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Research article

Waste *Moringa oleifera* seed pods as green sorbent for efficient removal of toxic aquatic pollutants

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ABSTRACT

In the present study, biosorption of chromium (Cr(VI)) ions and Naphthol blue black (NBB) dye using *Moringa oleifera* seed pods powder (MPP) as green biosorbent was investigated. Three different sizes of MPP viz. fine fraction (< 53 μm), coarse fraction (> 250 μm) and mixed fraction were investigated. The biosorbent was characterized by pHzpc, Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM) in order to get an insight of the surface charge, functional groups, and morphology of the biosorbent, respectively. The biosorption studies were conducted with Cr(VI) and NBB dye and different parameters, such as solution pH, contact time, initial concentration of the pollutant, adsorbent dosage and co-existing ions were examined. Experimental results revealed that the maximum removal of Cr(VI) and NBB dye was observed at pH 1 and 2, respectively and the equilibrium was achieved in ca. 180 min. The removal efficiency of Cr(VI) by fine, mixed and coarse fraction was 91.8, 74.9, 52.6%, respectively, whereas for NBB dye, the removal efficiency for the same fractions was 97.5, 33.6, 18.9%, respectively. The removal efficiency of Cr(VI) and NBB dye was influenced in the presence of competing ions. The biosorption isotherm and kinetic data were best correlated with Langmuir isotherm and pseudo-second order kinetic model, respectively. Column studies were also conducted with MPP by studying different flow rates and adsorbates concentrations to check the practical applicability of MPP in removing target metal and dye pollutants.

1. Introduction

Water resources are highly required by the commercial, agricultural, industrial as well as domestic sectors and among these, agriculture and domestic activities account for more than 70% of worldwide withdrawals of the freshwater (Maina et al., 2016). The type of contaminants of water differs based on their source, for example, in industrial sectors such as leather, textiles as well as foodstuffs, azo dyes are used extensively, and the final concentration of azo dyes found in wastewater is approximately 10–15% (Padhi, 2012). Since dyes can have a detrimental effect on the ecosystem, these are therefore, considered as hazardous pollutants. Moreover, dyes absorb and reflect the sunlight (Reck et al., 2018) thus, these affect the waterbodies in several ways e.g., decreasing the penetration of light, as well as the solubility of the gas in the water and having an impact on the water transparency (Natarajan et al., 2018).

In addition to dyes, heavy metals, present in the wastewater, are another important aquatic pollutant which should be removed from the wastewater. Several sources can be responsible for the presence of heavy metals in water, for example, these can occur naturally or might leach from industrial sites or from domestic wastes into the groundwater. In developed and developing countries, Cr(VI) compounds have a wide range of application, for example for wood preservation, dyeing, paints and pigments, steel fabrication metal refining, wood preservatives, ink, fungicide, textile dyeing, leather tanning and electroplating (Abbas et al., 2014b; Chen et al., 2013). The European Union and U.S. Environmental Protection Agency (USEPA) recommended the discharge water criteria for Cr(VI) to be under 0.05 mg L^{-1} (Hlihor et al., 2017).

Several approaches have been utilized for removing dyes and heavy metals from the wastewater such as advanced oxidation process (Xu et al., 2013), membrane filtration (Xu et al., 2012), and photo-electrochemical process (Sala et al., 2014), etc. Moreover, various techniques, such as, ion exchange, chemical precipitation, membrane

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filtration, adsorption and reverse osmosis have been used for removal of heavy metals (Gunatilake, 2015). However, these methods have some drawbacks such as, generation of toxic by-products, expensive (Mitra et al., 2017), high energy requirements and tedious process, etc. (Shafiq et al., 2018).

In recent years, the focus has been shifted to use sustainable ways to remediate the wastewater. In this scenario, use of biomaterials offers great potential. Biomaterials offer many benefits such as easily accessible, show good adsorption capacity for a variety of pollutants (even at low concentrations), do not require any processing, being environmentally friendly and locally available at very low cost (Cardoso et al., 2017), show selective adsorption for certain contaminants such as metal ions and finally have the potential to be conveniently regenerated (Maina et al., 2016). Several biomaterials have been used for decolorization of dyes such as bagasse fly ash, pith carbon and rice husk (Kannan et al., 2016). However, the success of these adsorbents is limited for treating the industrial effluents. In addition, the equilibrium data obtained from batch experiments are vital but not adequate for real-time process application which indicates the necessity of obtaining engineering data through fixed bed column studies in order to improve from mere laboratory-scale level to the pilot-scale stage.

The *Moringa oleifera* is from the family of the *Moringaceae*, a small size tree native to the Indian sub-continent in sub-Himalayan regions of north-west India and it has been naturalized in the subtropical as well as tropical areas around the world such as Asia, South America, Africa and the Pacific as well as Caribbean Islands (Abdull et al., 2014). *Moringa oleifera* seeds have been used as a coagulant for purifying water (Shan et al., 2017), for instance Carvalho et al. studied the efficiency of seeds for the removal of Acid black 1 and Basic red 2 (de Carvalho et al., 2015), Jafari et al. (Jafari and Mahvi, 2015) and Santos et al. (Souza dos Santos et al., 2016) examined the ability of seeds in the removal of reactive dyes. Reck et al. (2018) did the similar studies for identifying the potential of seeds to remove atrazine. Besides, several other studies have been done using the seeds in order to remove heavy metals from the aqueous media (Khorsand et al., 2017) and removal of organic pollutants from aqueous solutions (Obuseng et al., 2012). However, the pods of seeds are usually regarded as useless. There are few studies reporting the use of *Moringa oleifera* pods as sorbent for removing the organics such as benzene and ethylbenzene (Akhtar et al., 2007), atrazine (Coldebella et al., 2017) and heavy metals such as lead (Tavares et al., 2017), cadmium, copper, manganese, iron, zinc, and magnesium (Maina et al., 2016; Matouq et al., 2015) because of being inexpensive and effective in pollutants removal. However, most of these studies focused on no or only one or two particle sizes/fraction of pod powder. Also, in most of the previous studies, same types of pollutants were studied (either metals or dyes) with no comparison between different types of pollutants (such as metals and dyes). Moreover, most of the studies were limited to batch-scale only and the efficiency of pods powder was not examined in column-scale.

In this study, *Moringa oleifera* seed pod powder (MPP), which is the unexploited part of *M. oleifera* seeds, was used for the removal of two aquatic pollutants, Cr(VI) (metal pollutant) and Naphthol blue black (NBB) dye (organic pollutant). Three different sizes of MPP viz. fine fraction (FF) (< 53 μm), coarse fraction (CF) (> 250 μm) and mixed fraction (MF) were investigated and compared for their efficacy in removing target pollutants. To the best of our knowledge, this is the first study where *Moringa oleifera* seed pod powder in three specific size fractions has been studied for the removal of different types of aquatic pollutants (metal and dye). The biosorbent was characterized by pH_{zpc}, FT-IR, and SEM analyses to gain an insight of physico-chemical properties. The experimental conditions were optimized through batch experiments by studying different parameters, viz. effect of contact time, solution pH, biosorbent dosage, and initial concentration of the adsorbate. In addition, the effect of competing ions on adsorption was also studied and discussed in detail. Finally, fixed bed column studies were performed to know the practical applicability of MPP.

2. Experimental section

Naphthol blue black (NBB), potassium dichromate, phosphoric acid, 1,5-diphenylcarbohydrazide and acetone were purchased from Sigma Aldrich. *Moringa oleifera* seeds were obtained from a seller on eBay.com.

2.1. Moringa seed pod powder (MPP) as biosorbent

M. oleifera seeds were deshelled manually to remove the pods. The pods were washed with deionized water to remove any impurity from the pods and dried in an oven at 45 °C overnight. The washed pods were then ground with the grinder and the obtained *Moringa oleifera* pod powder (MPP) was again washed with deionized water for several times in order to remove the water-soluble impurities. Finally, the washed powder was dried in the oven for 48 h at 45 °C. The washed pod powder was then sieved into different sizes (250 and 53 μm) and three sizes were used (< 53 μm, > 250 μm and pod powder as it is (without sieving)). Samples were characterized using pHzpc, FT-IR, and SEM analyses. For SEM analysis, Zeiss sigma HDVP (Carl Zeiss GmbH, Oberkochen Germany) was used. Different voltages (2–6 kV) at (2.13 kX) magnification was used for taking the images. For FT-IR analysis, Thermo Nicolet Nexus 8700 model (Thermo electron, Madison USA) was used in the range of 400–4000 cm^{-1} at 64 scans and the spectra were recorded.

2.2. Batch adsorption studies

Stock solutions of Cr(VI) and NBB dye were prepared by dissolving an analytical grade of $K_2Cr_2O_7$ and NBB dye, respectively in deionized water. Adsorption studies were conducted via batch mode in polyethylene centrifuge tubes containing 10 mg L^{-1} of Cr(VI) and NBB dye solutions and a desired amount of biosorbent (MPP). Mixture was agitated at a speed of 80 rpm on a roller shaker. The adsorption parameters, such as solution pH (1–10), biosorbent dose (0.25–1.5 g L^{-1}), contact time (0–180 min), initial adsorbate (Cr(VI) and NBB dye) concentration (0.5–100 mg L^{-1}) were studied to optimize the process. The effect of different anions (Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{3-}) and cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) on adsorption was also investigated by the addition of a solution of competing anions and cations at two initial concentrations (25 and 50 mg L^{-1}) into adsorbate (Cr(VI) and NBB dye) solutions with fixed adsorbate concentration (10 mg L^{-1}). The experiments were conducted in duplicate, and the arithmetic mean values were calculated with the standard deviation less than ± 5%. The pH of the solution was adjusted by dropwise addition of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide. During the experiments, only one parameter was studied whereas all the others, that could influence the experiment, were kept constant. The mixture was then agitated for a predetermined period of time and after separation of the solid-liquid phases by centrifugation, filtration of the supernatants was done using 0.42 μm cellulose nitrate membrane filters. For measurement of Cr(VI) concentration in solution before and after adsorption, 1,5-diphenylcarbohydrazide method was applied and λ_{max} 540 nm was used for spectrophotometric measurements of Cr(VI) (Haupt, 1952). Moreover, λ_{max} of 620 nm was used for the spectrophotometric measurement of NBB dye concentration in the liquid phase before and after adsorption (Zazouli et al., 2014).

The adsorption percentage and equilibrium capacity of NBB dye and Cr(VI) by the MPP were measured via the following Eqs. (1) and (2):

$$Adsorption\% = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

$$q_e = \frac{v(C_i - C_e)}{W} \quad (2)$$

where C_i and C_e are the initial and equilibrium concentration of the