Journal of Environmental Chemical Engineering 6 (2018) 169–181

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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

Multifunctional activated carbon with antimicrobial property derived from *Delonix regia* biomaterial for treatment of wastewater

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ARTICLE INFO

Keywords:
Reactive dyes
Disinfection
Wastewater treatment
Adsorbent

ABSTRACT

In this work, we report the development of a multifunctional high surface area activated carbon (DRP), from a biomaterial, *Delonix regia*, with antimicrobial potential and demonstrated its applicability towards removal of two reactive dyes, Reactive Red (RR-120) and Reactive Blue (RB-4) with an adsorption capacity of ~6.36 and 24 $mg \cdot g^{-1}$ respectively. The newer multifunctional activated carbon was prepared from the deseeded pods of *Delonix regia* through thermo-chemical surface modification and characterized for surface and morphological characteristics, chemical composition, and thermal stability. DRP exhibited a high surface area of 1577 $m^2 \cdot g^{-1}$ with various active functional groups. The decolourisation efficiency achieved was very high, ~98% for both the dyes. The effects of various operating parameters like pH, initial dye concentration, adsorbent dosage, surfactant, salt etc. were investigated and the batch adsorption equilibrium data in each dye system was analyzed with various isotherms-Langmuir, Freundlich, and Tempkin. The kinetics of the adsorption process was best represented by pseudo-second order kinetic model and the adsorption efficiency was also illustrated in the binary system of varying dye compositions. DRP could successfully reduce the microbial growth of Gram positive *B. subtilis* with a higher zone of inhibition.

1. Introduction

Activated carbons are one of the most promising materials used in the tertiary step of wastewater treatment due to its high surface area, and high capacity for removal of organic pollutants from water. They are also employed in water filters [1] and cartridges to treat water of different uses ranging from potable to indirect use at point sources. However, due to its extended surface area, well-developed network of pores (micro, meso and macroporous), they are highly biocompatible and prone to breed various bacteria, fungi, and other common pathogens. The contamination of treated water with these microorganisms is undesirable and for safe water use, the reduction of only chemical oxygen demand (COD) or high pollutant removal capacity is not sufficient and there is a need for water available for reuse to be free from bacteria and pathogens. It has been observed that due to the mixing of sewage run off or availability of rich nutrients, nitrates, phosphates and other organic material in effluents or surface waters, wastewater is often contaminated with different kinds of faecal coliforms and is a huge problem in the reuse and recycling process of wastewater and are also known to spread several water borne diseases. They are responsible for degrading the quality of the water, membrane fouling, pores clogging, fouling of the water where these effluents are released. Even water for irrigation purpose in certain cases has to be free from microbes. To make the treated water safe for reuse and other indirect potable applications, these microorganisms must also be eliminated by processes which involve low cost and less energy input yielding clean and safe water [2]. Although disinfection of water is important for various safe water applications [3,4], the current available disinfection technologies like UV, ozone or chlorination are either cost intensive or produce harmful carcinogenic by-products [5]. Hence, if activated carbons are designed in such a fashion that itself possess biocidal properties, it is always an added advantage in the treatment process

Among the organic pollutants, dyes and dyestuffs from textile industry belong to one of the most polluting substance. Their presence in surface water is a great nuisance as most of them are non-biodegradable or degrade with the release of harmful carcinogenic [6,7] products or either themselves are toxic, mutagenic and carcinogenic. Dyes are usually released from the textile, leather, printing, paper, food, rubber, plastic and cosmetic industries [8–10], etc. These dyes are classified into several types, of which reactive dyes belong to the class of anionic

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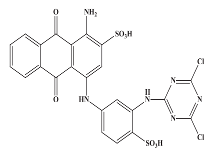
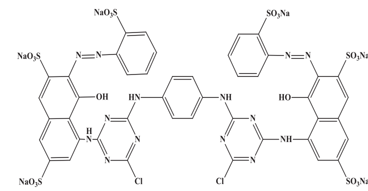
https://doi.org/10.1016/j.jece.2017.11.056
Received 3 August 2017; Received in revised form 3 November 2017; Accepted 17 November 2017
Available online 21 November 2017

Table 1
Physico-chemical specification of RB-4 and RR-120.

Dye	RB-4	RR-120
Other name	Procion Blue	Triazine dye red
Class	Anthraquinone	Diazo
Water solubility (g.L^{-1})	45	70
Maximum adsorption wavelength (nm)	591	535
Molecular weight(g.mol^{-1})	637.43	1470
Molecular structure		

polyaromatic structures which are widely applied in the textile industries due to their industrially beneficial properties like bright colours, wide colour range, high water solubility, tolerance to various degradation processes, easy and powerful application [11,12]. Reactive dyes constitute more than 20-40% of the dyes and contain one or more reactive groups that form covalent bonds with either the hydroxyl or amino group in fabric materials [13]. They are one of the most recalcitrant/persistent dyes due to their higher water solubility, non-biodegradability and occurrence in higher concentrations than any other dyes [12]. They may be removed through adsorption process using activated carbon as adsorbents which are versatile and a widely applied in industries and is associated with benefits of high efficiency and ease of operation, over the other processes. However, the high cost of the conventional commercial adsorbents is a bottleneck in its application. It is imperative to identify cheaper sources of activated carbon. The process can be made economical by involving biomaterial/bio-waste/agro waste as the raw material source of activated carbon. In addition, these biomass materials provide a renewable, non-toxic, regenerating, sustainable, biodegradable source to treat the waste water. The dyeing process uses various chemicals, acids, alkalis, salts, surfactants and it becomes instructive to study the efficiency of the treatment process under these different parameters.

The pods of *Delonix regia* (Gulmohar or Flamboyant) forms one such sustainable source of adsorbent material as they have limited valuable use other than the seed dispersal [14,15]. *Delonix regia*, is a dicotyledonous plant belonging to the Fabaceae family which is widely distributed in countries like India, Taiwan, Caribbean, the United States, Hawaii, Puerto Rico, the Virgin Islands, the Canary Islands, Hong Kong, Southern China, South Brazil, Australia [16] etc. These pods are rich in lignocellulosic material which may provide sites for the binding of the dye molecules or removal of other organic pollutants and hence a good precursor for preparation of activated carbons. Delonix regia have been reported as source of catalyst for the transesterification of the Hevea brasiliensis oil. There are few reports on the application in the removal of oil spills, methylene blue and acid dyes like Acid Yellow and Acid Red [15–17] where different parts of the plant are explored. However, chemico-thermal modification and activation of *Delonix regia* using phosphoric acid has not been reported for removal of reactive dyes. Further, it is desirable that the activated carbon used for the treatment of water be imparted with antimicrobial property which may be considered to be superlative.

The objective of the present study is to develop a multifunctional activated carbon having high surface area and antimicrobial property with capability for treating two model pollutants of reactive dyes, viz., Reactive Blue (RB-4) and Reactive Red (RR-120). The investigation involves studying the equilibrium and kinetics of adsorption of the two reactive dyes (Reactive blue 4 and Reactive red 120), and investigation of antimicrobial properties of the developed material using two model microbes, *E.coli* and *B. subtilis*. To determine the applicability of the prepared adsorbent in real waste water system, the adsorption process was conducted in presence of various interfering conditions like varying pH, salt, and surfactant concentrations and also in binary system.

2. Experimental

2.1. Materials and methods

All the chemicals used throughout the experiments were of analytical reagent grade and consisted of Phosphoric acid (98%, BDH), Cetyltetraammonium bromide, CTAB (98%, LOBA Chemie), Sodium lauryl sulphate, SDS (CAS No.151-21-3, Fisher Scientific), Sodium hydroxide ($\geq$97%, Merck, India), Hydrochloric acid, (35%, Fischer scientific), Sodium chloride (Fisher scientific), Sodium sulphate (99%, Fischer Scientific),Reactive Blue 4 or Procion Blue (Alfa Aesar), and Reactive Red-120 (Sigma-Aldrich). Commercial activated carbon (AC) was procured from Merck (CAS No. 7440-44-0, Methylene blue adsorption $\geq$180 mg·g^{-1}), India and another AC (Min. Methylene blue value of 400) was obtained from Sisco Research Laboratories Pvt Ltd, India. All the chemicals were used without further purification. The detail chemical specifications of both the dyes are given in Table 1. The working standard solutions were prepared from the stock solutions of 500 mg·L^{-1} by subsequent dilution method to the required concentration. Dye concentrations were then measured using Uv–vis spectrophotometer at their absorbance maximum.

As seen from the molecular structure in Table 1, RB-4 consisted of two sulphonyl group, one quinone, two chloro and one amino group whereas RR-120 consisted of six sulphonyl groups, two azo, one hydroxyl and two chloro groups.

2.2. Preparation of adsorbent

The deseeded woody brown pods of *Delonix regia* were chosen as the starting material as it is easily and abundantly present and often discarded as waste material. The present study employs phosphoric acid treated pods of *Delonix regia* in the preparation of a bio-adsorbent to target reactive dyes and bacterial pollutants. Dry pods of *Delonix regia* (DR) were collected from the local area of Maharashtra region of India. These pods were washed thoroughly and sun dried, broken down into small pieces, seeds were separated and finally ground in a blender to fine dry powder. The clean and dry powder was then mixed with orthophosphoric acid (1:1, w/v) for 3 h at 80° C on a hot plate, with intermittent stirring. Chemical activation of precursor material has been reported to increase the adsorbent surface area and porosity, creating sites available for the adsorption of the pollutant molecule. Many chemical activating agents like KOH, NaOH, $ZnCl_2$, K_2CO_3, H_2SO_4, etc. have been reported for chemical activation of adsorbent materials. Phosphoric acid is considered to be a good activating agent for carbonization of biomass material which mainly contains lignocellulosic