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Research article

Efficacy of spent black tea for the removal of nitrobenzene from aqueous media

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ABSTRACT

Nitrobenzene (NB) is a kind of persistent organic pollutant. A ubiquitous and cost-effective substance spent black tea (SBT) was investigated for the removal of nitrobenzene from aqueous media. The maximum uptake potential of dried biomass (SBT) for NB was found to be 14.86 mg per gram (q_{max}) in a batch experimental set-up. Equilibration time for NB sorption was about 50 min, and optimal removal efficiency was achieved at a dosage of 2 g/L with an initial concentration of 100 mg/L of NB. Findings revealed that NB uptake increased with an increase in the temperature from 273 K to 353 K. Sorption was also found to be pH sensitive, sorption improved as the pH value changes from alkaline to acidic (from 10 to 2). Different isotherm (Langmuir, Freundlich, Temkin and Dubinin Radushkevich) and kinetic models (pseudo-1st order, pseudo-2nd order and Elovich models) were applied to experimental results; the sorption mechanism was well described by the Freundlich and pseudo-2nd order models. Moreover, Scanning electron micrographs, ATR-FTIR spectra and the results of elemental analysis also supported the efficacy of SBT as an efficient bio-sorbent for the elimination of NB from water.

1. Introduction

Nitrobenzene is widely used as a precursor in many chemical industries. It is consumed in the preparation of certain technologically important products like pesticides, drugs, polymers, textile, explosives and lubricating oils etc. It is also used as a solvent in different chemical reactions. Moreover, it has been frequently used in many consumer products as well, such as for shoe, metal and furniture polishes, in particular inks and dyes, in paints, disinfectants and deodorants etc. (Saxena and Saxena, 2010; Davies, 2003; Basheer, 2018; Naumczyk et al., 1996; Ali and Aboul-Enein, 2006; Ali et al., 2009). However, during various production routes of the aforementioned products, the un-reacted nitrobenzene is expected to be released into the effluents. The major part of it goes untreated and thus discharged as such into the vicinal water bodies. Nitrobenzene is also resistant enough to withstand for a long time in the environment (Davies, 2003) and likely to pose a serious health risk to bionomics.

EPA Cancer Guidelines (U.S. EPA, 1986) have classified nitrobenzene (CAS No. 98-95-3) as “B2 carcinogen”. It can also be categorized as a humanoid carcinogen (Nitrobenzene Carcinogenicity (CAS No. 98-95-3), National Center for Environmental Assessment-Washington Office, Office of Research and Development U.S. Environmental Protection Agency Washington, DC, EPA/600/R-95/100 April 1998 (accessed on December 02, 2016)){Nitrobenzene Carcinogenicity- CAS No. 98-95-3, National Center for Environmental Assessment-Washington Office, Office of Research and Development U.S. Environmental Protection Agency Washington, DC, EPA/600/R-95/100 April 1998 (accessed on December 02, 2016)}. Though no human test data is available, carcinogenicity has been observed in animals. Due to its hazardous nature along with great industrial importance, nitrobenzene has been selected as a model organic compound for the present study.

Wastewater treatment is a global concern and when it comes to organic pollutants, biological treatments are not much rated for organic compounds due to their resilient nature. Thus, physical, chemical, electrochemical and other methods are generally applied (Reza and Abedin, 2011; Chakinala et al., 2008; Rajkumar and Palanivelu, 2004; Ali et al. 2012a, 2018; Ali and Jain, 2004; Dehghani et al., 2016; Burakova et al., 2018). All these methods are effective to a certain extent, but every method has its own pros and cons. However, adsorption is still considered as a low-cost and effective method for the removal of various contaminants from wastewater (Xiang et al., 2018; Ali et al. 2012b, 2014, 2016c, 2017a, 2017b; Sharma and Ali, 2011). Activated carbon is believed to be a renowned and an efficient bio-

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sorbent but due to its higher initial and regeneration cost; economically it is not much suitable. Thus, the need to explore more inexpensive and potential bio-sorbent materials is inevitable. Researchers are investing their efforts to come up with proposals of significant and non-conventional bio-sorbents, both synthetic and natural (Ng et al., 2018; Asfaram et al., 2018; Ali et al. 2015, 2016a, 2016b, 2016d, 2016e; Yousefi, 2018; Dhingra et al., 2018). In an attempt to join this struggle, the potential of "spent black tea" as an unconventional bio-sorbent was tested for the removal of nitrobenzene.

Tea is considered the second largest consumed drink in the world after water (Pirbazari et al., 2015; Girelli et al., 2017). Out of total tea produced and consumed globally, 76–78% is black tea, 20–22% is green, while < 2% is oolong (Z.-M. Wang et al., 2011). The worldwide tea consumption is constantly increasing (for instance; between 2009 and 2013, tea consumption increased by 24% and reach from 3.9 to 4.8 million tons in 2013 (Chang, 2015). In Pakistan, approximately 140–150 thousand tons of tea are being imported every year (GOP. 2011). Hence, being a much-consumed item, spent black tea can be easily available after domestic use, from cafeterias, tea stalls and restaurants etc. And can be used for the adsorptive studies.

The utilization of tea waste/spent tea has been explored for the removal of heavy metals like Pb, Ni, Cr, As etc. (Wasewar et al., 2009; Hossain et al., 2016; Mahvi et al., 2005; Ali et al., 2012a) and for some textile dyes (Zuorro et al., 2013) from water. But tea waste is rarely investigated for the removal of organic solvents/pollutants (Ahmaruzzaman and Gayatri, 2010; Ho et al., 2000) from industrial wastewater.

Adsorption of nitrobenzene so far have been studied using *Moringa oleifera* seeds, furnace ash and slags, organoclays, wetland soil, crop biological waste and some modified substrates like activated sludge, aminated lignin and activated carbons from various sources (Hause et al., 2011; Pan and Guan, 2010; Tavengwa et al., 2016; S. Wang et al., 2010; Yin et al., 2008; D. Wang et al., 2018). To the best of our knowledge, no studies have been reported yet on the removal of nitrobenzene from water/wastewater using spent black tea (SBT) as bio-sorbent. Utilization of SBT, a leftover biomass, will not only reduce the solid waste, but its re-use for the mitigation of industrial effluent will also help in reducing the water pollution.

The recent work is an initial contribution to exploring the effectiveness of SBT as an economic, novel and unconventional bio-sorbent for the removal of nitrobenzene from aqueous media. Optimum conditions for maximum sorption have been investigated. Furthermore, kinetic and isotherm models were applied to assess their validity on the experimental data.

2. Materials and methods

Nitrobenzene (Panreac), Methanol, HPLC grade (Sigma Aldrich), Sodium Hydroxide (Merck) Sodium Chloride (Sigma Aldrich) and Hydrochloric acid (Merck) were the chemicals, used in this study. All the chemicals used during experiments were of analytical grade and used without further purification. Structure of nitrobenzene (adsorbate) is shown in Fig. 1.

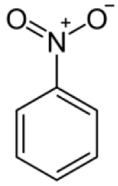

Fig. 1. Structure of nitrobenzene ($C_6H_5NO_2$).

2.1. Adsorbate preparation

All the solutions were prepared using deionized water. A stock solution of nitrobenzene was prepared by adding its certain amount to a specific volume of water. It was then stirred overnight using magnetic stirrer (Lab Tech, MSL-100) for uniform and thorough mixing. Standard solutions of required concentration were further prepared from stock. The pH meter (JENWAY 3510) was used to monitor pH during pH related experiments. An orbital shaker (Wise mix SHO-1D) with a capacity of 6-flasks was used for the adsorption experiments.

2.2. Adsorbent preparation

The bio-sorbent (spent black tea) used in the present study was obtained through the household tea making process. Collected tea waste was washed in boiling water to remove surface impurities, soluble and colored components. It was then repeatedly subjected to rinsing until the rinsed water was colour free. After thorough washing, the adsorbent was sun-dried. Dried and clean tea waste was then ground in a grinder, passed through a sieve and stored in a zip-locked polythene bag for the future use. Particle size was 16–60 mesh.

2.3. Instrumentation

An HPLC (Shimadzu Japan LC-20AT) coupled with a UV detector was used to analyze nitrobenzene (NB) samples before and after treatment. C-18 column (25 cm × 4.6 mm × 5 µm) was used at 280 nm. Methanol-water (70:30, v/v) mixture was a mobile phase; flow rate of1 mL/min was maintained in isocratic mode, while 20 µL sample injection volume was used for each run at 30 °C. Retention time was approximately 9 min.

The surface morphology and elemental composition of spent black tea were explored using scanning electron microscope, (JSM-6490 LA-JEOL Ltd- Tokyo, Japan) coupled with EDS at 20 kV. CNHS analysis was carried out through Vario MICRO cube Elementar.

Functional groups' data for loaded and unloaded bio-sorbent was obtained using Agilent Technologies Cary-630, Attenuated total reflection (ATR) FTIR. The scanning range was from 4000 to 400 cm^{-1}. Point of zero charge (pH_{pzc}) was also determined by means of salt addition method (Anderson and Rubin, 1981).

2.4. Analytical method

Nitrobenzene samples were analyzed using HPLC (before and after sorption). Peak areas obtained for NB standard solutions were used to draw the calibration curve against the initial concentration. This data was further used to determine the equilibrium concentration of nitrobenzene samples during all the experiments.

2.5. Batch adsorption studies

For sorption equilibrium experiments, 500 mg of the bio-sorbent dose was added to 200 mL of NB solution (100 mg/L) into a series of 250 mL Erlenmeyer flasks. Flasks were then fitted in an orbital shaker at 200 rpm for different time intervals (10–150 min). Samples were taken off after a particular time period and the contents were immediately filtered. The obtained filtrate samples were analyzed using HPLC-UV under specific operating conditions. Nitrobenzene uptake from aqueous media was calculated using Eqs. (1) and (2).

$$R(\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

where; initial NB concentration (mg/L) is denoted as C_o, the