Removal of methylene blue dye from aqueous waste by iron oxide activated carbon nanocomposites

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ABSTRACT
The removal of methylene blue dye from aqueous waste by Magnetic nanoparticle activated carbon (MNPAC) was investigated. Magnetic nanoparticle activated carbon (MNPAC) was synthesized by mixing aqueous suspension of activated carbon (AC) and Fe_3O_4 by chemical co-precipitation method. This Magnetic Nanoparticle Activated carbon (MNPAC) was characterized by X-ray Diffraction (XRD), Transmission Electron Microscope (TEM), Fourier Transform Infrared Spectroscopy (FTIR) and Vibrating Sample Magnetometer (VSM). The result of XRD characterization was indicated Fe_3O_4 as the product. FT-IR Spectrum of MNPAC shows the presence of various surface groups. TEM image of the Fe_3O_4 showed nanoparticles Fe_3O_4 have the mean diameter 5-20 nm. MNPAC exhibits super magnetic properties under external magnetic field with saturation magnetization value of 22.80emu/g at room temperature. The adsorption equilibrium was represented with Langmuir, Freundlich, and BET isotherm models. The adsorption data shows that the adsorption capacity was investigated by absorbing Methylene blue (MB) dye from aqueous waste, which demonstrated an excellent adsorption capacity of MNPAC (500 mg g^{-1}). A Langmuir kinetic model is fitted well for methylene blue adsorption on MNPAC.

KEY-WORDS: Magnetic nanoparticle activated carbon, Methylene blue dye, adsorption isotherms and kinetics.

INTRODUCTION

Dyes are used in large quantities in many industries such as textiles, leather, paper, plastics, etc. to colour their final products. The textile industries are the greatest generators of liquid effluent, due to high quantity of water used in the dyeing processes [1].Methylene blue is a common dye mostly used by industries involve in textile, paper, rubber, plastics, leather, cosmetics, pharmaceutical and food industries. Effluents discharged from such industries contain residues of dyes. Consequently, the presence of very low concentrations in effluent is highly visible [2]. Methylene blue (MB) dye causes eye burns, which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation [3,4]. Discharge of MB into the hydrosphere can cause environmental degradation as it gives undesirable colour to water and reduces sunlight penetration. The consumption of MB has many adverse effects due to its carcinogenic, genotoxic, mutagenic and teratogenic properties. Methylene Blue (MB) Dyes removal from wastewater effluent is a major environmental problem because of the difficulty of treating such streams by conventional physical, chemical, physicochemical and biological treatment methods. Many physical and chemical treatment methods including adsorption, coagulation, precipitation filtration, electro dialysis, membrane separation and chemical oxidation have been used for the treatment of dye-containing effluents [5-8]. Among the treatment methods, adsorption on commercial activated carbon is a very effective removal technique which produces effluents containing very low levels of dissolved organic compounds [9]. However, the expensive price of the commercial activated carbon had encouraged many researchers to investigate the use of cheap and efficient alternative substitutes to remove dyes from wastewater [10]. In recent years, many researchers and scientists has been interested in Magnetic Nanoparticle Activated carbons. Nanoparticles are not only widely applied in the fields of medicine, molecular biology and bioinorganic chemistry, but they are also well known in environmental science [11]. Magnetic materials have gained special attention in water treatment [12-13], based on their advantage such as easy separation, simple manipulation process, kind operation conditions and easy specifically functional modifications. The present work is an attempt to prepare Magnetic Nanoparticle Activated carbon (MNPAC) by using activated carbon and Fe_3O_4 magnetic nanoparticles by chemical coprecipitation method for the removal of Methylene Blue (MB) dyes from aqueous solution.

MATERIALS AND METHODS

Materials

Nitric acid (HNO_3, 63%), Ferric Chloride ($FeCl_3$), Ferrous chloride ($FeCl_2$), Sodium hydroxide (NaOH) and methylene blue (MB) dye (Merck, India) were procured from Nagpur, India.

Preparation of Magnetic Nanoparticles activated carbon (MNPAC)

The magnetic nanoparticle activated carbon (MNPAC) was prepared by a chemical co-precipitation method. Synthesis of Fe_3O_4 magnetic nanoparticles was carried out by co-precipitation method of ferric and ferrous salts under the presence of N_2 gas. To prepare MNPAC, Fe_3O_4 magnetic nanoparticles were combined with aqueous suspension of activated carbon. In the first step, a known quantity of activated carbon was impregnated with nitric acid (63%) and kept undisturbed for 3h at 80°C by using an ultrasonic bath. The sample was then filtered and dried in a room temperature. Subsequently, aqueous suspension of 5g obtained activated carbon was added into 200 ml of aqueous solution containing $Fe_3O_4.9H_2O$ and placed in ultrasonic bath for 1 h at 80°C. Then the sample was filtered and dehydrated in an oven at 105°C for 1 h. The sample was heated in a muffle furnace at 750°C for 3h under nitrogen gas atmosphere. The synthesized MNPAC was washed with deionised water for four times and then dried at a 105°C in a moisture oven and kept in a desiccator for use.

Method for Adsorption Isotherm and Kinetics study

To evaluate adsorption equilibrium data for Methylene Blue (MB) Dye, experiments were carried out in a batch system. 100mL of MB solution of known concentration was placed in 300 ml BOD bottles and accurately 0.1 gm Magnetic Nanoparticle Activated carbons (MNPAC) were added into each bottle. The BOD bottles were placed on a mechanical shaker with shaking speed of 600+-20 rpm and stirred for 48 hours. After equilibrium reached, solutions from each bottle were withdrawn and adsorbate concentration, C_e was determined by UV/visible spectrophotometer (Model Lambda 35, Perkin Elmer UV/VIS spectrophotometer) with wavelength 667 nm.

The specific amount of methylene blue adsorbed was calculated from the following equation;

$$Qe = (C_0 - C_e) \times V/W$$

Where Qe is the adsorption amount (mg/g) in the solid at equilibrium, C_0 & C_e are initial equilibrium concentration of Methylene Blue (mg/L) respectively; V is volume (L) of aqueous solution of methylene blue and W is weight (g) of Magnetic Nanoparticle Activated carbon.

For kinetics study, a cylindrical vessel of 5L capacity fitted with 8 baffles was used. 2gm of accurately weight prepared Magnetic Nanoparticle Activated carbon was introduced into 2L of MB solution of known concentration with constant stirring. The adsorbate was taken out from the vessel at regular time intervals and concentration was determined by using UV/visible spectrophotometer.

RESULT & DISCUSSION

Characterization of prepared MNPAC

The X-ray diffraction (XRD) patterns of Magnetic Nanoparticle Activated carbon were obtained on a powder X-ray diffraction system from analytical model XPERT-PRO diffractometer. Powder X-ray diffraction patterns are presented in figure-1. The X-ray diffraction patterns for MNPAC display a number of sharp peaks which are compatible with the presence of $Fe(OH)_2$ and $Fe(OH)_3$ and of Fe_2O_3. This illustrates that domain of iron species exist which is crystalline in the MNPAC sample.

To resolve the functional groups present and its wave numbers, FTIR of MAC were carried out by using Fourier transform infrared spectrophotometer (FTIR) (Perkin Elmer,PE-RXI) in the range of 450-4000cm^{-1}. The FTIR spectra in Figure-2 show the presence of various surface groups like phenolic –OH, carboxylic, aliphatic amines, Fe-O bond vibration of Fe_3O_4 compatible with the presence of iron oxides (Fe_3O_4) in the sample [14].

The size and shape of nanoparticles of MNPAC were observed by Transmission electron microscope (TEM) and high resolution TEM (HRTEM) on a JEOL JEM-2010F.TEM micrographs for the prepared MNPAC and are shown in figure- 3 (a-b). From these micrographs it is observed that the particle size of the nanoparticles lie in the range of 5-20 nm. Fe_3O_4 nanoparticles with a cubic structure are clearly visible in the micrographs. The particles formed tend to cluster as they are magnetic in nature. Recording of higher resolution images of the carbon might be quite difficult owing to its highly disordered structure [15].

The magnetic properties of a ferromagnetic material are represented by the plots of magnetization (M) against the field strengths giving the hysteresis loop. The hysteresis loop was carried out using Lakeshore vibrating sample magnetometer (VSM) 7410 at room temperature. The suitability of ferromagnetic materials for application depends on characteristics shown by their hysteresis loops [16] obtained from plots of magnetization (M) against the field strengths. The saturation magnetization of Magnetic Nanoparticle Activated carbon is 22.80emu/g at room temperature as shown in figure-4

Adsorption isotherms

In order to study the dominant adsorption mechanism and to compute various adsorption parameters three adsorption models, namely Langmuir, Freundlich and BET were used.

The Langmuir adsorption model [17] is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the sorbed molecules. The linear form of the Langmuir isotherm is given by the following equation:

$$1/Q_e = (1/Q_0) + (1/Q_0b) \times 1/C_e$$

The plot of Qe (mg/g) verses the equilibrium concentration of adsorbate in solution Ce (mg/L) in figure-5. Where Q_e is the maximum amount of the Methylene Blue (MB) adsorbed per unit weight of the adsorbent at equilibrium, Q_0 is the monolayer capacity of adsorbent, C_e is the concentration of adsorbate at equilibrium, and b is a Langmuir constant. Langmuir parameters Q_0 and b were calculated from the slope and intercept of the linear plots of $1/Q_e$ vs. $1/C_e$ as given in figure-6 and value shown in table-1.

The adsorption data for Methylene Blue (MB) was also analyzed by the Freundlich adsorption model. The Freundlich isotherm [19] is an empirical equation employed to describe heterogeneous systems. The linear form of Freundlich adsorption model is as follows:

$$\text{Log}(Q_e) = \text{Log}K_f + 1/n\ \text{Log}(C_e)$$

Where, K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively. The value of K_f and 1/n are obtained from the slope and intercept of the linear Freundlich plot of Log Qe vs. Log Ce in figure-7 and the values shown in Table-1.

The BET adsorption model can be derived similar to the Langmuir adsorption model, but by considering multilayered gas/solid molecule adsorption, where it is not required for a layer to be completed before an upper layer formation starts. The Langmuir adsorption isotherm is usually better for chemisorptions and the BET adsorption isotherm works better for physisorption for non-micro porous surfaces. The BET adsorption equation can represented as:

$$C_e/Q_e (C_s-C_e) = 1/Q_0z + (z-1/Q_0z)*C_e/C_s$$

Where C_e, Q_e, Q_0, have the same meaning as in Langmuir model, C_s is the saturated concentration of the adsorbate and z is BET constant. BET parameters Q_0 and z were calculated from the graph

Plotted between C_e/C_s vs $C_e/Q_e (C_s-C_e)$ in Figure-8.The values shown in Table-1

Kinetic study for MNPAC:

A simplified rate expression based on Langmuir adsorption theory has also been used to evaluate the adsorption rate constant using Langmuir kinetic model [18]. Kinetic data were evaluated using following Langmuir Kinetic equations,

$$\ln[(C_t-C_e)/(C_t+a)] = -kC_et + \ln[(C_0-C_e)/(C_0+a)]$$

Where, $a = (C_0/kC_e)$ and $k = Ka/Kd$

The rate of adsorption in kinetics of MNPAC is more at initial time intervals shown in figure-9. The adsorption rate constant 'Ka' and desorption rate constants 'Kd' thus evaluated by plotting

$\ln[(C_t-C_e)/(C_t+a)]$ against t, (figure-10) and the value of adsorption rate constants for MNPAC are given in Table-1.

CONCLUSION

The materials described in this work showed the adsorption features of Activated carbon combined with Fe_3O_4 nanoparticles to produce Magnetic Nanoparticle Activated carbon (MNPAC) by chemical coprecipitation method. MNPAC were prepared, characterised and evaluated for removal of Methylene Blue dye from aqueous waste. These magnetic adsorbents have very good adsorption efficiency for Methylene Blue (MB) contaminants in water. XRD analysis of MNPAC shows the presence of $Fe(OH)_2$ and $Fe(OH)_3$ and of Fe_2O_3. The FTIR spectra show the presence of various surface groups like phenolic –OH, carboxylic, aliphatic amines, Fe-O bond vibration of Fe_3O_4 compatible with the presence of iron oxides (Fe_3O_4) in the sample. The TEM of MNPAC shows Fe_3O_4 nanoparticles of size 5-20 nm. MNPAC exhibits super magnetic properties under external magnetic field with saturation magnetization value of 22.80emu/g

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Figure-1 XRD of MNPAC

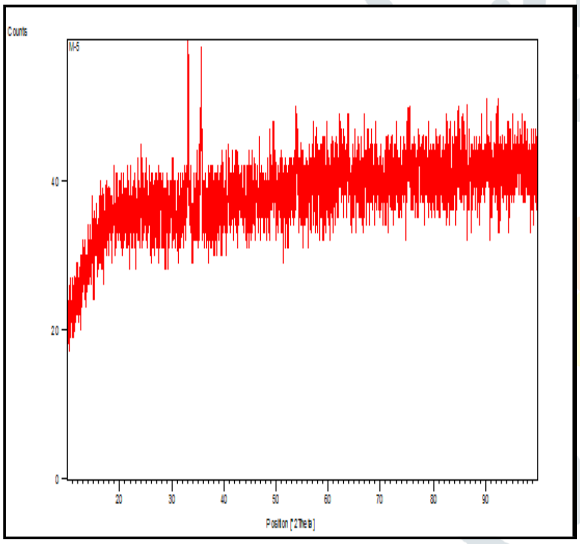

Figure-2 FTIR images of MNPAC

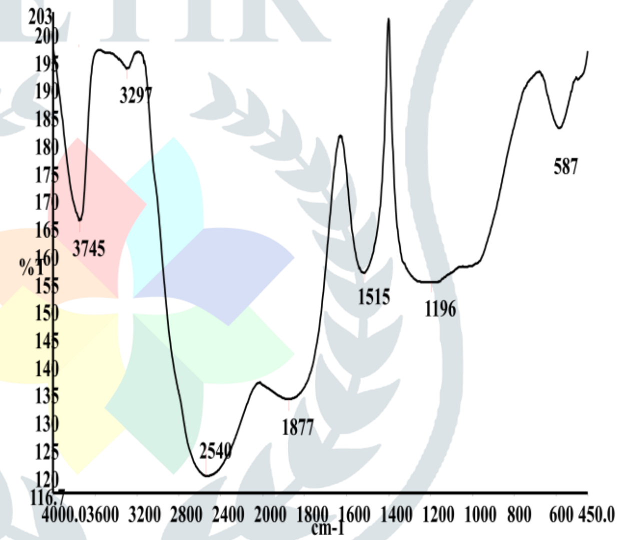

Figure-3 (a), (b) TEM images of MNPA

Figure-4 VSM Magnetisation Curve of MNPAC

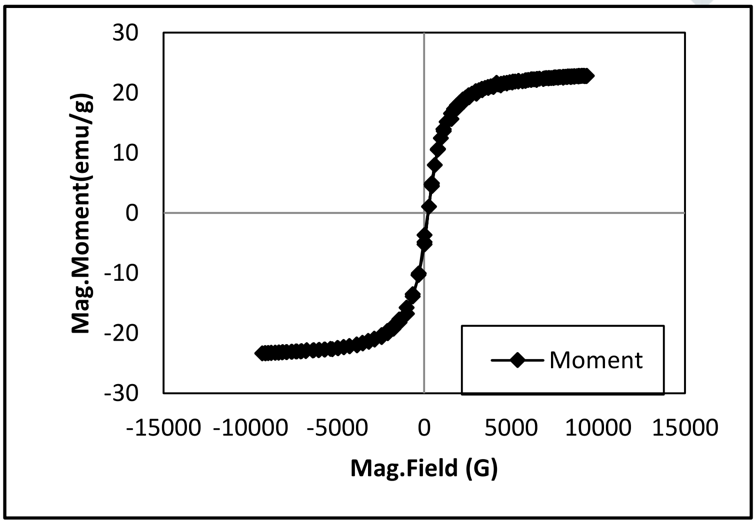

Figure-6 Langmuir Adsorption graph of MNPAC

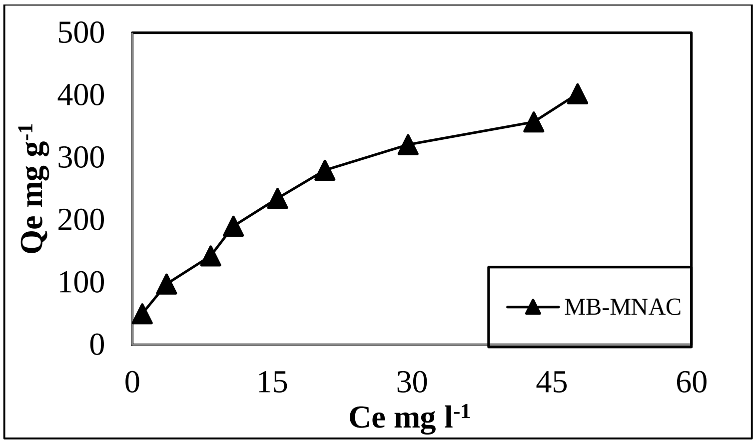

Figure-5 General Adsorption graph of MNPAC

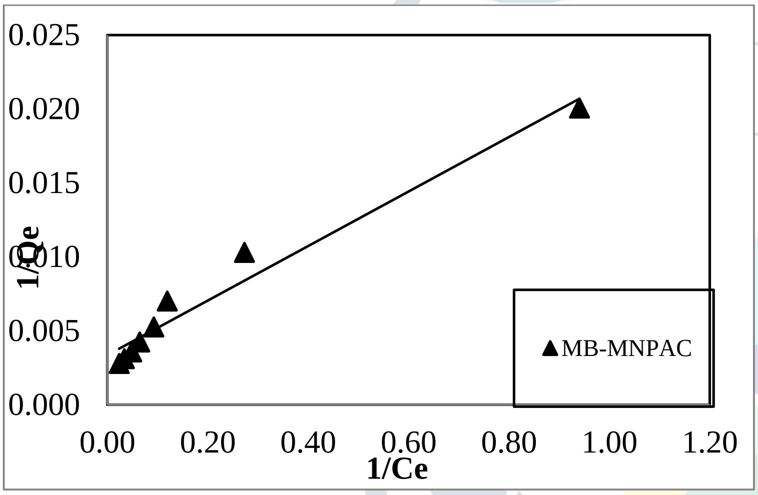

Figure -7 Freundlich Adsorption graph of MNPAC

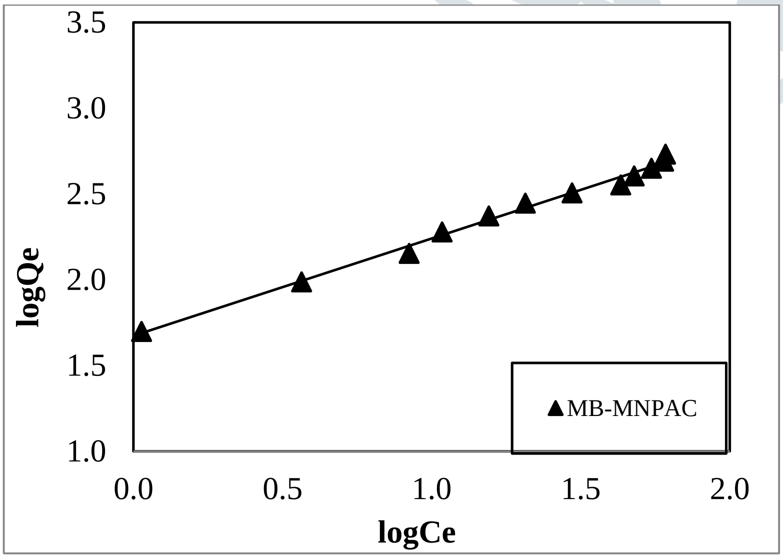

Figure-8 BET Adsorption graph of MNPAC

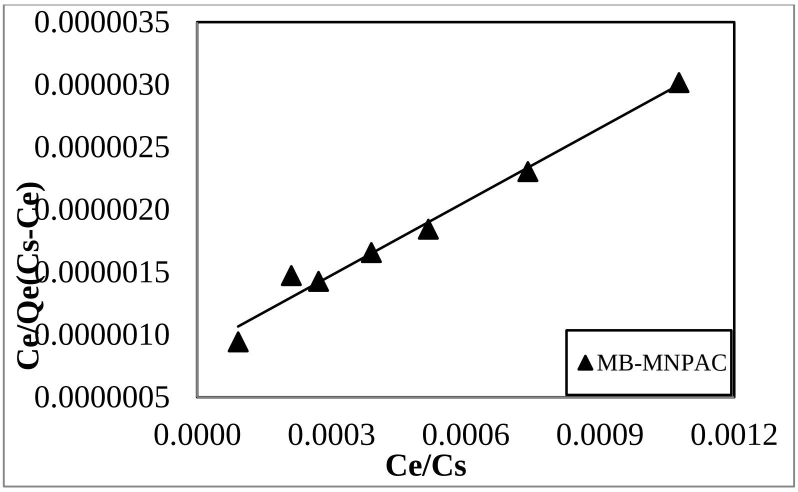

Figure-9 General Kinetics graph of MNPAC

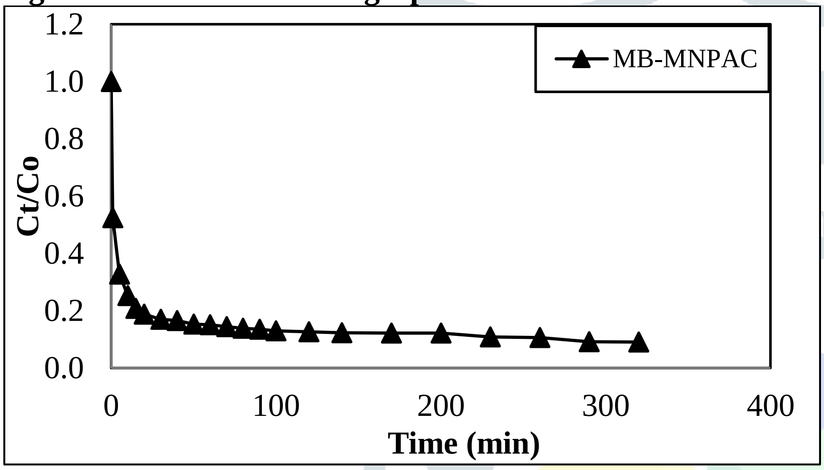

Figure-10 Langmuir kinetics graph of MNPAC

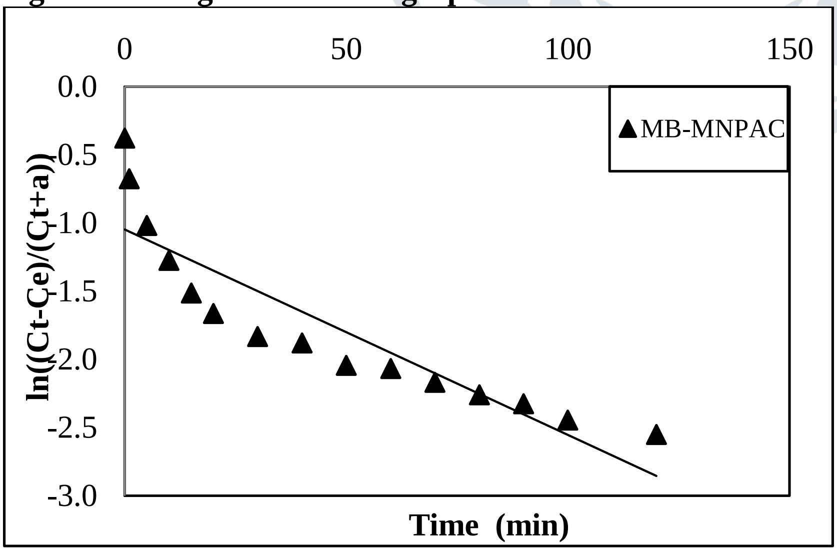

Table-1 Adsorption isotherm and Kinetic data for MNPAC

Adsorbent	Adsorbate	Langmuir Constant		Freundlich Constant		BET Constant		Langmuir Kinetic Constant	
MNPAC	Methylene Blue (MB)	Q^o (mg/g)	b	K_f	1/n	Q^0	z	Ka	Kd
		500	0.166	47.09	0.567	500	2221	262.68	0.00493

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