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Carbonaceous adsorbent prepared from waste tires: Experimental and computational evaluations of organic dye methyl orange

Tawfik A. Saleh [a], Abdulaziz A. Al-Saadi [a], Vinod Kumar Gupta [b,*]

[a] Chemistry Department, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia
[b] Chemistry Department, Indian Institute of Technology Roorkee, Roorkee 247 667, India

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ABSTRACT

This work reports the recycling of waste rubber tires (WRT) to produce a carbonaceous material as adsorbent of an environmental value. The produced material was activated by thermal–chemical process. The WRT-derived carbonaceous adsorbent (CA) was characterized by means of scanning electron microscope, energy-dispersive X-ray spectroscopy and infrared and Raman spectroscopic techniques. The developed CA was tested and evaluated as potential adsorbent for methyl orange (MO) removal. A series of MO stock solutions whose concentrations range from 1×10^{-6} to 1×10^{-4} M was prepared to investigate the possible activity of CA. Experimental parameters such as dosage amount, initial concentration and temperature were optimized. A rapid and fast equilibrium has been observed. The maximum adsorption took place in the pH range of 3–5. The temperature-effect study revealed that the process is exothermic. A possible adsorption mechanism has been suggested on the view of calculated frontier molecular orbitals of the methyl orange molecule.

1. Introduction

The remarkable increase in the number of vehicles manufactured worldwide and the lack of both technical and economical mechanisms of proper disposal make waste tires a serious source of pollution. Waste rubber tires (WRT) are almost non-biodegradable and, hence, have become a serious source of environmental pollution. Since most of the WRT are stockpiled or put in landfills, hazards associated with scrap tires can cause health and environmental problems. Land filling the waste tires is an uneconomical and non-environmentally friendly strategy of disposal [1]. The disposal of WRT represents major environmental issue throughout the world because they occupy large volumes and cause the destabilization of compacted landfill sites due to their flexible nature [2]. Consequently, the environmentally friendly disposal of WRT seems to be impossible in terms of economy and health.

A feasible solution would be to recycle them so that they can be used as raw materials for various useful applications. In addition to their availability at lower costs, WRT are embodied with a high amount of carbon. The typical compositions of tire rubber are: 60–65% SBR (and natural rubber), 29–31% carbon black, 2–3% zinc oxide, and 1–2% sulfur [3]. Carbon black is used to strengthen the rubber, to improve its abrasion resistance and to reduce its degradation by UV rays [4]. Approximately 55% oil, 10% gas, and 35% char can be produced from the WRT [5,6]. Gases have been used to heat the reactor. Calorific values between 34.6 and 40.0 MJ/m^3 have been reported. The gases were identified as a mixture of hydrogen, carbon mono- and di-oxides, methane and ethane with lower concentrations of other hydrocarbon gases. Analysis of the oils indicated the presence of alkanes, ketones or aldehydes, and aromatic, polyaromatic, and substituted aromatic groups.

Therefore, WRT represent an interesting source of raw material for the preparation of mesoporous carbonaceous adsorbent (CA). These materials can be defined as nano-porous adsorbent which are widely used in both gas and liquid phase separation processes [7–11]. They can be produced from various carbonaceous precursors such as coal coconut shell, wood, and polymer scrap. Research into the conversion of low-cost waste materials to adsorbent has recently increased; firstly for the need to meet the increasing demand for carbonaceous adsorbent (CA) especially in the wastewater treatment industry and secondly to stick to economic values of waste materials, especially WRT. The use of inexpensive materials such as wastes with such an aim will certainly lower the production cost of the adsorbent. At present, in fact, low-cost adsorbents are being frequently tested for organic and inorganic pollutant removal from contaminated water [12–14].

There are many ways to reuse waste tires. One potential recycling process is pyrolysis which involves the heating of tires under inert conditions, usually at high temperatures. This is followed by chemical activation process. These tire-derived carbonaceous adsorbents (CAs) have been applied in removing pollutants such as phenols, dyes, copper, lead, and other pollutants [15–24] from wastewater.

Among the adsorbents, CA is an effective adsorbent for water treatment [25–29]. Nano-materials like carbon nanotubes and their composites have been reported to have high adsorption capacity toward removal of pollutants like heavy metals and dyes from wastewaters [30–34]. However, the disadvantage of such materials is their high cost.

* Corresponding author. Fax: +91 1332273560.
E-mail addresses: vinodfcy@gmail.com, vinodfcy@iitr.ac.in (V.K. Gupta).

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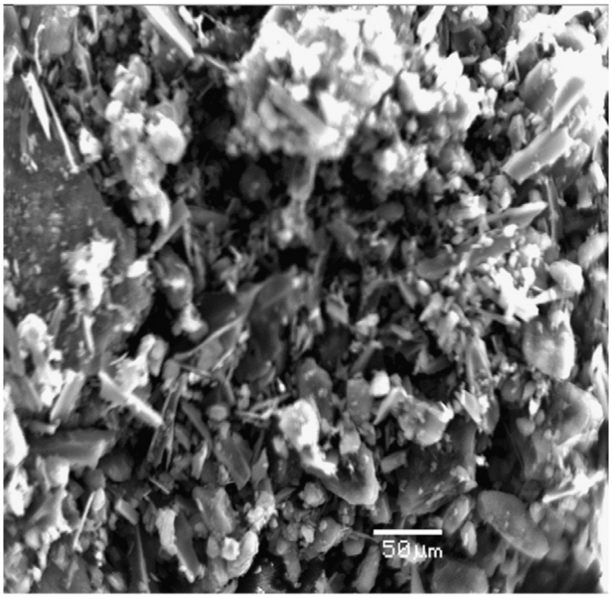

Fig. 1. The SEM image showing the surface structure of the tire-derived carbonaceous adsorbent.

Activated carbon is the most widely used adsorbent due to its large surface area, microporous structure, and high-adsorption capacity. However, its use is limited because of its high cost. Alternatively, waste tire derived-activated carbon as sorbents has the advantages of being less inexpensive. Moreover, recycling this cheap and plentiful resource as raw materials in alternative processes is considered to be a possible solution to overcome tire problems.

Methyl orange (MO) is released into the environment not only from natural sources but also from human activities. There are various methods to remove MO from wastewater including filtration, chemical precipitation, ion exchange and adsorption. One of the main drawbacks in such techniques is associated with the high production cost of adsorbents. To some extent, it may be palliated using cheap precursors, namely WRT.

To the authors' knowledge, the use of WRT-derived carbonaceous adsorbent (CA) for removal of methyl orange (MO) has not been well investigated. The present study aims to assess the applicability of CA derived from the WRT for the adsorptive removal of MO from aqueous solution and to investigate the effect of operating parameters on the adsorption process. The parameters studied include dosage amount, methyl orange concentration and temperature.

2. Experimental

2.1. Reagents and chemicals

The starting material used in the study was size-reduced residual rubber obtained from waste rubber tires (WRT). Methyl orange (MO) was obtained from Fisher Scientific Company (M-216 76166 LOT 726294), and was used as received. The water employed in all the studies was doubly distilled. The other reagents obtained from Sigma Aldrich were of analytical purity and were used as received. MO solutions of different initial concentrations were prepared by diluting the stock solution in appropriate proportions. In order to prevent metal contamination from laboratory glassware, glassware was kept overnight in a 10% (v/v) HNO_3 solution. All commercial reagents were purchased from Sigma-Aldrich and used as received unless otherwise stated. For the adsorption part, two solutions of methyl orange (1×10^{-4} M and 1×10^{-5} M) were prepared. Other concentrations were prepared in situ.

2.2. Preparation of adsorbent

Carbonaceous adsorbent (CA) was prepared from waste rubber tires via carbonization, chemical treatment and steam activation. The waste rubber tires were cleaned, thoroughly washed with deionized water, and then dried in an oven at 120 °C for 4 h. For carbonization, the dried material was then heated to approximately 800 °C for 6 h. This was followed by treatment with hydrogen peroxide solution (6%) for 24 h to oxidize adhering organic impurities. The material was washed with deionized water and dried in vacuum oven. The dried material was activated to 900 °C for 2 h (N_2 flow rate = 225 mL min^{-1}). It was then removed from the furnace and cooled in desiccators. After cooling, the material was treated with a 4 M nitric acid solution to remove the ash content and was then washed with deionized water. Then, it was treated with 10% hydrogen peroxide for 24 h and washed again with deionized water. The product was finally dried in an oven at 100 °C.

2.3. Equipment and characterization

The IR spectra of the samples were recorded on a Nicolet FTIR-100 spectrophotometer in the chemistry department using KBr pellets

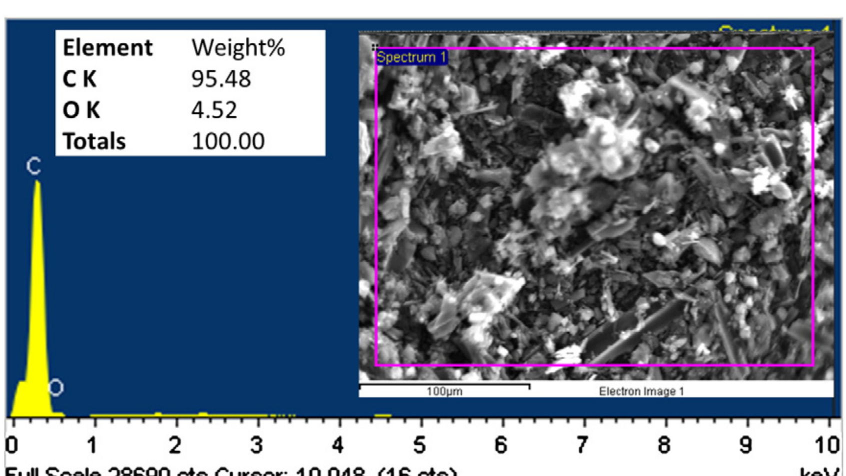

Fig. 2. The EDX spectrum with low magnification SEM image of the tire-derived carbonaceous adsorbent; inset: represent the quantitative analysis of the same.