Contents lists available at ScienceDirect

Process Safety and Environmental Protection

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

Feasibility test of waste oyster shell powder for water treatment

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ARTICLE INFO

Article history:
Received 23 September 2015
Received in revised form 12 February 2016
Accepted 6 March 2016
Available online 12 March 2016

Keywords:
Oyster shell powder (OSP)
Agarose
Methylene blue (MB)
Carbon nanodots
Metal detection
Water treatment

ABSTRACT

In Korea, the huge amounts of abandoned oyster shells have caused problems including their noxious odor and illegal dumping into the sea. It is an urgent requirement, therefore, to find environmentally safe and profitable uses for waste oyster shells. Although organic and inorganic pollutant removal and biodiesel production by oyster shell powder (OSP) have been reporting recently, its utilization for water-treatment purposes still remains highly blooming to be explored. In the present study, we evaluated methylene blue (MB) removal by OSP in the bath mode, which showed a ~2.0 mg/g removal capacity according to the Langmuir equation and pseudo-first-order kinetics. In continuous one-dimensional column tests, two modes, namely OSP-layer deposition on top of and OSP-encapsulated agarose gel packing in the column, were compared in their different MB-removal mechanisms and removal capacities. In the OSP–agarose gel packing, the breakthrough curves were delayed compared with the case of only-OSP-layer deposition, resulting in a significantly enhanced MB-removal capacity. Further, carbon nanodots-entrapped OSP–agarose gel was colorimetrically detected for the existence of Mn^{2+} or Fe^{3+} ions. As for the bacterial growth effect with OSP adsorbed with MB (OSP–MB), it showed no or little toxicity. Thus, technically, OSP can have potential with unique metal oxides for degradation of organic matter and for killing of pathogens in future advanced water treatment applications.

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http://dx.doi.org/10.1016/j.psep.2016.03.004
0957-5820/

1. Introduction

In water-treatment engineering, advanced adsorption technologies have attracted intensive interest from the academic and industrial sectors due to their usage of low-cost adsorbents and simple protocols (Ali and Gupta, 2006; Ezechi et al., 2015). Among many low-cost adsorbents and beyond the various pretreated ones (Gupta and Suhas, 2009), aquacultural oyster shell is encountering significant problems due to its nasty smell and environmentally damaging mass-abandonment. In fact, huge untreated amounts have been dumped into water bodies in China, Taiwan, and Korea (Hsu, 2009; Wu et al., 2014; Shih and Chang, 2015). In Korea, ~250,000 t are produced annually, of which only ~50% and ~10% is reused in the seeding of oyster beds and as agricultural fertilizer, respectively. Approximately 40% of those 250,000 t of oyster shell waste, therefore, remain to be beneficially up-recycled somehow (Moon et al., 2015).

As a possible solution to the problem of the utilization of oyster shell waste, oyster shell powder (OSP), consisting of ~97% calcium carbonate, has potential applications as a materials filler as well as in the chemical and food industries and biomedical, energy, and environmental fields (Boyjoo et al., 2014). Owing to its low price and basicity, OSP has been employed in environmental areas for stabilization/solidification of heavy metals (As, Pb, and Cu etc.) (Hsu, 2009; Wu et al., 2014; Moon et al., 2015; Ahmad et al., 2012; Ahmad et al., 2014), removal of phosphate (Oladoja et al., 2015; Namasivayam et al., 2005; Chen et al., 2013) and desulfurization (Simón et al., 2010). Secondarily, and very recently, OSP has been earmarked for use in bioenergy production, specifically for recycling of low cost and solid catalysts (Nakatani et al., 2009; Hu et al., 2011; Boro et al., 2012; Rezaei et al., 2013; Sirisomboonchai et al., 2015; Whyte et al., 2015).

In the present study, OSP in the batch and column modes was applied to methylene blue (MB) removal as part of a water treatment application. Some pollutants removal by OPS from aqueous solution was investigated (Table 1), Tsai et al. (2009), reported that MB removal by OSP showed 0.084 mg/g of q_{max} at 25 °C, indicating that different OSP conditions can result in different removal capacity. Further, in the continuous one-dimensional column mode (Lee et al., 2014), it was utilized in the form of column-packed chopped OSP–encapsulated agarose gel fragments. Finally, quantum dot-like carbon nanodots-entrapped OSP–agarose gel film (Gogoi et al., 2015) was tested for detection of heavy metals and for its feasibility, thus, as a filter membrane.

2. Materials and methods

2.1. Materials (chemicals)

In this study, oyster shell powder (OSP, ball-milled, market price <3.36 $/1 L on August 26 2015) was supplied. Methylene blue (MB, $C_{16}H_{18}ClN_3S{\cdot}3H_2O$, MW: 373.90 g/mol) as the model pollutant and low-gelling-temperature agarose for gel preparation with OSP were purchased from Sigma-Aldrich (MO, USA). Also, manganese (2+) chloride tetrahydrate (ACS reagent, ≥98%, MW: 197.91 g/mol) and iron (3+) chloride hexahydrate (ACS reagent, 97%, MW: 270.30 g/mol), as model metal ions detectable in groundwater, also were obtained from Sigma-Aldrich. Carbon nanodots were produced by a polyethylene glycol ultrasonication method modified by Lee et al. (Park et al., 2015). A one-dimensional glass chromatography column (SciLab®Duran) was acquired from DAIHAN Scientific (Korea). Double-distilled water (resistance of 18.2 MΩ cm@25 °C) was utilized in all of the experiments.

2.2. Basic characterizations of OSP

The morphologies and elemental compositions of OSP and MB–adsorbed OSP samples were examined under cold-type field-emission scanning electron microscopy (FE-SEM-4700) with an energy-dispersive X-ray (EDX) spectrometer. For the SEM analysis of *Pseudomonas aeruginosa*, first, a buffer solution (0.2 M monobasic sodium phosphate, 0.2 M dibasic [$Na_2HPO_4{\cdot}7H_2O$] sodium phosphate) was washed completely two times with culture medium. After removal of the buffer solution, 500 μL of 2.5% glutaraldehyde was added, followed by pre-fixation for 1 h at 4 °C. The fixative was removed by washing two times with buffer solution. After removal of the buffer solution, it was fixed for 1 h at room temperature with 500 μL of 1% OsO_4. The fixing solution was removed by a buffer solution twice and de-hydrated by 10 min reaction with ethanol gradient concentrations of 70, 90, 95, and 100%. After evaporation of the ethanol, 500 μL of hexamethyldisilazane was treated for 15 min. The OSP–MB-pre-treated *P. aeruginosa* was then analyzed by E-SEM (environmental-scanning electron microscopy; LEO 1455 VP, Carl Zeiss, Germany).

For confirmation of the crystalline structure, impurities, and identities of the OSP sample, powder X-ray diffraction (XRD) patterns were detected from 3 to 80° at 2θ/degree using powder micro-area X-ray diffractometry (D/MAX-2500; Rigaku, 40 kV and 300 mA). The N_2 gas sorption/desorption data on the OSP was obtained by a gas sorption analyzer (NOVA 4200 Instrument, Florida, USA). Specifically, the Brunauer, Emmett, and Teller (BET) surface area, pore size, and pore volume were obtained. In order to effect organic bonding in the organic functional groups in OSP, pellet-mode Fourier transform infrared (FT-IR) spectrometry was utilized for samples with 90 wt% KBr and 10 wt% OSP. In order to determine the thermal mass loss of OSP, thermogravimetric (TG) analysis/derivative thermogravimetric analysis (dTG) curves were recorded within the 60–1000 °C temperature range at a rate of 10 °C/min by a TG analyzer (TGA; Shinco, TGA-N1000, USA).

2.3. Adsorption isotherms

This study employed 100 mg/L of MB stock solution. Subsequently, the solution was adjusted by dilution with DI water. The entire working volume of MB solution was fixed at 10 mL and room temperature (25 °C). The initial MB solution concentrations prepared were 3, 5, 7, 10, 20, 30, and 50 mg/L, respectively, at 0.02 g of OSP loading for 2 h of stirring which is MB adsorption/desorption equilibrium time. Likewise, 0.1 g of OSP–agarose gel loading at various pHs (2.0, 4.0, 6.0, 8.0, and 10.0) were tested for MB removal capacities after 12 h equilibrium time.

2.4. Kinetic and thermodynamic studies

The adsorption kinetics of MB removal by OSP was carried out by shaking at 30 rpm in a 25 °C water bath according to 0, 0.33, 0.66, 1.0, 2.0, and 3 h. 10 mL of 1, 3, 5, 10, and 20 mg/L MB solution was mixed with 0.02 g of OSP in five glass vials, respectively. The five vial samples per each MB concentration