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Bio-waste derived adsorbent material for methylene blue adsorption

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ABSTRACT

Corn cobs were used as a source to prepare activated carbon by physical activation methods with CO_2 and steam at high temperature of 1173 K. The adsorption studies of a basic dye, methylene blue, on the activated carbon were investigated. The effects of various experimental parameters like contact time, adsorbent dosage, MB concentration and temperature were studied using batch adsorption experiments. The characterization of the activated carbon was accomplished by using BET-N_2 adsorption, Temperature programmed decomposition (TPD) and Thermogravimetric analysis (TGA). The results obtained from adsorption studies follow Langmuir adsorption isotherm with maximum monolayer capacity of 100 mg/g for CCC and 75.5 mg/g for SCC. The kinetics of adsorption was analyzed by different kinetic models like pseudo first order, pseudo second order, intraparticle diffusion and Evolich. Among these, pseudo second order was found to be the most appropriate to study the adsorption of MB on physically activated carbon. The process was found to be endothermic with enthalpy change, ΔH (kJ/ mol) of 43.27 (CCC), 38.45 (SCC), and entropy change, ΔS (kJ/ mol) of 1.57 (CCC), 1.33 (SCC) for a temperature change of 300–330 K. The negative value of $\boldsymbol{\Delta G^{\circ}}$ (kJ/ mol), of −29.92 (CCC), −11.14 (SCC), −7.09 (NCC) and −2.14 (PCC), suggests the spontaneous adsorption of MB on activated carbon.

1. Introduction

Water from textile industries is a cause of serious environmental concern, since they generate large amount of waste water in various steps of dyeing and finishing processes. According to an estimate, about 20% of industrial water pollution is caused due to treatment and dyeing of textiles. The water is found to be rich in color and consists of residues of reactive dyes (intermediates) and a large number of different compounds [1]. Dyes released from various sources, *e.g.*, textile industries, cosmetics, pharmaceuticals, paper and pulp industries are regarded as one of the potent pollutants being added to the natural water resources. The textile industry is believed to be the major polluter of clean water by the usage of about more than 8000 chemicals in various processes of dyeing and printing. During these processes a major proportion of dye dissipates into the water stream, which makes the discharge distinctly colored which cannot be removed by traditional water treatment methods [1]. Since majority of dyes possess high water solubility, they pass through drains and rivers and hence affect the quality of water, making it unfit for consumption [2,3].

The presence of dyes in water is unenviable, not only because of their color but also due to their hazardous effects on human health and environment [4,5]. Some adverse effects on human health include respiratory sensitization, allergic problems like dermatitis, irritation to eyes, mucous membrane and respiratory tract. Their degraded products are found to be toxic, carcinogenic and mutagenic due to presence of carcinogens like benzidine, toluidine and several other aromatic compounds [1]. Moreover, their presence can interfere with aquatic ecosystem by depleting the level of dissolved oxygen (DO) that can endanger the life of aquatic plants and animals.

Dye is a colored organic substance that imparts color to various substrates. It is classified on the basis of nature of chromophore present, acidic and basic groups, nature of origin, chemical composition and application. Methylene blue is a heterocyclic basic dye which contains three water molecules in hydrated form which is commonly employed in textile industries for dyeing purposes. The dye has molecular formula of $C_{16}H_{18}N_3SCl.3H_2O$ with the structure shown in Fig. 1.

Methylene blue has also found use in medical applications for staining tissues and as an antidote for cyanide poisoning [6,7]. At therapeutic doses, it can treat *methemoglobinemia*, which decreases the oxygen carrying capacity of hemoglobin in body. Continuous research is going on to find its potential role for the treatment of malaria and alzheimer's disease. It also exhibits antiseptic properties against bacterial infection. Apart from these medical applications, its presence in water can affect human health in various ways. It is one of the

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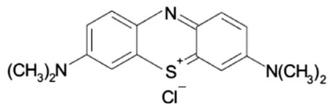

Fig. 1. Chemical structure of methylene blue.

most commonly used cationic dyes for dyeing cotton, wool and silk. Although the dye is not strongly hazardous, still it can generate some negative effects on human health. Chronic exposure to skin can cause discoloration, redness or dryness. Exposure to eyes induces irritation, watering and burning sensation to eyelids, or may lead to permanent damage in humans and animals. Ingestion may lead to irritation of gastrointestinal tract along with symptoms of headache, dizziness, nausea and vomiting. It may give rise to convulsions, cyanosis, confusion and sweating, if inhaled. Its degradation products like toluidine, benzidine and other aromatic components induce several chemical and biological changes in body; can lead to cancer and mutations. Hence, it is prerequisite to remove methylene blue from waste water.

The various methods available for the treatment of dye contaminated water are chemical precipitation, membrane filtration, ion exchange, membrane bioreactor, carbon adsorption and co-precipitation/adsorption [6,8–13]. However, chemical and biological methods cannot be used because of the non biodegradable nature of most of the dyes [14]. Hence adsorption using activated carbon is the most preferred process for removal of dyes from aqueous solutions with respect to methodology and efficiency. This is due to its highly porous structure and high surface area to volume ratio.

But the cost and the non-regenerability of the activated carbon hamper its use on large scale as an adsorbent. Hence there is an urge to develop low cost activated carbon using agricultural and other bio waste materials. Agricultural and bio-waste materials which have been used for the production of activated carbons are rice husk, peanut shell, fruit shell [15], sawdust [16], palm tree cobs and ground nutshells [17], sugarcane bagasse [18], coffee beans [19] etc. The carbon developed from these agricultural wastes can be used to remove toxic metal ions, dyes, organic pollutants from water. Modifications can be done in the carbon prepared from agricultural waste to make them more efficient and applicable at industrial scale. The present study utilized maize corn cob as a source of raw material to prepare activated carbon.

India is the fifth largest producer of corn in the world with an average production of about 22 million tons every year, and thousands of tons of corn cobs continue to exist as agricultural waste in fields and factories. They are known to have highest residual to product ratio (RPR) of 4.3 among all the agricultural waste. Thus, they possess a great potential to be used as raw material for the production of activated carbon.

The present study demonstrates the use of corn cob, a bio waste material obtained from maize/corn, for the production of activated carbon by physical activation with steam (H_2O) and carbon dioxide (CO_2) [20].

The activated carbon was characterized by using Thermogravimetric analysis (TGA), Brunauer–Emmett–Teller (BET) surface area. The thermal stability and decomposition products of oxygen functionalities are explored by Temperature Programmed Decomposition (TPD) coupled to mass spectroscopy. The main objective of present study is to develop activated carbon from agricultural waste, corn cobs and to test the efficacy of carbon to remove dye from waste water. The present study differs from the earlier reports due to the fact that a systematic approach of activation was followed by physical methods. The correlation of surface area and the surface functionality of the carbon prepared were estimated by nitrogen adsorption and temperature programmed decomposition. In order to ensure the effectiveness of the activation steps, a model dye methylene blue, is selected as a prototype for assessing the potential of corn cob carbon to remove dye from waste water. The impact of various parameters like temperature, contact time, different concentrations of adsorbent and adsorbate was studied in detail. The equilibrium data thus obtained was interpreted to study the kinetics, adsorption isotherms and thermodynamic parameters.

2. Methods and materials

2.1. Adsorbate

Methylene blue ($C_{16}H_{18}N_3ClS$, molecular weight 319.85 g/mol) was selected as an adsorbate for carrying out the adsorption studies on prepared activated carbon. It has absorption maxima at 668 nm. The 1000 ppm (1000 mg/L) stock solution of dye was prepared by dissolving 1 g of methylene blue in 1 L of deionized water (taken from Direct-Q 3 MILLIPORE water purification system). Required initial concentrations of the dye were prepared by diluting the stock solution in accurate proportion. The concentration of methylene blue in solution was monitored before and after adsorption using a double beam UV spectrophotometer (Shimadzu, Japan). The solutions of known concentration of methylene blue were used for calibration curve.

2.2. Preparation of raw carbons

The carbonization and activation of carbon were carried out independently. Corn cobs used in the present study were obtained from the nearby market. It was washed and cut into small pieces and kept overnight in oven to remove moisture content. It was then subjected to carbonization in furnace at 1173 K under N_2 atmosphere for 6 h. The flow of nitrogen gas and the heating rate was kept constant at 100 mL/min and 10 K/min respectively. After completion of treatment, sample was allowed to cool down at room temperature with continuous supply of N_2 gas through the sample. The produced carbon was collected and used for further activation processes. Physical activation involves the use of gaseous activation agents like carbon dioxide, steam or air that generally necessitates high temperature conditions.

2.3. Physical activation

In this method, carbon is allowed to interact with oxidizing gases like steam, CO_2 and air. It involves the development of molecular porous structure with high surface area in the presence of high temperature of about 600–800 °C. This method of activation can be considered as eco-friendly since it does not produce waste water; however consumption of large amount of energy and time can be called as its negative impacts. Due to high temperature requirements and low reaction rate between the oxidizing gas and the sample, usually low product yield is obtained through physical activation.

The process was initiated by packing raw carbon, CC, in quartz tube with gun cotton followed by placing it into furnace. The inlet of the tube was affixed with N_2 generator and furnace was switched on. N_2 gas was passed through the sample till the furnace temperature reached to the required set value in order to ensure the complete absence of oxygen. For all activation process the flow rate of N_2 gas and the heating rate of furnace were kept constant at 100 mL/min and 10 K/min respectively. After the attainment of the required temperature, the N_2 generator was switched off and CO_2 gas was passed through for 2 h at 700 °C. After completion of the treatment, again N_2 generator was switched on and the sample was allowed to cool down. Finally, the sample was collected and used for further analysis.

The same process was followed for the other physical activation treatments. In addition, N_2 gas was bubbled through water for steam treatment while CO2 was bubbled through water for a combination of CO_2+steam activation. **The carbon derived from CO_2 activation**