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# Acid washed black cumin seed powder preparation for adsorption of methylene blue dye from aqueous solution: Thermodynamic, kinetic and isotherm studies

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The present study deals with the preparation, characterization of a green natural product-based adsorbent, acid washed black cumin seeds (AWBC), and its application for adsorption of Methylene blue (MB) dye from aqueous solution. AWBC was prepared by washing black cumin (BC) seed powder with hydrochloric acid which was characterized using Fourier transform infrared (FT-IR), X-ray diffraction (XRD), scanning electron microscopy equipped with Energy-dispersive X-ray spectroscopy (SEM-EDAX) and transmission electron microscopy (TEM) techniques. Batch experiments were performed with varying adsorbent dose (1–5 g $L^{-1}$), pH of the solutions (2—10), contact time (15–120 min), concentration (10–60 $mgL^{-1}$), temperature (27, 35 and 45 °C) and agitation at 215 rpm. Langmuir, Freundlich, Temkin, and D-R isotherm models were used to determine the adsorption capacity, mechanism and other various parameters related to temperature effects. Results of the study indicated that the AWBC adsorption data fitted well with the Langmuir and Freundlich isotherms. The maximum Langmuir adsorption capacity of acid washed BC seeds for methylene blue was found to be 73.529 mg $g^{-1}$ at 27 °C which decreased slightly with the rise of solution temperature. The pseudo-first-order, pseudo-second-order and Elovich kinetic models were used to demonstrate the reaction kinetics. Adsorption reaction followed the pseudo-second order kinetics. Overall, hydrochloric acid washed BC seeds offered low-cost adsorbent for MB removal from water.



## 1. Introduction

The discharge of coloured wastewater into the water bodies without proper treatment poses a big risk to the natural aquatic system and flora/fauna present inside [1–3]. The coloured water possesses variety of organic substances having stable molecular structure and many of them are bio-resistant, accumulate in human body, and toxic to the ecosystem [4–6]. Regular exposure to coloured water has been associated with several acute and chronic disease including skin sensitization and cancer [3,4]. Among plethora of dyes, methylene blue (MB) is most discharged colour substance in water which has been associated with high heart rate, vomiting, nausea, jaundice, tissue necrosis, and quadriplegia etc. [7–9]. Therefore, for removal of such toxic dyes from the effluents, before discharging into river/sea, the development of proper water treatment technique is highly desirable. Coagulation and flocculation, membrane separation, reverse osmosis, oxidation, and co-precipitation are the methods of choice. However, considering the cost, technical challenges, and effectiveness of the methods, none of them are ideal and are laced with one or more drawbacks [10]. Contrarily, adsorption of dyes from coloured water has been most versatile, inexpensive, ecofriendly, and widely used method [11–13]. The sorption of molecule or ions onto the carbonic substances is a promising approach as it offers low cost and high removal efficacy [14–17]. Biomasses derived from plants are abundant, non-toxic, eco-friendly, sustainable and inexpensive which interacts with charged molecules or ions via oxygen functionalities present at their cellular surface [18–20]. However, one of the drawbacks of plant materials is that they release organic compounds into the water during adsorption process, which leads to change in odour, colour, and taste of the water [18]. Moreover, most of plant matrices contain heavy metals that can be released into the water during the adsorption which may leads to toxicity. Fortunately, this drawback associated with plant materials can be sorted out by modification through treatment with acids or bases [21–23]. Acid or base treatment can help in breaking the existing bonds between the surface of plant material and the less strongly bonded organic compounds as well as heavy metals.

The efficacy of black cumin seeds (BC) was explored by considering the challenges persisting in the dye removal and the advantages offered by the biomasses. These seeds are highly abundant, inexpensive, biologically favourable, and possess a number of oxygenous groups (carboxyl, hydroxyl and phenolic) at the surface, which can be advantageous for

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the adsorption technology [24,25]. Hardly any adsorption study is available in the literature where black cumin seed material has been used for the adsorption application. The seeds were crushed to powder and for detaching already attached heavy metals and organic compounds on the surface that might be released into the water; powder material was treated with hydrochloric acid [26]. The acid washed black cumin seed powder was investigated for the adsorption of MB from aqueous solution. The adsorption was studied as function of pH, temperature, adsorbent dosage, and MB concentration. The adsorption data were tested for Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherms to establish suitable removal conditions. The kinetic data was tested using various kinetic models to propose mechanism of the process.

## 2. Experimental

### 2.1. Materials and methods

BC seeds were purchased from local market, New Delhi, India. The seeds were washed with double distilled water several times to remove dirt, and then dried at 65 °C in an oven for 48 h. AR grade hydrochloric acid (HCl), sodium hydroxide (NaOH), and MB were purchased from Merck India Ltd. Stock solution of MB (1000 mg $L^{-1}$) was prepared and diluted to appropriate concentration for adsorption experiments.

### 2.2. Preparation of bio-adsorbent

Previous reported studies revealed that black cumin seeds possess predominantly potassium, phosphorus, sodium, and iron while zinc, calcium, magnesium, manganese, and copper at lower levels [25]. Therefore, for leaching out these elements the seed material needs chemical treatment. Generally, heavy metals present in the plant material can be extracted or leached using acid, which was achieved by following a reported method available in the literature [27]. In brief, the dried seeds were grinded to appropriate sizes 0.8–1.0 mm with high-speed disintegrator and separated with standard sieves and named BC. The powder was treated with common inorganic acid, hydrochloric acid (HCl) as reported by Zhao et al. [27] and named as acid washed black cumin seed powder (AWBC) and stored in desiccator for characterization and adsorption.

### 2.3. Characterization

#### 2.3.1. Surface characterization

The active functional groups on the surface of biomaterial were analyzed by Fourier transform infrared spectra (FT-IR). The spectra was recorded in KBr in the range of 4000–400 $cm^{-1}$ using a VERTEX 70/70v, FT-IR spectrometer (BRUKER). The X-ray diffraction (XRD) of the material was recorded on a Rigaku Ultimav-IV, Cu, Kα radiation ($\lambda = 1.54060$) in 2θ range 10 to 80°. The morphology of the AWBC was analyzed from field emission scanning electron microscopy (FESEM (Nova Nano SEM 450, FE1) equipped with EDAX (Bruker 127 eV) and transmission electron microscopy analysis using electron microscope (Tecnai T-30 (300 kV FEGTEM) operated at 80 kV.

#### 2.3.2. Determination of point of zero charge of AWBC

Zero point charge (ZPC) of solid explains the pH condition of water at which the surface of an adsorbent has zero charge density, and below or above this pH, the surface gets positive and negative charge due to protonation and deprotonation of oxygenous groups, respectively. ZPC controls the adsorptive interaction between solid surface and the charged molecule. Although, various methods are available for the determination of ZPC, salt addition method was employed in the present study [28]. In this method, 20 mL of 0.1 M $KNO_3$ solution was transferred in a series of 50 mL Erlenmeyer flasks and pH of each solution was adjusted from 2 to 10 by adding either 0.1 M HCl or 0.1 M NaOH solutions. The initial pH of these solutions was noted as $pH_i$ using EQUIP-TRONIC pH meter (model EQ-610). 0.2 g of AWBC powder was added to each of the flasks and these flasks were placed on water bath shaker at 27 °C and agitated at 215 rpm until no difference in pH values was observed between two successive readings. The equilibrium pH value was noted as $pH_e$ and ZPC value of surface was calculated from the plot of ΔpH ($pH_i$-$pH_e$) vs $pH_i$.

### 2.4. Determination of adsorption capacity and removal rate

MB adsorption experiment was carried out in batch manner for contact time of 0–120 min at neutral pH, and room temperature. A series of 50 mL of Erlenmeyer flasks having 10 mL of MB solution of an initial concentration varying from 10 to 60 mg $L^{-1}$ and 1.0 g $L^{-1}$ of AWBC powder were mechanically agitated at 215 rpm followed by the centrifugation of MB loaded AWBC from agitated MB solution. The final concentration of supernatant (MB solution) was estimated by analyzing their absorbance using ultraviolet-visible (UV–Vis) spectrophotometer at 660 nm. The obtained adsorption data was applied to explore the removal capacity of AWBC for MB. Initial concentration of MB solution was estimated from the calibration curve plotted between absorbance and concentration of MB solution [Supplementary file (Fig. S1)]. The initial and the final concentration of MB in supernatant gave the uptake capacity as follows [29]:

$$\text{Maximum uptake of MB}, Q_e = (C_o - C_e)\frac{V}{m} \quad (1)$$

where, $C_0$ and $C_e$ are the initial and equilibrium concentrations of MB, respectively. V is the volume of MB solution in liter and m (g) is the amount of AWBC powder.

$$\text{Percentage removal}, R\% = \left(\frac{C_o - C_e}{C_o}\right)100 \quad (2)$$

Experiments were carried out in triplicate and the mean values of $C_e$ and $Q_e$ were applied for optimization of MB uptake capacity in terms of AWBC amount, initial MB concentration, pH, time, and temperature. Ultimately, adsorption data obtained from above study was verified by fitting in various isotherms, kinetic and thermodynamic relationships to design the appropriate water treatment system using bio-adsorbent.

## 3. Results and discussion

### 3.1. Characterization of AWBC

Previous study on black cumin seed contents reported that BC seed contains the certain composition of protein, fat, crude fibre, and carbohydrates [25]. The major unsaturated fatty acids present in seeds are linoleic and oleic acid while the main saturated fatty acid is palmitic acid. The main amino acids present in seeds are glutamic acid, arginine and aspartic acid while cystine and methionine are the minor amino acids, thus having high nutritional potential [25].

FT-IR spectroscopy gave the information about the functional groups present on the surface of AWBC which provides adsorptive sites for MB molecules. The FT-IR spectrum of AWBC (Fig. 1) showed various bands at different frequencies. The broad peak around 3305 $cm^{-1}$ might be attributed to –OH stretching frequency. Two strong peaks at 2926 and 2852 $cm^{-1}$ were assigned for C—H stretching of $—CH_3$, and $—CH_2$ groups, respectively [30–33]. The presence of C═O group was confirmed from the strong band around 1713 $cm^{-1}$. The absorption peaks about 1651 and 1536 $cm^{-1}$ were attributed to the C═O and N—H bonds of amide groups [33]. The —C═C— stretching frequency was assigned at 1450 $cm^{-1}$and —COOH group was confirmed from the peak at 1412 $cm^{-1}$ [31,33]. The peak at near 1232 $cm^{-1}$ was assigned