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Novel adsorbent from agricultural waste (cashew NUT shell) for methylene blue dye removal: Optimization by response surface methodology

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ABSTRACT

Activated carbon, prepared from an agricultural waste, cashew nut shell (CNS) was utilized as an adsorbent for the removal of methylene blue (MB) dye from aqueous solution. Batch adsorption study was carried out with variables like pH, adsorbent dose, initial dye concentration and time. The response surface methodology (RSM) was applied to design the experiments, model the process and optimize the variable. A 2^4 full factorial central composite design was successfully employed for experimental design and analysis of the results. The parameters pH, adsorbent dose, initial dye concentration, and time considered for this investigation play an important role in the adsorption studies of methylene blue dye removal. The experimental values were in good agreement with the model predicted values. The optimum values of pH, adsorbent dose, initial dye concentration and time are found to be 10, 2.1846 g/L, 50 mg/L and 63 min for complete removal of MB dye respectively.

1. Introduction

Synthetic dyes are being extensively used in various industrial dyeing and printing processes. The textile industry is the largest consumer of synthetic dyes utilizing about 56% of the total world dyes production per annum (7×10^5 t) [1,2]. The dye effluents are considered to be highly toxic to the aquatic species and affect the symbiotic process by disturbing the natural equilibrium by reducing photosynthetic activity and primary production due to the colorization of the water [3]. Effluents contain significant level of organic contaminants, which are toxic as they create odor, bad taste, unsightly color, foaming, etc. These substances are often resistant to degradation by biological methods and are not removed effectively by conventional physico-chemical treatment methods. Removal of these dyes from effluents in an economic fashion remains a major problem for textile industries [4,5]. The most commonly used methods for color removal are biological and chemical precipitation. However, these processes are effective and economic only in cases where solute concentrations are relatively high [6]. There are advantages and disadvantages of various methods of dye removal from the wastewaters [7]. Many physicochemical methods have been tested, but only that of adsorption was considered to be superior to other techniques. This is attributed to its low cost, easy availability, simplicity of design, high efficiency, easy operation, biodegradability and ability to treat dyes in more concentrated forms [8,9]. The adsorption technique has been proven to be an excellent way to treat effluents, offering advantages over conventional process, especially from the environmental point of view [4]. Weber and Morris [4] had identified many advantages of adsorption over several other conventional treatment methods. The adsorption of dyes onto various types of materials has been studied in detail. These include activated carbon [10], peat [11], chitin [12], silica [13], hardwood [14], hardwood sawdust [15], bagasse pith [16], fly ash [17,18], mixture of fly ash and coal [19], chitosan fiber [20], paddy straw [21], rice husk [22], slag [23], chitosan [24], acid treated spent bleaching earth [25], palm fruit bunch [26], bone char [27], copper-doped zinc sulfide nanoparticles loaded on activated carbon [28], gold nanoparticles loaded on activated carbon [29], copper nanowires loaded on activated carbon [30] and tin sulfide nanoparticle loaded on activated carbon [31]. Activated carbon adsorption is one such method which has a great potential for the removal of dyes from wastewater [32–37]. Carbon is being used as a potential adsorbent because of its high efficiency [38]. Commercially available activated carbons are usually derived from natural materials such as wood or coal which is considered expensive [39]. Enhancement of the price of activated carbon results in economic difficulties for developing countries like India. Hence, alternate adsorbents with an equivalent potential of activated carbon are the current thrust area of research. Consequently, low-cost activated carbons based on agricultural solid wastes are being investigated for a long time.

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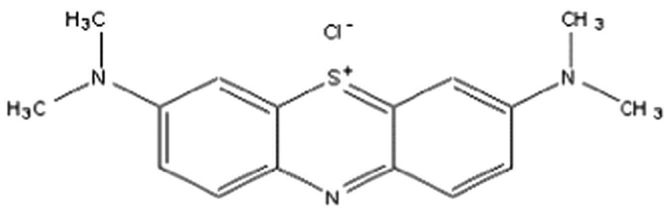

Fig.1. Structure of methylene blue dye.

Agricultural byproducts and waste materials used for the production of activated carbons include plum kernels [40], cassava peel [41], bagasse [42], jute fiber [43], palm-tree cobs [44], rice husks [45], olive stones [46], date pits [47], fruit stones and nutshells [48], rattan sawdust [49], peach stones [50], oil palm shell [51], orange peel carbon [52] and Egyptian rice hull [53].

Methylene blue, a basic dye, used for dyeing of silk, leather, plastics, paper, and cotton mordant with tannin, as well as for the production of ink and copying paper in the office supplies industry [54–61]. The discharge of this dye to the environment is distressing for both toxicological and aesthetical reasons as dyes impede light penetration, damage the quality of the receiving streams and are toxic to food chain organisms [62]. The chemical structure of methylene blue dye is given in Fig.1. Since this dye has a synthetic origin and complex aromatic molecular structures, it is an inert and difficult to biodegrade when discharged into waste streams. This aspect has always been overlooked in their discharge [63]. The removal of synthetic dyes is of great concern, since some dyes and their degradation products may be carcinogens and toxic and, consequently, their treatment cannot depend on biodegradation alone [64,65].

The present investigation deals with removal of methylene blue dye from the aqueous solution by adsorption onto activated carbon prepared from the new, low-cost agricultural waste, cashew nut shell and optimization of process variables such as solution pH, adsorbent dose, initial dye concentration, and time using Response Surface Methodology. The conventional and classical methods of studying a process by changing one variable at a time and maintaining other factors of the process at a constant level does not depict the combined effect of all the factors involved. This method is also time consuming and requires large number of experiments to determine optimum levels, which are unreliable. These limitations of the classical method can be eliminated by optimizing all the affecting parameters collectively by statistical experimental design such as Response Surface Methodology (RSM) [66]. Response surface methodology, first described by Box and Wilson [67], is an experimental approach to identify the optimum conditions for a multivariable system. RSM is a collection of mathematical and statistical techniques useful for developing, improving and optimizing processes and can be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions. The main objective of RSM is to determine the optimum operational conditions for the system or to determine a region that satisfies the operating specifications [68]. The application of statistical experimental design techniques in adsorption process development can result in improved product yields; reduce process variability, closer confirmation of the output response to nominal and target requirements and reduced development time and overall costs [69].

2. Experimental

2.1. Preparation and characterization of CNSAC

The CNS was collected from Pudukkottai District, Tamilnadu, India. It was washed with hot distilled water to remove the dust like impurities. After that it was dried and then the material was finally sieved to discrete sizes. The raw material was then carbonized at 700 °C under nitrogen atmosphere for 1 h. The produced char was then soaked with potassium hydroxide (KOH) at impregnation ratio of 1:1. The mixture was dehydrated overnight in an oven at 105 ± 1 °C, then pyrolysed in a stainless steel vertical tubular reactor and placed in a tube furnace under high-purity nitrogen (99.99%) at flow rate of 150 cm^3/min to a final temperature of 850 °C for 2 h soaking. Once the final temperature was reached, the nitrogen gas flow was switched to carbon dioxide and activation was continued for 2 h. The activated product was then cooled to room temperature and washed with deionized water to remove remaining chemical. Subsequently the sample was transferred to a beaker containing 250 mL solution of HCl (about 0.1 mol/L) stirred for 1 h, and then washed with hot deionized water. The textual characterization of the CNSAC was carried out by N_2 adsorption at 77 K using Autosorb I, supplied by Quantachrome Corporation, USA. The Brunauer Emmette Teller (BET) [70] (N_2, 77 K), the most usual standard procedure was used to find the BET surface area, average pore diameter and pore volume of the CNSAC are 984 m^2/g, 2.52 nm and 0.552 cm^3/g, respectively.

2.2. Adsorbate

Methylene blue dye supplied by Merck India was used as an adsorbate for the present adsorption studies. A stock solution of MB dye solution was prepared (500 mg/L) by dissolving the 0.5 g of dye powder in double distilled water then diluted with double distilled water to obtain desired dye concentration. MB dye has a molecular weight of 373.9 g/mol, which corresponds to methylene blue hydrochloride with three groups of water.

2.3. Analysis

The concentration of MB dye in the supernatant solution before and after adsorption was determined by using a double beam UV–vis Spectrophotometer (Shimadzu, Kyoto, Japan) at 668 nm. It was found that the supernatant from the CNSAC did not exhibit any absorbance at this wavelength and also that the calibration curve is very much reproducible and linear over the concentration range used in this work.

2.4. Adsorption experiment

Adsorption experiments were carried out as per the design developed with the response surface central composite design methodology. The experiments were conducted in 250 mL Erlenmeyer flasks with the working volume of 100 mL of aqueous solution. The initial pH of the solution was adjusted to the desired value by adding 0.1 M NaOH or HCl. The required amount of adsorbent dose was also taken in the flasks. The flasks were shaken for the specified time period in a temperature controlled incubation shaker at 120 rpm. The flasks were withdrawn from the shaker after the desired time of operation. The supernatant and the spent adsorbent were separated by using the centrifugation operation (5000 rpm, R-24 REMI Centrifuge, Mumbai, India). The residual dye concentration in the supernatant was analyzed by using the UV–vis spectrophotometer. Dye concentration in the supernatant was calculated from the calibration curve. The maximum wavelength (λ_{max}) values of the wastewater samples varied by ± 10 nm from the λ_{max} values of pure sample. Each determination is repeated three times and the results given were their average value. The percentage of CR removal was taken as a response (Y) of the experimental design and calculated as