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Research article

Rapid and high-performance adsorptive removal of hazardous acridine orange from aqueous environment using *Abelmoschus esculentus* seed powder: Single- and multi-parameter optimization studies

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A B S T R A C T

In this research, the performance of naturally abundant lignocellulosic by-product, *Abelmoschus esculentus*, and its processed seed powder referred as AESP, as a potential biosorbent for the removal of acridine orange (AO) from the aqueous environment was examined. The AESP biosorbent was characterized by field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) analysis, diffuse reflectance spectroscopy (DRS), Fourier transform infrared (FTIR) and pH_{ZPC} analyses. The average size of the biosorbent according to particle size distribution analysis was found to be ~132 µm. The batch adsorption experiments were conducted by altering the parameters such as contact time, solution pH, biosorbent dosage, initial dye concentration, stirring speed and temperature. Sorption of cationic AO dye onto AESP was found to be rapid, and the equilibrium condition reached within 30 min. The isotherms (Langmuir, Freundlich, Redlich-Peterson and Sips), kinetic models (pseudo-first order, pseudo-second order, Elovich, intra-particle diffusion, Bangham and modified-Freundlich models) and thermodynamic parameters were also evaluated. High values of determination coefficients (R^2) and minimal values of non-linear error functions (i.e. HYBRD, RMSE, MPSD, ARE, APE and χ^2) indicated that experimental data were best fitted with Sips isotherm and pseudo-second order kinetic model. Accordingly, the maximum loading capacity of AESP was found to be 259.4, 284.3 and 346.5 mg/g for the temperatures of 15, 30 and 45 °C, respectively. The thermodynamic parameters showed that the adsorption of AO onto the AESP surface was an endothermic and spontaneous process. Besides these, the central composite experimental design (CCD) superimposed with response surface methodology (RSM) modeling was also employed to investigate the effect of four significant parameters (solution pH, contact time, initial AO concentration and AESP dosage) and their interaction-term effects on the adsorption capacity of AESP and to formulate the mathematical model for the experimental data using multi-variate statistical analysis. Maximum dye uptake capacity under the optimum conditions of variables (pH 8.96, contact time 32.06 min, initial dye concentration 867.71 mg/L and AESP dosage 1.89 g/L) was 312.1 mg/g at temperature 30 °C, and it was found to be very close to the experimentally determined values (313.4 ± 0.057 mg/g). The promising reusability potential of AESP using 0.1 M HCl, implied that, the lignocellulosic biosorbent AESP might be helpful for the appropriate designing of the environmental-friendly purification systems.

1. Introduction

In the recent scenario, the environmental pollution caused due to the release of colourant wastewater is one of the foremost concerns. Many industries like textiles, leather, cosmetics, paper, food and mineral processing divisions have regularly employed the dye substances as colouring agents for their production outcome, and subsequently, a huge amount of dye-bearing effluent is heedlessly emitted into the surface water streams without any significant treatment (Gong et al., 2005). From an enormous number of dyes in exercise, the toxic acridine orange (AO) which is a nucleic acid selective fluorescent cationic dye, is of much concern. As

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compared with other dyes, it can be observed that its extensive applications for printing, dyeing leather, lithography and biological staining can cause severe problems in the ecosystem. This is because of its hazardous biological effects (Saetzler et al., 1997). Since they are designed to be chemically stable, less biodegradable and resistant to fading, the treatment of dye bearing effluents has been a challenging task for the environmental scientists (Robinson et al., 2001). Besides these, the toxicological investigations have indicated their mutagenic potential (Dhiman et al., 2017). Thus, the removal of these colourant substances from effluents in an economic way remains as a primary issue in dye handling industries. Various decolourisation techniques used to treat the dye-bearing wastewater include electrochemical oxidation, ion-exchange, photo irradiation, precipitation, reverse osmosis, biological methods (using fungi or bacteria), and many others; however, high operational cost, possibility of secondary pollutant formation, requirement of huge toxic reagents and long processing time limit the implementation of these conventional technologies in large scale (Gupta and Suhas, 2009). In this context, adsorption is considered as an effective treatment technique for removing dyes from industrial wastewater. The reliability and affordability of the adsorption method has further broadened its research scope towards a greener approach by employing the natural biomaterial resources for the treatment process. This is due to their high abundance and renewable feature which are the most important aspects for sustainability development.

In recent years, a variety of natural biomaterials have been used for dye removal (Bhatnagar et al., 2015; Bharathi and Ramesh, 2013). For instance, agricultural materials like oak acorn peel (Kuppusamy et al., 2017), rye straw (Baldikova et al., 2015) and spent coffee grounds (Safarik et al., 2012) were employed to give satisfactory results in the removal of AO dyes from aqueous solution. Thus the continuous investigations are in the limelight to find the novel, cost-effective and efficient alternative biomaterials which are easily available in nearby localities. Moreover, the lignocellulosic materials which are abundantly available in nature, possessed uneven morphology, pores of different sizes, and availability of active functional groups on their surface might have an immense adsorptive potential. In this context *Abelmoschus esculentus* (or lady's finger), which contains an attractive lignocellulosic fibre material could be obtained in large quantity and at low price. It is cultivated in the countries like India, Turkey, Nigeria, and others, under the tropical and subtropical climatic conditions. In 2014, the maximum *A. esculentus* production quantity has been reached up to 6,346,370 tons from 532,660 hectare of harvested land in India, which has a world share of 66.0% (Factfish, 2017). These naturally occurring fibrous materials consisting of cellulose, hemicellulose and lignin constituents are composed of acid functional groups (i.e. hydroxylic, carboxylic and phenolic groups), and they have high affinity towards the cationic dye molecules which help to remove them from their aqueous solution (Nayak and Pal, 2017). Moreover, considering the efficiency and cost, the seeds explored the best adsorption behaviour toward the dye sequestration as compared to other segregated materials (i.e. outer shell and kernel) of *A. esculentus* seed pods. The material was procured from a local market. It is abundantly available and cheap. In continuation with our earlier efforts, this lignocellulosic fiber material has been employed here for the purpose of AO dye removal from the polluted water resources.

However, just the selection of a paramount agricultural-based biosorbent for the removal of harmful dyes may not lead to a well-organized treatment technique. Therefore it is necessary to assemble and optimize the process parameters that acquire desired and efficient results. The conventional system by changing one parameter at a time towards process optimization has become more time consuming and would not correspond to the accurate optimum conditions due to lack of exploring the interaction effects involved in-between the process parameters. These drawbacks of the conventional method can be overcome by simultaneously changing all the influencing parameters by means of a statistical experimental design acknowledged as the response surface methodology (RSM). RSM technique is a collection of mathematical and statistical techniques employed for modeling and designing the experimental system in order to establish the functional relationships between the response variable and a set of independent process variables, and also to optimize the operational conditions through numerical optimization for desired results with minimal number of experimental runs (Khobragade et al., 2016). The incorporation of statistical experimental design approaches in adsorption process can lead to enhanced response outcome, reduced reaction time as well as materials consumption, minimised process changeability and overall operational costs. On the other hand, the importance of the selection of central composite design (CCD) over other existing experimental design models is that, it possesses flexible, robust and efficient properties (Azila et al., 2008).

In view of this, the present research is mainly focused on the investigation on the effectiveness of *A. esculentus* seeds powder (AESP) for the removal of AO dye from aqueous solution in batch operational system. The effects of different process parameters including solution pH, biosorbent dosage, initial dye concentration and contact time were studied. In addition, a detailed kinetics, isotherm and thermodynamic studies of AO dye adsorption have been carried out to examine the adsorption behaviour. The current study has also elucidated the relative significance of the above-mentioned parameters involved on the adsorption process using multiple regression analysis technique in the CCD-RSM modeling.

2. Materials and methods

2.1. Reagents and adsorbate preparation

Acridine orange (AO) (Basic Orange 14; C.I. 46005) was purchased from LOBA Chemie (India). AO showed an intense absorption peak at ~451 nm. A stock solution of AO having concentration 1000 mg/L was prepared using distilled water (DW), and was employed further to acquire the desired dye concentrations by diluting the stock solution. The pH of each solution was adjusted to the desired value by using 0.1 M NaOH or HCl solutions.

2.2. Biosorbent preparation

A. esculentus seed pods were procured from local areas close to the IIT Kharagpur campus. The seeds were segregated manually from each seed pod, and repeatedly washed with tap water and subsequently with deionized water to remove dust and other surface impurities. Further, the wet biomass was dried in an air oven at 60 °C until a constant weight was attained, and finally it was grounded using mortar and pestle in order to increase the surface area and the active functional sites on the biosorbent surface, and finally the fraction of <300 μm was selected for our purpose. The prepared biosorbent (designated as AESP) was kept stored in an air tight container to prevent moisture from environment.

2.3. Instrumentation

UV–Vis spectrophotometer (SPECTRASCAN UV 2600, Chemito, India) was employed to record the absorbance values through a 1-cm well stoppered glass cuvette. A digital pH meter (GENEI, India) was employed for pH measurement. An electronic balance (Afcoset,