



Pine Cone biomass as an efficient precursor for the synthesis of activated biocarbon for adsorption of anionic dye from aqueous solution: Isotherm, kinetic, thermodynamic and regeneration studies

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ABSTRACT

This study describes the synthesis of activated biocarbon from *Pinus kesiya* cone by $ZnCl_2$ activation and its efficacy in the removal of Alizarin Red S (ARS) dye. The prepared biocarbon was characterized using Elemental analysis, Scanning Electron Microscopy (SEM), FT-IR spectroscopy, Brunauer-Emmett-Teller (BET) surface area analysis and zero point charge. BET surface area and total pore volume of the synthesized carbon was found to be $878.07 \text{ m}^2 \text{ g}^{-1}$ and $0.412 \text{ cm}^3 \text{ g}^{-1}$ respectively. The impact of process parameters like adsorbent dosage, pH, initial concentration, and contact time were determined using batch experiments and an increase in adsorption capacity was observed with increase in the initial dye concentration, adsorbent dosage and contact time. The adsorption isotherm was well defined by Langmuir model with a maximum adsorption capacity of 118.06 mg g^{-1} . Pseudo-second order kinetics gave the best correlation value ($R^2 > 0.99$) reflecting the chemical nature of the adsorption process. Thermodynamic studies showed that adsorption was spontaneous (negative ΔG°) and endothermic in nature (positive ΔH°). Regeneration of spent carbon was also evaluated in order to assess the reusability which shows that the regenerated carbon can be used till the third cycle.

1. Introduction

Water is an important resource for sustenance of this planet; yet the accessibility to clean water has become a continuous increasing problem in recent years. The continuous expansion in human population and their increasing needs has led to serious contamination of water with various undesirable substances or so called pollutants. These pollutants in water are generally brought about by industries, domestic discharges, urban runoff, sewage disposal, hospitals and other human activities and thus threatens water supplies. Out of the many pollutants, the discharge of dyes into the water bodies from various industries such as textile, rubber, paper, plastic, cosmetics and printing etc have become one of the major source of water pollution (Kumar and Jena, 2016). It is estimated that over 7×10^5 tonnes production of around 10^5 types of commercial dyes occur per annum (Khan et al., 2011). These dyes are mostly toxic, and have prolonged and intricate degradation processes because of their high chemical and photolytic stability, and release probable carcinogenic and mutagenic products (Gautam et al., 2014, 2013; Wanassi et al., 2017a). Besides, the presence of dyes in water leads to increase in turbidity levels which

obstruct the ability of aquatic animals to locate food and also leads to reduction in photosynthetic activity of the aquatic ecosystem (Spagnoli et al., 2017). Among many dyes, Alizarin Red S (ARS), an anthraquinonoid dye is unique as it belongs to a group of the most durable dyes because of its complex structures of aromatic rings. It has high physiochemical, optical and thermal stability which makes its degradation somewhat difficult (Liang et al., 2018). Therefore, treatment of wastewater containing such a dye has an importance of its own. Among the various technologies developed over the years for removal of dyes from wastewater, like biological treatment, photocatalysis, ultrafiltration, electrochemical processes, adsorption etc. (Gupta et al., 2013; Gupta et al., 2012a, 2012b; Gupta et al., 2011; Gupta and Suhas, 2009; Mittal et al., 2010, 2009a, 2009b; Mohammadi et al., 2011; Salleh et al., 2011; Saravanan et al., 2013a, 2013b, 2016, 2014), adsorption techniques has received an enormous attention because of its cost-effectiveness, simple operation and high efficiency for removal of contaminants from wastewater (Ghosh and Bandyopadhyay, 2017; Kumar and Jena, 2016; Liu et al., 2013; Spagnoli et al., 2017; Yagub et al., 2014). Adsorption by activated biocarbon is most frequently used as a favorable method for the removal of various dyes from aqueous solutions because of its

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well-developed pore structure, high surface area and surface chemical functional groups (Kumar and Jena, 2016; Nourmoradi et al., 2015).

However, the production of commercial activated carbon is quite expensive and thus there has been a growing research interest towards development of low cost and efficient activated carbon through utilization of various alternative sources. Activated carbon prepared from natural or agro-industrial wastes are found to be promising as they are renewable, highly available and cost-effective thus making them a cleaner and highly effective material for environmental applications (Bhomick et al., 2017; Divband Hafshejani et al., 2016). In this regard, lots of work have been reported in recent years, to the preparation of activated carbon from various biomass such as palm shells (Hamza et al., 2016), snail shell (Gumus and Okpeku, 2015), wood chips (Thue et al., 2016), mushroom roots (Cheng et al., 2016), rice husk (Bishnoi et al., 2004), coconut shell (Li et al., 2008), Fox nut (Kumar and Jena, 2015), pecan shells (Shawabkeh et al., 2002), banana peel (Getachew et al., 2015), Waste Tea leaves (Peng et al., 2013), almond shells (Mohan et al., 2011), Plum Kernel (Treviño-Cordero et al., 2013), *Mucuna pruriens* (Pongener et al., 2017) and *Manihot esculenta* (Pongener et al., 2018).

For the present study, the cones of *Pinus kesiya* was used as the raw precursor for the preparation of activated carbon. Pine cone is one of the most readily available biomass and is generally treated as a waste (Aksakal and Uzun, 2010; Ofomaja et al., 2009; Sen et al., 2011; Uzun et al., 2009, 2003). Magnitude quantities of pine cones are formed annually as agricultural by-product around the globe. Therefore, pine cone from *Pinus kesiya* was selected as a biomass of interest owing to their vast availability, easy collection, and renewable character.

To the best of our knowledge, Alizarin Red S adsorption onto activated biocarbon synthesized from cones of *Pinus kesiya* has not been reported to date. Therefore, the work presented in this paper was designed with an aim to investigate a viable and efficient method for removal of Alizarin Red S (ARS) from water by activated biocarbon synthesized from low-cost and extensively available pinecones. Characterization of the prepared adsorbent was done using various analytical techniques and also the influence of initial concentration, contact time, adsorbent dosage, pH on ARS adsorption has been investigated. The equilibrium isotherm, kinetic and thermodynamic of the adsorption process of the Alizarin Red on the prepared activated carbon were also studied. In addition, regeneration studies of the saturated carbon were also investigated.

2. Materials and methods

2.1. Materials

Pine cones of *Pinus kesiya* were obtained locally from the vicinity of Nagaland University, Lumami Campus, Zunheboto, Nagaland, India. The cones were washed repeatedly with distilled water for removing any dirt or impurities adhering to them and oven dried at 110 °C till the cones became completely dry. The dried pine cones were grounded into smaller pieces; labeled and stored for further use as PKB (*Pinus kesiya* Biomass).

2.2. Preparation of Pine Cone activated biocarbon

For preparation of biocarbon, 10 g of PKB was mixed with a 200ml of ZnCl₂ solution (20 g of ZnCl₂ in 200 ml of double distilled water) and the mixture was continuously agitated at 80 °C for 3 h and then dried at 110 °C for 24 h. The dried sample was then grounded into fine powder using a planetary ball mill. The mixture was then pyrolyzed in a muffle furnace at 500 °C at the heating rate of 10 °C min⁻¹ from ambient temperature to 500 °C and was kept at 500 °C for 90 min. The activated sample was then washed with HCl (0.5 M) and hot distilled water to make the residual solution pH neutral and dried at 110 °C. The activated sample was labeled as pine cone activated biocarbon (PAB)

and stored in a desiccator for further use. The yield percentage of the obtained biocarbon was determined using Eq. (1)

$$\text{yield percentage} = \frac{W_{\text{PAB}}}{W_{\text{PKB}}} \times 100 \quad (1)$$

where W_{PAB} = weight of the prepared activated biocarbon in grams, W_{PKB} = weight of *Pinus kesiya* biomass in grams.

2.3. Characterization of activated biocarbon

Proximate analysis of PAB was achieved using ASTM method (ASTM, 1990) while ultimate analysis was done using CHN analyzer (Model: PE 2400 Series II, Make: Perkin Elmer). Surface area and total pore volume were measured using BET surface analyzer (Smart instrument, SS93/02) by degassing PAB at 300 °C for 60 min and measuring N₂ adsorption-desorption isotherm at -195.79 °C (liquid nitrogen temperature). Scanning electron microscopy (SEM) (Model: JSM-6360; JEOL) technique was used for surface textural studies of the activated biocarbon. The functional groups present on the surface were identified by Fourier Transform infrared (FT-IR) spectrometer (Model: Spectrum Two, Made: Perkin Elmer). Zero-point charge (pHzpc) was measured by batch equilibrium method (Babic et al., 1999). For pHzpc measurement, 50 ml of KNO₃ solution (0.1 M) was put in a conical flask containing PAB and the initial pH values were adjusted between 2 and 12 by adding HCl or NaOH (0.1 N) and continuously stirred for 2 days on a magnetic stirrer. Later, the ultimate pH values were measured and the difference between the initial and final pH values ($\Delta\text{pH} = \text{pH}_{\text{initial}} - \text{pH}_{\text{final}}$) was plotted against the $\text{pH}_{\text{initial}}$.

2.4. Preparation of adsorbate

For this present study the dye used namely Alizarin Red S (ARS) (Fig. 1) (Molecular weight = 342.26; C₁₄H₇NaO₇S) was purchased from Merck India. 1000 mg L⁻¹ of stock solution of the dye was prepared by taking 1000 mg of solid dye and dissolving it in 1000 ml of double distilled water. The working initial dye solutions (50 mg L⁻¹, 100 mg L⁻¹ and 200 mg L⁻¹) were prepared daily by diluting the stock solution with double distilled water to give the desired concentration. All other chemicals used were of analytical grade.

2.5. Adsorption studies

All experiments were studied using batch adsorption method and for this study, 50 ml of the desired concentration (50 mg L⁻¹, 100 mg L⁻¹ and 200 mg L⁻¹) of dye solution was taken in 250 ml flasks with variant adsorbent doses (0.01–0.05 g) The mixtures were then stirred in a rotary shaker from 0 to 140 min at varying pH (2–10) at 30 °C. The solution was filtered using Whatman filter paper and the residual dye concentration in each aliquot was determined by using a double beam UV-visible spectrophotometer (Perkin Elmer, Lambda 25) at 423 nm. The amount of ARS adsorbed by PAB and the removal percentage was calculated by Eqs. (1) and (2) respectively:

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (2)$$

$$\text{Removal \%} = \frac{C_0 - C_e}{C_0} \times 100 \quad (3)$$

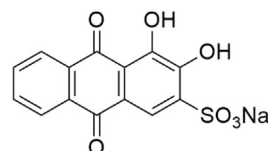


Fig. 1. Chemical structure of Alizarin Red S.

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