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Research article

Efficient removal of Acid Green 25 dye from wastewater using activated *Prunus Dulcis* as biosorbent: Batch and column studies

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Biosorbent synthesized from dead leaves of *Prunus Dulcis* with chemical activation during the synthesis was applied for the removal of Acid Green 25 dye from wastewater. The obtained biosorbent was characterized using Brunauer-Emmett-Teller analysis, Fourier transform-infrared spectroscopy and scanning electron microscopy measurements. It was demonstrated that alkali treatment during the synthesis significantly increased surface area of biosorbent from 67.205 to 426.346 m^2/g. The effect of various operating parameters on dye removal was investigated in batch operation and optimum values of parameters were established as pH of 2, 14 g/L as the dose of natural biosorbent and 6 g/L as the dose of alkali treated biosorbent. Relative error values were determined to check fitting of obtained data to the different kinetic and isotherm models. It was established that pseudo-second order kinetic model and Langmuir isotherm fitted suitably to the obtained batch experimental data. Maximum biosorption capacity values were estimated as 22.68 and 50.79 mg/g for natural biosorbent and for alkali activated *Prunus Dulcis*, respectively. Adsorption was observed as endothermic and activation energy of 6.22 kJ/mol confirmed physical type of adsorption. Column experiments were also conducted to probe the effectiveness of biosorbent for practical applications in continuous operation. Breakthrough parameters were established by studying the effect of biosorbent height, flow rate of dye solution and initial dye concentration on the extent of dye removal. The maximum biosorption capacity under optimized conditions in the column operation was estimated as 28.57 mg/g. Thomas and Yoon-Nelson models were found to be suitably fitted to obtained column data. Reusability study carried out in batch and continuous column operations confirmed that synthesized biosorbent can be used repeatedly for dye removal from wastewater.

1. Introduction

Dyes are color bearing organic compounds which are used to apply color to various substrates such as textile materials, paper, cosmetics and plastics. Dyes impart color to substrate by binding themselves to fabrics or surfaces (Ngulube et al., 2017). Dye uses as colorant in different industries like textile, paper, plastic, etc. are increasing worldwide. About 56% of the annual worldwide production of the total synthetic dyes is consumed by textile industries. During the process of dye production and also dyeing, a large quantity of dye is released/lost into the effluent due to improper handling and/or incomplete dye fixation onto the fabric. Dyes are recalcitrant and stable towards the environment and thus are harmful to human being and living species including microorganisms (Moussavi and Khosravi, 2011). Some of the dyes are also carcinogenic and teratogenic offering significant risk to the aquatic species and human beings (Song et al., 2017). Presence of dyes in the effluents also reduces the photosynthetic activity of aquatic plants and thus disturbs the equilibrium of nature. Dyes also impart bad taste and give significant odor to water bodies (Santos et al., 2017; Subramaniam and Ponnusamy, 2015). Severe health disorders in terms of dysfunction of liver, kidney and nervous system can be caused by dyes (Zhou et al., 2015). Discharge of dye effluents directly into the water bodies can affect the health of the people who are using this water for drinking purpose (Adegoke and Bello, 2015). Dye removal from effluents is a major problem faced by textile industries. It is challenging to address the environmental issues created by dye effluents and in this regard, there is a need to develop effective treatment methods to destroy or isolate the dyes from the effluents before discharge into the water bodies to protect

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ecosystem.

Several physical methods such as ultrafiltration (Ng et al., 2017), electrodialysis (Xue et al., 2015), reverse osmosis (Nataraj et al., 2009) and chemical methods such as electroflotation (Balla et al., 2010) and electrochemical oxidation (Singh et al., 2016) have been applied by researchers for dye removal from aqueous solution. However these treatment methods are not found to be cost effective and also some of these treatment techniques involve use of excessive chemicals which also create additional environmental concerns (Demirbas, 2009). These limitations may be overcome by the method of adsorption. In adsorption, activated carbon is commonly used for dye removal due to its effectiveness, but this offers drawbacks of high cost of the treatment process, difficulty in regeneration after exhaustion during the use and reduced adsorption efficiency after regeneration (Srivastava et al., 2007). Hence research into development of low cost, sustainable and efficient adsorbent for dye removal is on the forefront in recent years. Different adsorbents in their natural form such as *Xanthium strumarium* L. seed hull (Khamparia and Jaspal, 2017), bagasse fly ash (Mall et al., 2005), coconut mesocarp (Monteiro et al., 2017) as well as in the activated form such as oxalic acid treated *Artocarpus odoratissimus* peel (Dahri et al., 2017), surfactant treated saponite (Tangaraj et al., 2017) and H_3PO_4 activated cattail (Shi et al., 2010) have been utilized for removal of dyes from wastewater. In the present study, removal of Acid Green 25 (AG 25) dye has been studied using biosorbent synthesized from dead (fallen) leaves of *Prunus Dulcis* (PD) in raw form and using NaOH (alkali) treatment during the synthesis. The literature analysis established that utilization of dead leaves of *Prunus Dulcis* (DLPD) has not been explored for the biosorbent synthesis and application for AG 25 dye removal from wastewater. The advantage of biosorbent selected in the present study in comparison with other biosorbents is its availability in large quantity at minimal cost, especially in the agriculture dominated countries. Also the use of such agricultural waste (biomass) as a biosorbent can reduce the volume of solid waste as it follows the principle of wealth from waste. AG 25, an organic sulphonic acid dye, selected as pollutant in the present study finds applications in textile, leather and cosmetic industry. AG 25 dye containing effluent can cause eye and skin irritation and also the compound is toxic to aquatic organisms. Hence removal of AG 25 dye from wastewater is necessary to protect the ecosystem and there is always a need to develop effective and economical treatment approaches. In present study, batch experiments have been carried out initially to investigate the effect of operating parameters on dye removal. The industrial processes of adsorption typically need to be conducted in column mode due to the large volumes of the effluent to be handled and hence column experiments have also been conducted to probe the effectiveness of synthesized NaOH activated *Prunus Dulcis* (NAPD) for operation in continuous manner. The effect of operating parameters in the column operation on AG 25 dye removal was also investigated to establish breakthrough conditions, which are important design parameters.

2. Materials and methods

2.1. Biosorbent synthesis

Dead (fallen) leaves of *Prunus Dulcis* (DLPD) were collected, washed, dried and crushed. The obtained powder was screened in sieve shaker to get particles in the size range of 53–106 μm. The obtained biosorbent was used as such in the natural form and also subjected to activation. In the process of activation, Lignin from the powder (DLPD) was removed by activation of powder with NaOH solution. 1 part of obtained powder was treated with 5 parts of NaOH solution (1% by weight) for 4 h in a reactor at temperature of 323 K. The mixture was then filtered, washed with distilled water for removing colored lignin and then again heated at 323 K in oven. The synthesized NaOH activated *Prunus Dulcis* (NAPD) biosorbent in this manner was then stored in glass bottles to be used for further studies.

2.2. Pollutant dye

An anionic dye, Acid Green 25 [Molecular formula = $C_{28}H_{20}N_2Na_2O_8S_2$, molecular weight = 622.57 g/mol], was obtained from Sigma-Aldrich, India. 1000 mg/L of stock dye solution was prepared and then diluted to obtain desired dye solutions required for batch and column study.

2.3. Biosorbent characterization

Scanning electron microscopy (SEM, JEOL 6380, USA) was used to examine surface morphology of NAPD biosorbent before and after the adsorption of AG 25 dye as well as of the natural form of DLPD. The functional groups involved in the process of AG 25 dye adsorption on synthesized NAPD biosorbent were analyzed using Fourier transform-infrared spectroscopy (FT-IR, Perkin Elmer BX, USA). BET parameters for the DLPD and NAPD biosorbents were evaluated using the Brunauer-Emmett-Teller (PMI BET Sorptometer-201AEL-2OSEL, USA) method. UV Spectrophotometer (Shimadzu-1800, Japan) was used for determining the concentration of AG 25 dye in the solution by recording the UV absorbance at λ_{max} of 642 nm. Limit of detection and limit of quantification, which are the validation parameters for data were also evaluated as 0.0995 and 0.3318 mg/L respectively.

2.4. Batch equilibrium studies

Batch equilibrium studies were performed in orbital shaker (Bio-Technics, Mumbai). Desired amount of synthesized biosorbent was added in 50 mL of aqueous solution of AG 25 dye having a specific concentration and at the desired pH value. The pH of the dye solution was adjusted to the required value by adding 0.1 N HCl/0.1 N NaOH as required for pH adjustment. The shaking was performed at constant speed of 150 rpm. The effect of operating parameters like pH of dye solution, biosorbent loading, time, AG 25 dye concentration and temperature on the extent of dye removal have been investigated. Samples were withdrawn from the shaker at specific time intervals and analyzed using UV spectrophotometer. Reusability study of the biosorbent was also performed by first desorbing AG 25 dye from NAPD biosorbent based on the regeneration approach and reusing the biosorbent again in the study. Dye loaded NAPD biosorbent was thoroughly mixed with 0.1 mol/L NaOH solution applied as a desorbing agent (Guo et al., 2012) in orbital shaker. After desorption, reusability of the recovered biosorbent was further checked in five consecutive cycles.

Biosorption capacity (q_t) defined as ratio of dye adsorbed (mg) to biosorbent mass (g) was estimated using the equation given below:

$$q_t = \frac{(C_i - C_t)}{m} \tag{1}$$

where C_i and C_t (mg/L) are initial concentration and concentration at any time, t of AG 25 dye in the solution, respectively and m is biosorbent load (g/L).

The extent of dye removal (%) was evaluated using equation as given below:

$$Extent\ of\ removal(\%) = \frac{C_i - C_t}{C_i} \times 100 \tag{2}$$