ\text{C}$  in 20 min. The flow rate was  $1.1 \text{ mL min}^{-1}$  with a total run time of 77.5 min. An Agilent HP-5MS capillary column with 5% (v/w) phenyl-substituted methyl siloxane nonpolar stationary phase, cross-linked and double bonded to the capillary wall with excellent thermal stability and low bleed levels was used. The dimensions of the column were  $30 \text{ m} \times 250 \mu\text{m} \times 0.25 \mu\text{m}$ . From the obtained

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