Process Safety and Environmental Protection 117 (2018) 125–142

Contents lists available at ScienceDirect

Process Safety and Environmental Protection

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

Adsorption characteristics of phosphoric acid induced activation of bio-carbon: Equilibrium, kinetics, thermodynamics and batch adsorber design

Sankhadeep Basu, Gourab Ghosh, Sudeshna Saha*

Department of Chemical Engineering Department, Jadavpur University, Kolkata, India

ARTICLE INFO

Article history:
Received 5 January 2018
Received in revised form 22 April 2018
Accepted 25 April 2018
Available online 30 April 2018

Keywords:
Adsorption
Methylene blue
Activated carbon
Sterculia foetida
Isotherm
Film diffusion
Batch adsorber

ABSTRACT

Activated carbon from *Sterculia foetida* was prepared using phosphoric acid as activating agent for efficient removal of methylene blue (MB). The effect of different operational parameters like pH (2–12), loading (1–4 g/l), initial dye concentration (50–500 ppm), temperature (298–328 K), and contact time (0–24 h) were investigated for the adsorption of MB. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich models were used to analyse the equilibrium data. The Langmuir model fitted well with maximum monolayer adsorption capacity of 181.81 mg/g. Adsorption kinetics followed pseudo-second order kinetic model. The adsorption process was found to be governed both by intra-particle and film diffusion. Thermodynamic parameters like entropy, enthalpy, and Gibb's free energy were also evaluated. It was found that the adsorption was spontaneous, endothermic and physisorption in nature. The liquid phase volumetric mass transfer coefficient was found to decrease from 1.03 min^{-1} to 0.088 min^{-1} with increase in initial concentration from 50 ppm to 300 ppm. A single-stage batch adsorber design for dye adsorption has been proposed based on the Langmuir isotherm model equation. The reusability study demonstrated that the prepared adsorbent could effectively be used up to 5 cycles without regeneration. The study showed that the activated carbon prepared from *Sterculia foetida* can be effectively used as an adsorbent for methylene blue removal from aqueous solutions.

1. Introduction

The discharge of coloured wastewater into the environment is a major source of pollution, eutrophication and imbalance in the marine ecosystem. The presence of dye in the effluents of wastewaters of various industries like textile, leather and paper originates during the colouring process where a significant percentage of dye does not bind to the material surface and is lost to the waste stream (Métivier-Pignon et al., 2003). Estimates indicate that about 12% of the dye used annually are lost to waste streams during manufacturing and processing operations and 20% of these losses usually enters the environment through effluents of the wastewater treatment plants (Ratna, 2012). The release of these dyes in the environment not only reduces the penetration of sunlight but also has harmful effects on living organisms (Carmen and Daniel, 2012; Process et al., 2010; Ratna, 2012, Bulut and Aydin, 2006). Methylene blue (MB), a cationic dye, commonly used for colouring of textiles can causes eye burns, and if swallowed causes irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea. If inhaled it may also cause methaemoglobinemia, cyanosis, convulsions and dyspnoea (Tan et al., 2007). Therefore treatment of wastewater containing such dye becomes imperative due to its hazardous effects.

Conventional physical, chemical and biological methods such as membrane separation, coagulation, advanced oxidation, microbial oxidation have been exploited for treatment of dye containing wastewater (Padmesh et al., 2006, Sharma et al., 2016). However the major drawbacks of these methods are their high cost, formation of secondary waste products and intensive energy requirements (Nandi et al., 2009). Among other techniques adsorption has been identified to be efficient for the treatment of wastewaters containing dyes, pigments and other colorants due to its simplicity and cost effective nature (Sharma et al., 2017). Different types of adsorbent materials like zeolites (Khan et al., 2015), brown macroalga (Daneshvar et al., 2017), activated lignin-chitosan blends (Albadarin et al., 2017), pine nut shells (Naushad et al., 2016), palm kernel shells (Ming-Twang et al., 2017), nickel ferrite (Naushad et al., 2017) and ferric oxide-TSC (Alqadami et al.,

* Corresponding author.
E-mail addresses: sudeshna.saha@jadavpuruniversity.in, sudeshnas@chemical.jdvu.ac.in (S. Saha).

https://doi.org/10.1016/j.psep.2018.04.015
0957-5820/

2016) have been utilized for the removal of toxic dyes from wastewater. However among the adsorbents, activated carbon has received much attention for the removal of dye containing wastewater owing to its large active surface area and porous nature. But commercial activated carbon is considered expensive. This is due to the use of non-renewable and relatively expensive raw material such as coal, which is unjustified in pollution control applications (Chakraborty et al., 2005). In recent years, this has prompted a growing research interest in the production of activated carbons from renewable and cheaper precursors such as industrial and agricultural waste products (Foo, 2018). These include rice husk (Gupta et al., 2006), waste rice straw (Sangon et al., 2018), denim fabric waste (Silva et al., 2018), peanut shell (Tanyildizi, 2011), leaves of Camellia sinensis (Mahmood et al., 2017), orange peel (Lam et al., 2017), eggshell waste (Daraei et al., 2013), bottom ash (Mittal et al., 2014), lignocellulosic waste (Noreen et al., 2013), hen feather waste (Mittal et al., 2013) and coconut bunch waste (Hameed et al., 2008).

Sterculia foetida is a tropical plant belonging to the *Sterculiaceae* family which is also called as 'Java-Olive'. Its seed, oil, leaves, bark, and gum have considerable medicinal value; the leaves of this plant are used as herbal medicine as aperient, diuretic and as insect repellent. Seed oil exhibits antifungal, insecticide, antibiotic activities. The gum from the trunk is used for book binding purposes (Kale and Vijaya Darade, 2011). However the fruit shells of *Sterculia foetida* have no economic value and are considered as a garden waste. To make use of this cheap abundant waste, it is proposed to produce activated carbon from it. This will lead to the conversion of unwanted agricultural waste to useful, value added adsorbents which will contribute to solving part of the wastewater treatment problem.

The aim of the present study was to evaluate the adsorption potential of *Sterculia foetida* based activated carbon for methylene blue dye. The study investigates the effects of contact time, concentration, initial solution pH, adsorbent dosage and temperature on methylene blue dye adsorption. Adsorption kinetics, isotherms and thermodynamics were also evaluated and reported along with an adsorber design process based on Langmuir adsorption isotherm.

2. Materials and methods

2.1. Methylene blue

Methylene Blue ($C_{16}H_{18}N_3SCl{\cdot}3H_2O$) obtained from E. Merck, India was used as the model dye without further purification. The solutions were prepared by dissolving the required amount of dye in distilled water. Methylene blue was chosen in this study because of its known strong adsorption onto solids. It has a molecular mass of 373.9 g/mol, which corresponds to methylene blue hydrochloric acid with three groups of water.

2.2. Preparation and characterization of activated carbon

Shells of *Sterculia foetida* were cleaned and were then dried for 12 h at a temperature of 100–120 °C in order to remove free moisture. Dried shells were crushed prior to activation. The raw material was then soaked in phosphoric acid solution (40% w/v) with an impregnation ratio of 1:1. The mixture was dehydrated overnight in an oven at 105 °C followed by carbonization at a temperature of 600 °C with constant heating rate of 10 °C/min under nitrogen flow of 150m^3/min in a stainless steel vertical tubular reactor. Once the temperature reached the desired value, the activation was held for various times e.g., 30 min (AC1), 1 h (AC2) and 2 h (AC3) in order to investigate the effect of activation time on adsorption characteristics. The activated carbon was then cooled to room temperature under continuous flow of nitrogen. The same was washed with deionized water until the pH of the washing solution reached 7.

Surface area and porosity measurement of the activated carbon was carried out by N_2 adsorption at 77 K using Autosorb I (Quantachrome Corporation, USA). The samples were degassed at 130 °C for 4 h prior to nitrogen adsorption measurements. Field Emission Scanning Electron Microscope-EDAX (JEOL JSM-7600F) analyses were carried out for the prepared activated carbon and also MB loaded activated carbon after adsorption to study the surface morphology. The samples were gold-palladium coated prior to FESEM-EDAX analysis. The structural variations were examined by FTIR spectroscopy using a Shimadzu IRPrestige-21 Spectrophotometer. The FTIR spectrum of the samples was noted in the transmittance mode in the range of 4000–450 cm^{-1}. XPS spectra were taken with an Omicron Multiprobe spectrometer (Omicron NanoTechnology GmbH.) fitted with an EA125 hemispherical analyzer. A monochromated Al Kα X-ray source operated at 150W was used for XPS.

2.3. Adsorption experiments

The effect of pH on the removal of dye was investigated over the pH range of 2.0–12.0 with 1 g/L of the adsorbent dosage for a contact time of 24 h with a dye solution concentration of 200 ppm. The initial solution pH was adjusted using 0.05 M HCl or 0.05 M NaOH.

The effect of adsorbent dosage on the removal of dye was studied with different adsorbent dosages (0.1–0.4 g) in 100 mL dye solution of 100 ppm concentration at pH 12.0 till equilibrium time (24 h).

The effect of contact time and initial concentration was also studied by using 3 g/L of the adsorbent at 25 °C and pH 12.0 for various time intervals and different initial dye concentrations varying from 50 ppm to 500ppm.

Adsorption kinetic experiments were carried out using 100 mL of aqueous dye solution of various initial concentrations in a series of 250 mL flasks, maintained at different temperatures (25 °C, 40 °C, and 55° C). The flasks were shaken at 120 rpm for an equilibrium time of 24 h in an incubator shaker.

The effects of temperature on the adsorption isotherms behaviour were studied by performing the adsorption experiments at various temperatures (25 °C, 40 °C, and 55° C) with 3 g/L of the adsorbent at pH 12.0 and different dye concentrations.

For reusability studies, experiments were performed with 200 ppm dye concentration with a loading of 3 g/L, pH 12 at a temperature of 25° C. After each cycle the adsorbent particles were

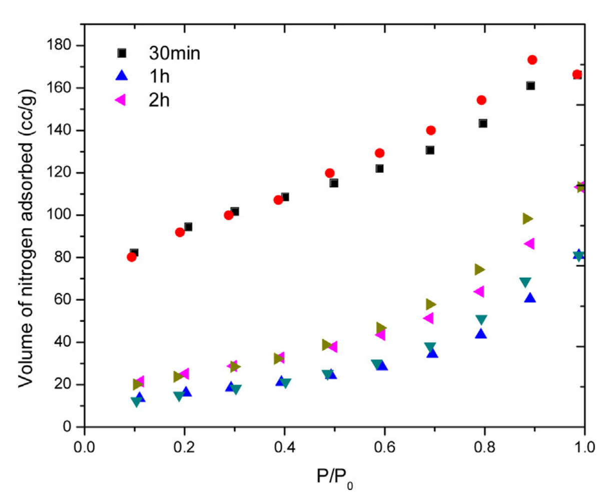

Fig. 1. Adsorption desorption isotherms for activation time of 30 min, 1 h and 2 h at 77 K.