Ecotoxicology and Environmental Safety 128 (2016) 109–117

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Adsorption of methyl orange from aqueous solution by aminated pumpkin seed powder: Kinetics, isotherms, and thermodynamic studies

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ARTICLE INFO

Article history:
Received 19 October 2015
Received in revised form
1 February 2016
Accepted 2 February 2016
Available online 25 February 2016

Keywords:
Adsorption
Methyl orange
Kinetics
Isotherms
Thermodynamics

ABSTRACT

Present research discussed the utilization of aminated pumpkin seed powder (APSP) as an adsorbent for methyl orange (MO) removal from aqueous solution. Batch sorption experiments were carried to evaluate the influence of pH, initial dye concentration, contact time, and temperature. The APSP was characterized by using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The experimental equilibrium adsorption data were fitted using two two-parameter models (Langmuir and Freundlich) and two three-parameter models (Sips and Toth). Langmuir and Sips isotherms provided the best model for MO adsorption data. The maximum monolayer sorption capacity was found to be 200.3 mg/g based on the Langmuir isotherm model. The pseudo-first-order and pseudo-second-order model equations were used to analyze the kinetic data of the adsorption process and the data was fitted well with the pseudo-second-order kinetic model ($R^2 > 0.97$). The calculated thermodynamic parameters such as ΔG^0, ΔH^0 and ΔS^0 from experimental data showed that the sorption of MO onto APSP was feasible, spontaneous and endothermic in the temperature range 298–318 K. The FTIR results revealed that amine and carboxyl functional groups present on the surface of APSP. The SEM results show that APSP has an irregular and porous surface which is adequate morphology for dye adsorption. Desorption experiments were carried to explore the feasibility of adsorbent regeneration and the adsorbed MO from APSP was desorbed using 0.1 M NaOH with an efficiency of 93.5%. Findings of the present study indicated that APSP can be successfully used for removal of MO from aqueous solution.

1. Introduction

Water pollution due to the release of various toxic chemicals from industrialization and urbanization is a global problem (Gupta et al., 2004). Among the various notorious toxic chemicals, dyes, organics and pharmaceuticals are of highly concerned (Gupta and Nayak, 2012; Gupta et al., 1998, 2011a, 2011b, 2011c, 2012a, 2012b, 2005, 2015a, 2015b). However, industrial effluents released from textile, paint, paper, varnishes, ink, plastics, pulp, cosmetics, tannery, and plastic are one of the key causes of water pollution, since these runoffs comprises highly colored substances. Their discharge into the hydrosphere possesses a significant source of pollution due to their visibility even at very low concentrations. This is due to their recalcitrance nature, giving undesirable color to the water, reducing sunlight penetration, resisting photochemical and biological attack, and their degradation products being toxic or even mutagenic, and carcinogenic (Gupta et al., 2013a, 2013b).

Over 7×10^5 tons and approximately 10,000 different types of dyes and pigments are produced worldwide annually. It is estimated that 10–15% of the dye is lost in the effluent during the dyeing process (Gupta et al., 2011a, 2011b, 2011c). In general, dyes are classified as anionic (direct, acid and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes and vat dyes) (Zheng et al., 2015). Among them, azo dyes (anionic) with the existence of nitrogen-nitrogen double bonds, are considered to be the largest and most versatile class of organic dyes (Netpradit et al., 2004; Gao et al., 2013). But their degradation is difficult due to their complicated aromatic structure and poor biodegradability (Fang et al., 2010). Methyl orange (MO), a typical water-soluble anionic azo dye, with IUPAC name of Sodium 4-[[4-(dimethyl amino) phenyl] diazenyl] benzene sulfonate. MO is commonly present in effluent discharges from textile, food, pharmaceutical, printing and paper manufacturing industries (Cheah et al., 2013). Due to the toxicity and persistence, these discharges can cause a serious threat to physic-chemical properties of fresh water and to aquatic life. Therefore, it is necessary to provide suitable technology for the wastewater treatment.

The conventional methods for the removal of dyes from

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http://dx.doi.org/10.1016/j.ecoenv.2016.02.016
0147-6513/

wastewaters include coagulation and flocculation (Panswad and Wongchaisuwan, 1986), oxidation or ozonation (Malik and Saha, 2003; Koch et al., 2002), membrane separation (Ciardelli et al., 2000). However, most of these techniques suffer from high operating cost and sludge generation. Adsorption is one of the most successful technique for color removal from wastewater among all the techniques so far developed for dye removal (Ali and Gupta, 2007; Gupta et al., 2009). The major advantages of adsorption over conventional treatment methods include; low cost, ease of operation, high efficiency, minimization of chemical or biological sludge, no additional nutrient requirement, regeneration of biosorbent and possibility of sorbate recovery (Saleh et al., 2011; Khani et al., 2010; Gupta et al., 2011a, 2011b, 2011c, 2012a, 2012b). The agricultural and forestry products have a great potential to be used as biosorbents. Some of the reported low cost biosorbents include palm ash (Ahmad et al., 2007), de-oiled soya (Mittal et al., 2005), broad bean peels (Hameed and EI-Khaiary, 2008), durian peel (Hameed and Hakimi, 2008), rice husk (McKay et al., 1999), almond shell (Senturk et al., 2010) and neem sawdust (Khattri and Singh, 2000), etc. These types of biosorbents contain polysaccharides and proteins having various functional groups such as carboxyl, hydroxyl, and phosphates (Bharathi and Ramesh, 2013; Asgher, 2012). The biosorption of dye molecules by these materials might be associated with these functional groups.

Pumpkin, a gourd-like squash of *Cucurbitaceae's* family, is one of the widely cultivated plant species for its fruit. The fruit of pumpkin is one the most important vegetables in traditional agricultural systems in the world. The fruit represents rich sources of pectin-type dietary fiber, antioxidants (carotenoids), vitamins (C, E, B6, K, thiamine, and riboflavin), and minerals (potassium, phosphorus, magnesium, iron, zinc and selenium) (Celekli et al., 2014). Pumpkin seeds have been valued as a special source of the mineral zinc, and the World Health Organization recommends their consumption as a good way of obtaining this nutrient. Pumpkin seeds, pumpkin seed extracts, and pumpkin seed oil have long been valued for their anti-microbial benefits, including their anti-fungal and anti-viral properties. Thus, in the present study we have chosen pumpkin seeds as biomass source for manufacturing efficient adsorbent.

Although adsorbents have been regarded as promising materials for pollutant removal, raw adsorbents (without modification) suffer from their low sorption efficiencies. In recent years, increased interest has been focused on enhancing the sorption capacity of biomass by introducing various chemical functional groups (Reddy et al., 2012; Sajab et al., 2013; Kumar et al., 2014). As sorption mainly takes place on the biomass surface, enhancing/activating the binding sites on the surface would be an effective approach for improving the adsorption capacity. Considering the aforesaid reasons in the present study we have chosen pumpkin seeds a raw biomass sources and the surface of biomass was further functionalized to enhance the sorption capacity.

The main objective of the present work is to investigate the potential of APSP as an adsorbent material for the removal of MO from aqueous solutions. The different parameters such as effect of the pH, initial dye concentration, contact time, and temperature that influences the sorption processes of MO onto APSP were evaluated. The isotherm, kinetics as well as thermodynamic parameters for the adsorption of MO onto the APSP were calculated. Characterization of adsorbent was carried using FTIR and SEM analysis.

2. Materials and methods

2.1. Adsorbent preparation and chemical modification

Pumpkin seeds were used as the raw biomass for the preparation of adsorbent, and the seeds were collected from a local market in South Korea. The collected seeds were washed several times with boiled water and finally with deionized water to remove any adhering dirt. It was then oven dried at 70 °C for 24 h to a constant weight. The oven dried seeds were ground well to a fine powder, sieved to 20–30 mesh fractions. This pumpkin seed powder was named as PSP.

The aminated biomass was prepared by employing a reported method (Brady and Duncan, 1994) of esterification. For the preparation of aminated pumpkin seed powder (APSP), 5 g of the well washed raw PSP was suspended in 100 mL of ethanolamine, and 20.8 mL of concentrated hydrochloric (HCl) acid was added to the suspension. The reaction mixture was agitated on a rotary shaker at 150 rpm for 6 h. This treatment was expected to result in the increase of amine groups on the biomass by the ester link to the carboxyl groups via the general equation:

$$\text{Biomass} - \text{COOH} + \text{NH}_2\text{CH}_2\text{CH}_2\text{OH} \overset{\text{HCl, room temp}}{\underset{6\text{h}}{\rightarrow}} \text{Biomas s} - \text{COOCH}_2\text{CH}_2\text{NH}_2 + \text{H}_2\text{O}$$

The chemically treated suspension was then centrifuged and sequentially washed with distilled water. The treated biomass was dried at 60 °C inside a convection oven for 24 h. This treated biomass was named as APSP. The resultant dried APSP was stored in a desiccator, and subsequently used as an adsorbent in the sorption experiments.

2.2. Chemicals and equipment

All chemicals used in this work were of analytical reagent grade and used without purification. Double deionized water (Milli-Q Millipore 18.2 MΩ cm^{-1} conductivity) was used for all dilutions. MO dye [formula weight: $C_{14}H_{14}N_3NaO_3S$, molecular weight: 327.34, λ_{max}: 464 nm] was purchased from Junsei Chemicals, Japan. Working standards were prepared by progressive dilution of the stock MO solution. HCl, NaOH and buffer solutions (Dae Jung Chemicals, Korea) were used to adjust the solution pH. A pH meter (pH-240L, NEOMET, Korea) was used for pH measurements. The pH meter was calibrated using standard buffer solutions of pH 4.0, 7.0 and 10.0. Infrared spectra of the PSP and APSP sample were obtained using Fourier Transform Infrared Spectrometer (BIO-RAD, FTS-135, USA). For IR spectral studies, 10 mg of sample was mixed and ground with 100 mg of KBr and made into a pellet. The background absorbance was measured by busing a pure KBr pellet. The morphology of PSP and APSP was analyzed by Scanning Electron Microscopy (JEOL, JSM-7600F, Japan). The samples were first sputter-coated with homogeneous gold layer and then loaded onto a copper substrate. The dye concentrations in the samples were determined using UV/Vis spectrophotometer (Optizen Pop, Korea) at maximum wavelengths of 464 nm.

2.3. Batch adsorption procedure

The adsorption of MO on the APSP was investigated as an effect of pH, initial dye concentration, contact time, and temperature. 1000 mg/L of MO stock solution was prepared and was used further to obtain a standard solution by appropriate dilution of stock solution. In sorption experiments, 0.05 g of the sorbent was brought into contact with 30 mL of MO solution in a 50 mL falcon tube. The pH values of the solutions were adjusted using small