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# Adsorption of Methylene Blue onto activated carbon produced from steam activated bituminous coal: A study of equilibrium adsorption isotherm

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**Abstract**

Equilibrium adsorption isotherm for the removal of basic dye (Methylene Blue) from aqueous solution using bituminous coal-based activated carbon has been investigated. Liquid phase adsorption experiments were conducted and the maximum adsorptive capacity was determined. The effect of experimental parameters, namely, pH and adsorbent particle size were studied. Equilibrium data were mathematically modelled using the Langmuir, Freundlich and Redlich–Peterson adsorption models to describe the equilibrium isotherms at different solution pH values and particle sizes, and isotherm constants were determined. The results indicate the potential use of the adsorbent for the removal of Methylene Blue (MB) from aqueous solution. Maximum adsorption capacity of 580 mg/g at equilibrium was achieved. It was found that pH plays a major role in the adsorption process. The optimum pH for the removal of MB from aqueous solution under the experimental conditions used in this work was 11. The Redlich–Peterson isotherm was found to best fit the experimental data over the whole concentration range as indicating from the high values of the correlation coefficients ($r^2 > 0.99$).


*Keywords:* Activated carbon; Bituminous coal; Steam activation; Methylene Blue; Adsorption; Equilibrium isotherm

## 1. Introduction

Textile industry use dyes and pigments to colour their product. There are more than 100,000 commercially available dyes with over $7 \times 10^5$ tonnes of dyestuff are produced annually. Many types of dye are used in textile industries such as direct, reactive, acid and basic dyes. Most of these dyes represent acute problems to the ecological system as they considered toxic and have carcinogenic properties, which make the water inhibitory to aquatic life [1,2]. Due to their chemical structure, dyes possess a high potential to resist fading on exposure to light and water. The main sources of wastewater generated by the textile industry originate from the washing and bleaching of natural fibers and from the dyeing and finishing steps. Given the great variety of fibers, dyes and process aids, these processes generate wastewater of great chemical complexity and diversity, which are not adequately treated in conventional wastewater treatment plant [3].

Numerous studies have been conducted to assess the harm impacts of colorants on the ecosystem. It was found that colorants may cause problems in water in several ways: (i) dyes can have acute and/or chronic effects on exposed organisms with this depending on the dye concentration and on the exposure time; (ii) dyes are inherently highly visible, minor release of effluent may cause abnormal coloration of surface waters which captures the attention of both the public and the authorities; (iii) the ability of dyes to absorb/reflect sunlight entering the water, this has drastic effects on the growth of bacteria and upsets their biological activity [4,5]; (iv) dyes have many different and complicated molecular structures and therefore, are difficult to treat and interfere with municipal waste treatment operations [6,7]; (v) dyes in wastewater undergo chemical and biological changes, consume dissolved oxygen from the stream and destroy aquatic life [8]; (vi) dyes have a tendency to sequester metal ions producing microtoxicity to fish and other organisms [9].

Regarding the aforementioned problems, government legislation concerning the quality of textile industrial wastewater effluents is becoming increasingly strict, especially in developed countries. This forces textile industries to treat their waste effluent to an increasingly high standard. For example, environmental policy in UK, since September 1997, has stated that no

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synthetic chemical should be released into the marine environment [2]. This challenge has prompted intensive research in new and advanced treatment technologies, some of which are currently making their way to full-scale installation [3]. This is paralleled with increased demand currently being placed on water supply and waste disposal, and thus have necessitated broader concepts in the application of wastewater treatment.

Basic dyes were known from the past as synthetic dyes. Historically, basic dyes are important because the first synthetic dye, Mauvein (CI 50245), which was discovered in 1856 by William Perkin, belongs to this class of dye [10].

By definition, basic dyes are cationic dyes with cationic properties originating from positively charged nitrogen or sulfur atoms. The charge is generally delocalized throughout the chromophoric system, although it is probably more localized on the nitrogen atoms. In fact, basic dyes are so named because of their affinity to basic textile materials with net negative charge [11]. Most basic dyes are beautiful, shiny, crystalline compounds and their most outstanding property is brilliance. Their tinctorial value is very high; less than 1 ppm of the dye produces an obvious coloration [12,13]. According to Anliker et al. [14], basic dyes have been classified as toxic colorants.

The most important basic dye is Methylene Blue, discovered by Caro in 1878. Methylene Blue is a dark green powder or crystalline solid. It is widely used as a stain and has a number of biological uses. It dissociates in aqueous solution like electrolytes into Methylene Blue cation and the chloride ion. The coloured cation is adsorbed by several adsorbents preferentially to a very great extent [15]. For that reason, Methylene Blue was selected to be the adsorbate in this research. It has various harmful effects on the human beings, so it is of utmost importance to be removed from wastewater. In addition, it is used as a convenient indicator in the evaluation of active carbons [16].

Recently adsorption technology is rapidly gaining prominence as a technique for removing organic and inorganic micropollutants from aqueous effluents [17]. Adsorption processes may be classified as physical or chemical depending on the nature of forces involved. When adsorption occurs without any chemical reaction, it is generally termed as physical adsorption "physisorption". It is brought about as a result of Van der Waals forces [18,19]. These forces are electrostatic in origin, and are termed dispersion forces. Dispersion forces exist in all type of matter and are always present regardless of the nature of other interactions and often account for the major part of the adsorbate–adsorbent potential [20]. Many parameters can affect the quality of physical adsorption; these include properties of the adsorbed material (molecular size, boiling point, molecular mass and polarity) and properties of the surface of the adsorbent (polarity, pore size and spacing) [19]. If the adsorbate undergoes chemical interaction with the adsorbent, the phenomenon is referred to as chemical adsorption or "chemisorption". It involves a sharing of electrons between the adsorbate molecules and the surface of the adsorbent. It is restricted to just one layer of molecules on the surface, although it may be followed by additional layers of physically adsorbed molecules [21]. Under favourable conditions, both processes can occur simultaneously or alternatively.

Adsorption technology has been used extensively in industrial processes for many purposes of separation and purification. The removal of coloured and colourless organic pollutants from industrial wastewater is considered as an important application of adsorption process using suitable adsorbents [22]. Highly functional porous materials with high surface areas are generally used for such applications as they show excellent efficiency [23].

This work investigates the adsorption of Methylene Blue onto activated carbon produced from bituminous coal using equilibrium isotherms. A further aim is to describe equilibrium data using equilibrium isotherm models.

## 2. Experimental

### 2.1. Materials

Adsorption technique for the treatment of dye containing aqueous solution using low cost activated carbon has been investigated. The activated carbon (PAC2) was produced by the steam activation of New Zealand bituminous coal on an industrial scale. The adsorbent was washed and sieved into the desired particle size before coming in contact with dye aqueous solution. The ultimate and proximate analysis of the adsorbent was determined using the Perkin-Elmer 2400 Series 2 CHNC Elemental Analyzer and the Mettler Toledo TGA/SDTA 851e, respectively. Table 1 shows the physical and chemical characteristics of the adsorbent (PAC2) used in this work.

Methylene Blue C.I. 52015 (MB), supplied by ACROS Organics, USA, was used as an adsorbate in this work. It has molecular volume of 241.9 ($cm^3\,mol^{-1}$) and molecular diameter of 0.8 (nm). The chemical structure of Methylene Blue is shown in Fig. 1. Deionised water (18.2 μΩ) was used as a solvent in this work to prepare stock dye solutions.

### 2.2. Method

#### 2.2.1. Production of activated carbon

The production process pass through different stages which include preparation of the raw material and this included drying,

Table 1
The physical and chemical characteristics of PAC2 determined in this study

| | |
|---|---|
| Total surface area (BET) ($m^2\,g^{-1}$) | 857.1 |
| Micropore surface area ($m^2\,g^{-1}$) | 801.8 |
| Total pore volume ($cm^3\,g^{-1}$) | $4.5 \times 10^{-1}$ |
| Micropore volume ($cm^3\,g^{-1}$) | $3.9 \times 10^{-1}$ |
| Carbon content (%) | 81.8 |
| Hydrogen content (%) | 0.35 |
| Nitrogen content (%) | 0.38 |
| Oxygen content (%) | 16.8 |
| Moisture content (%) | 5.7 |
| Ash content (%) | 3.7 |
| Volatile content (%) | 2.2 |
| Fixed carbon | 88.4 |
| Surface acidity ($meq\,g^{-1}$) | 0.46 |
| Surface basicity ($meq\,g^{-1}$) | 0.56 |
| $pH_{solution}$ (10 mass%) | 8.2 |
| $pH_{zpc}$ | 6.3 |