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Removal Performance Assessment of Dyes in Solution Using Mesoporous MCM-41 Prepared from Iraqi Rice Husk

Abstract- In this study, mesoporous silica MCM-41 material was synthesized using Iraqi rice husk for the first time, as silica precursor and Cetyltrimethylammonium bromide (CTAB) as a template. MCM-41 was characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), BET surface area, Fourier transform infrared (FTIR) spectroscopy and Thermal Gravimetric Analysis (TGA). Then the ability of MCM-41 as adsorbents was tested to treat dyes as one of the organic pollutants from synthetic wastewater. The adsorption behavior of Gentian violet (GV), Methylene blue (MB) and Congo red (CR) dyes from synthetic wastewater onto mesoporous MCM-41 was tested. Batch adsorption was employed to determine the effects of pH (2-11), adsorbent dose (0.05-1g), contact time (0-200 min), initial concentration (25-300 mg/L) and temperature (293, 313, 333 K). It was found that MCM-41 has higher potential for adsorption of basic dyes (GV, MB) and lesser for acidic dye (CR) from aqueous solution in batch system. Adsorption isotherms were fitted with the Langmuir, Freundlich and Temkin models. It was found that the Langmuir adsorption isotherm model for GV and CR had the best fit with; on the other hand, the Freundlich adsorption isotherm model had the best fit for MB.

Keywords- MCM-41; rice husk; Gentian violet; methylene blue; Congo red; Adsorption.

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1. Introduction

Water can be respected contaminated when it changes its quality or organization either or therefore human exercises [1]. Among the diverse natural toxins of oceanic biological communities, colors are the huge and critical gathering of chemicals show in modern waste [2]. The level of colors even in low fixation is exceptionally obvious and will influence oceanic life and nourishment web. Many colors are hard to corrupt and they are for the most part stable to light and oxidizing specialists. Therefore, it is vital to decrease the color focus from squander water [3]. Colored wastewaters are released by a wide gathering of sources, for example, materials, printing, shading, dyestuff get-together, and nourishment plants. A few examinations have been led on the physical, synthetic, and natural strategies for expelling shading from colored wastewater [4]. Such as cutting edge oxidation and organic process, coagulants, electrochemical, and adsorption methods. For the above strategies, it was discovered that adsorption may be a productive and financial procedure to evacuate colors and furthermore to control the biochemical oxygen request [5]. Several adsorbents have been

tried for color expulsion, for example, enacted carbon, alumina, silica gel, zeolite [6].

Zeolite has wide applications in principal science, petrochemical science, pharmaceutical, air cleaning, normally kind composite structure and waste remediation. Despite these artificially appealing properties of zeolites, they wind up evidently deficient when reactants with sizes over the estimations of the pores must be dealt with. The mesoporous materials can resolve these issues [7]. The masterminding of mesoporous materials family M41S since 1992 beginning in the generally later past has opened a wide field of uses. Mesoporous sub-atomic sifters have sensibly clearing and uniform pore assess (15-100 Å), which break past the pore measure imperative (< 15 Å) of microporous zeolites, high surface zones (> 1000 m²·g⁻¹) [8]. MCM-41 mesoporous materials, as a subset of nanostructured adsorbent, have been the center of interest of many researchers throughout the world.

The M41S mesoporous family are often referred to as MCM materials such as MCM-41 with a 2-D hexagonal structure and the MCM-48 with a 3-D cubic structure and MCM-50 with a 3-D cubic

structure [9]. This is credited to their wide use in catalysis, reactant underpins, sensors, expulsion of organic (dyes) and nonorganic (substantial metals) and medication conveyance [7]. The MCM-41 nanomaterial is typically blended by utilizing research facility reagents as silicate sources, for example, sodium silicate and tetramethylammonium silicate (TEOS) and ludox. Research center reagents are yet costly for an extensive scale generation. Alluding to the writing, many endeavors are centered on the utilization of a waste source, for example, fly and base fiery debris, rice husk, rather than the lab reagents to diminish the cost of mesoporous materials [7]. Rice husk (RH) is a rural waste material that ought to be wiped out. Because of its high silica, content rice husk slag has turned into a hotspot for planning various silicon mixes, for example, mesoporous MCM-41 [10]. In this investigation, MCM-41 mesoporous silica was combined and portrayed to use as adsorbent to evacuate the fundamental and acidic colors from engineered wastewater in-group adsorption framework.

2. Materials and Methods

I. Materials

The reactants used in this study were [(Cetyltrimethylammoniumbromide) (CTAB) as a surfactant purchased from Sigma Aldrich Company and rice husk used to prepare silica was from Al-Najaf province, Hydrochloric corrosive (HCl, 37%), sulfuric corrosive (H₂SO₄, 98%) were bought from Thomas Baker/India, sodium hydroxide (NaOH, 99%) was from BDH England, gentian violet (GV), methylene Blue (MB) and Congo red (CR) were from SCRC China.

II. Synthesis of adsorbents

RH-MCM-41 was synthesized by hydrothermal method as follows [11].

- CTAB and refined water were blended and mixed for 30 min there after sodium silicate arrangement was included the type of drops to the surfactant arrangement under lively mixing. Subsequent to mixing for 30 min a little measure of 1 M H₂SO₄ was added to the blends to decrease the pH to 10.2 and mixed for 1 h. The silica-surfactant gel found was hydrothermally treated at 110 °C for 36 h.
- After cooling to room temperature, the subsequent strong item was recuperated by filtration on a Buchner channel, washed with refined water, and dried in the outside at 90 °C.

- Surfactant was removed by calcining the as-synthesized product at 550 °C for 5 h. with heating rate of 2°C/min in a furnace.

III. Preparation of Adsorbate Solution

The stock solutions with 500 ppm concentration of (GV), (MB) and (CR) were prepared. From the stock solution, different concentrations of GV, MB and CR were prepared by diluting with distilled water. The concentration of the dye solution (GV, MB, CR) were estimated using UV spectrophotometer at maximum wavelengths of the GV (λ_{\max} = 584 nm), for MB (λ_{\max} =664nm) and for CR (λ_{\max} =492nm).

IV. Characterization of Adsorbents

An x-ray diffraction spectrum was utilized to identify the crystal structure of MCM-41 samples, (XRD-6000 shimadzu, Japan). The FTIR instrument (FT-IR, Bruker-Tensor 27, Germany) spectrometer is a system that gives data about the distinguishing proof of certain utilitarian gatherings, for example, - OH, Si-OH, Si-O-Si and the practical gatherings joined on to the MCM-41 solids tests. The surface morphology of the mesoporous materials was procured by sifting electron microscopy (SEM, TESCAN Germany). The specific surface scopes of the examples were registered using the Brunauer-Emmett-Teller (BET) method (BET, Q-surf 9600 USA). A thermogravimetric examination (TGA) was finished using thermogravimetric Analyzer TG-DSC (STA PT1000 USA) to get information concerning the warm strength of MCM-41.

V. Batch Adsorption Experiments

Batch adsorption tests were performed in 100 ml cone like jugs containing 100ml of shading course of action of known concentration and pH. The pH was adjusted by techniques for 0.1M HCl and 0.1M NaOH plans. A known measure of adsorbent was incorporated the 100 ml containers at room temperature. The blend was mixed on electrical shaker at 250 rpm. The harmony ponder was completed by taking samples from the shaker at various time of intervals. Each sample, the adsorbent was isolated by utilizing syringe channel (0.2µm). The grouping of the color arrangement was evaluated by measuring absorbance utilizing UV spectrophotometer. The expulsion effectiveness was ascertained by the accompanying condition:

$$R\% = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

Where R is the removal efficiency and Co is the initial dye concentration and Ct the dye concentration in mg/l at t time

VI. Adsorption Isotherm

The adjust adsorption isotherm is vital in depicting among adsorbate and adsorbent, and it is fundamental in the arrangement of adsorption systems. The adsorption isotherm was found out at different mass of MCM-41 (0.05-1) g/l with 40mg/l MB and pH 7. The adsorption data for MB was fitted into Langmuir, Freundlich and Temkin isotherms conditions. The linearization type of the Langmuir condition [12] is as the following:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \quad (2)$$

Where q_m is the max. adsorption capacity(mg/g). K_L is a constant related to net enthalpy of adsorption l/mg.

The constants q_m and K_L can be calculated from slope and intercept of the straight plot of C_e/q_e versus C_e . The immediate kind of the Freundlich condition is given by [13]:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (3)$$

Where K_f and $1/n$ are Freundlich constants. The constant K_f and $1/n$ can be obtained from the slope and intercept of the plot of $\ln q_e$ versus $\ln C_e$. Temkin isotherm has the general form [14]:

$$q_e = B \ln K_t + B \ln C_e \quad (4)$$

Where steady $B=R_e T/b$. The adsorption information were broke down as per Eq.(4). A plot of q_e versus $\ln C_e$, empowers the assurance of the isotherm constants K_t and B.

3. Results and Discussion

I. Characterization of silica prepared from Iraqi rice husk

The structure of the silica was examined by X-beam diffraction and the state was uncovered by the state of the XRD design got. The X-Ray diffraction of silica is shown in Figure 1 with solid expansive pinnacle of immaculate silica around $(2\theta)= 23^\circ$, which are yielded with the solid wide pinnacle of a trademark nebulous SiO_2 , nonappearance of sharp pinnacles affirms the nonattendance of requested crystalline structure in the readied Silica. The outcome got in the present work is in great concurrence with the outcomes acquired by Nittaya and Apinon [15].

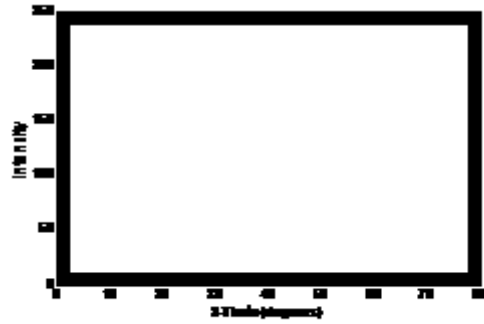


Figure 1: XRD pattern of rice husk silica

The FTIR range of test silica separated from rice husk was introduced in Figure 2, that demonstrates an exceptional topsy-turvy, symmetric extending and twisting vibration for Si-O-Si securities at wave numbers 1097, 806, and 467 cm^{-1} individually; while the assimilation band at around 3672 cm^{-1} identified with remain water atom. The ingestion band at around 960 cm^{-1} is not recognized. It uncovers that there is no silanol group [11].

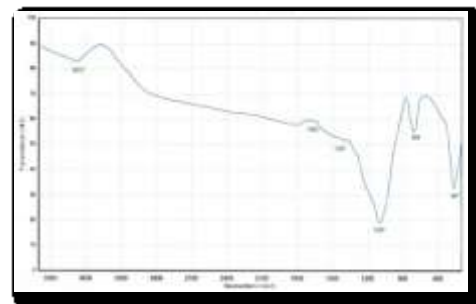


Figure 2: FT-IR spectra of rice husk silica

II. Characterization of calcined MCM-41 and uncalcined MCM-41

The XRD case of calcined MCM-41 and uncalcined MCM-41 is shown in Figure 3a,b. Three impressions of silicon dioxide valuable stones were found at 2θ in the region of 2° and 5° , contrasting with reflection planes 100, 110 and 200, independently. These sharp banners demonstrated the long-run solicitations of the uniform hexagonal mesoporous structure, which is the incredibly typical for MCM-41 sort. As showed by these results, it was contemplated that silica from Iraqi rice husk red-hot remains can be utilized for the amalgamation of MCM-41 material. The enlisted XRD examples of the calcined MCM-41 solids demonstrated that these later are preferable organized over before calcination this is because of the freedom of porosity following the corruption of the surfactant particles show inside the pores [16]. The outcome got in the present work is concurring admirably with that outcome acquired [17].

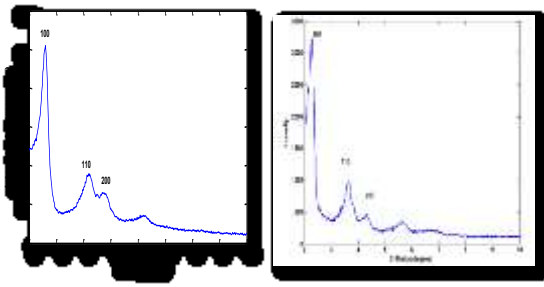


Figure 3: X-ray diffraction patterns of MCM-41, (a): calcined (b): Uncalcined MCM-41

The surface morphology of MCM-41 using SEM illustrate in Figure 4. It can be observed the presence of agglomerated spherical particles, sometimes distorted spherical shapes can be observed which are a typical feature of mesoporous materials [18].

The BET surface area and pore volume of MCM-41 were measured and presented in Table 1. These outcomes demonstrate that the arranged mesoporous material MCM-41, have a higher surface area in the range (700-1500 m²/g) and pore volume (>0.6 cm³/g) for MCM-41 [19]. Table 1 shows structure properties of MCM-41.

Figure 5 shows the FTIR spectra of the MCM-41 samples. The Si-O-Stretching band around 1227-1068 cm⁻¹ was assigned as the fingerprint region of MCM-41.

Figure 5b which represents the uncalcined MCM-41, absorption bands around 2918 and 2850 cm⁻¹ correspond to characteristics of alkanes groups, which were, disappear in calcined MCM-41 spectra. The absorption band at 1477, which is assigned to C-H stretching vibration of an alkyl group, it was clearly observed in the spectrum of uncalcined MCM-41. For uncalcined MCM-41 appearance of an expansive band at 3410 cm⁻¹ is because of O-H stretching of surface hydroxyl groups, spanned hydroxyl groups and adsorbed water particles which vanish from calcined MCM-41. For uncalcined MCM-41 the band at 727 cm⁻¹ is associated with vibrations by the organic template. Stretching Si-O-Si (800 cm⁻¹) is prominent in calcined MCM-41 [11].

Thermal gravimetric analysis of the MCM-41 sample is shown in Figure 6 the sample was heated from room temperature to 600 °C, at a rate of 10 °C/min. Thermal gravimetric curves showed no mass losses of MCM-41 this indicates that MCM-41 are thermostable. This outcome is in agreement with that of Kalash [20].

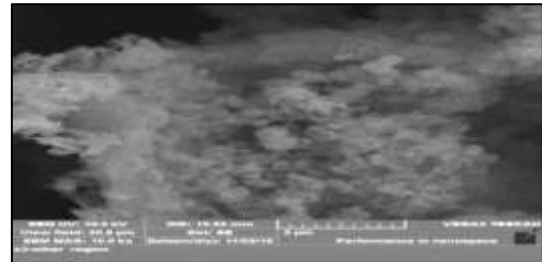


Figure 4: Typical SEM image for MCM-41

Table 1: Structure properties of MCM-41

Material	S _{BET} (m ² /g)	Pore volume (cm ³ /g)
MCM-41	1050.6	0.6709

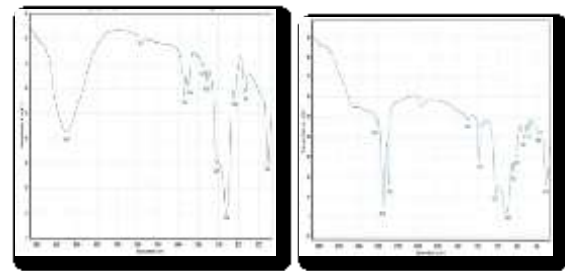


Figure 5: FT-IR spectra of MCM-41 (a): calcined (b): Uncalcined MCM-41.



Figure 6: Thermogravimetric analysis of MCM-41.

III. Batch Adsorption Studies

Figure 7, shows the effect of contact time on the adsorption removal of dyes. The removal percentage of GV, MB and CR dyes increases with the contact time and gradually reach to equilibrium. The removal percentage of GV, MB and CR dyes by MCM-41 increases rapidly during the first few minutes, then increases gradually until remains constant. The maximum removal percentages of dyes were 96.58%, 98.47 % and 80.21% at 190, 160 and 180 min for GV, MB and CR dye respectively. This could be because of the impressive number of abandoned surface locales are accessible for adsorption toward the start of contact. As the color particles fill the surface locales, just couple of ones are left vacant, so that, toward the finish of the adsorption procedure, removal percent of

colors remains practically consistent. Thus, 200min contact time was taken for the next experiments. In addition, it can be seen that the removal percentage for GV and MB is higher than CR for all time. This means that MCM-41 may be attractive adsorbent for the removal of basic dyes [21].

II. Effect of adsorbent dose

The adsorbent dosage has low effect on GV removal and higher removal percentage ($\approx 99\%$) was obtained for all amount of MCM-41 used. Figure 8 shows the removal percentage of MB and CR remarkably increases from 65.32% to 97.78 for MB and 58.32 % to 81.54 % for CR at increasing the MCM-41 dosage from 0.05 to 1 g. The increase in removal percentage of dyes is attributed to that higher dose of adsorbent in the solution means higher total surface area and more active sites are available on the surface of MCM-41 [22].

III. Effect of pH

PH is one of the basic factors that affect adsorption process. It influences the surface charge of the adsorbent, and in addition the ionization level of the adsorbate. The examinations for departure of hues were refined at different pH, going in the region of 2 to 12, and the results are sketched out in Figure 9. The departure level of hues extending at pH increase (5-11), (4-11) and (2-7) for GV, MB and CR independently. This is generally a result of updated relationship of the shading cations. It is related to the electrostatic interest drive of the dye solution with MCM-41. Augmentation in the pH of the course of action grows the electrostatic interest between the insistently charged shading and the surface of the adsorbent, which achieves extended adsorption of MB shading. Relative observations were at that point declared for the adsorption of MB on various adsorbents. [23].

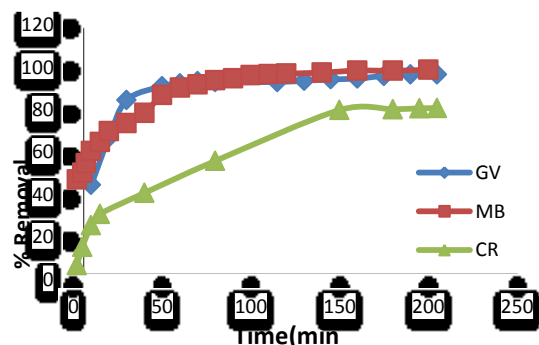


Figure 7: Effect of contact time on the adsorption removal of GV, MB and CR onto MCM-41

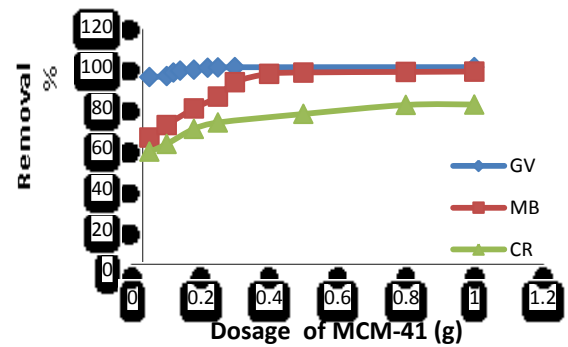


Figure 8: Effect of dosage on the adsorption removal of GV, MB and CR onto MCM-41

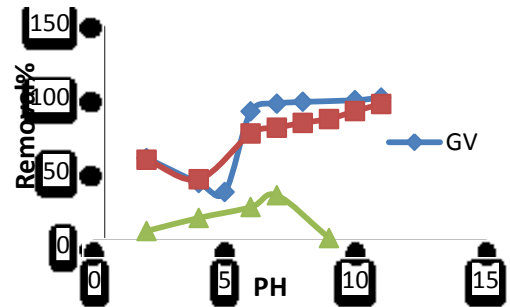


Figure 9: Effect of pH on the removal efficiency of GV, MB and CR onto MCM-41.

IV. Effect of initial concentration

The effect of initial concentrations of dye on the removal percentage at initial dye concentration from (20- 200) mg/l is shown in Figure 10. The removal percentage of GV and MB was found to be high at different concentration and approximate equal to 100%. This means that amount of MCM-41 used has enough adsorption surface and sites for this range of concentration. For CR, the removal percentage rapidly decreased with the increase in concentration. This means that MCM-41 has higher potential for the adsorption of basic dyes (GV, MB) than for acidic dye (CR).

V. Adsorption Isotherms

The isotherm constants and R^2 for each model are given in Table 2. It can be seen from this table that the coefficient of determination values for Langmuir, Freundlich and Temkin models indicate that the data shows a better fitting with experimental data. The Langmuir isotherm model for GV provided the best fitting to the experimental data for different temperature. Coefficient of determination ($R^2= 0.982-0.997$) were obtained. Thusly, the adsorption procedure can be depicted by the development of monolayer scope of the adsorbate on the homogeneous adsorbent surface. These outcomes are in a decent concurrence with the outcomes acquired by Juang et al, 2007. The higher K_L esteem at 60 °C shows higher solute adsorptivity because of higher restricting vitality

between GV color and MCM-41. The higher estimation of K_F shows that higher growth of take-up of GV at 60 °C and the lower estimation of $1/n$ at all temperatures infers that the qualities connected on the surface of the MCM-41 in the midst of GV shading adsorption are weak.

The test data got for MB and CR are fitted with the three isotherm models and the parameters got from these models are recorded in Table 2. The adsorption isotherms for methylene blue at temperature (293 K) are fitted well with all the three models, and the correlation coefficients (R^2) got for the Freundlich=0.937 are more prominent than the Langmuir and Temkin models (0.921, =0.903) and for Congo red, the correlation coefficients (R^2) got for Langmuir=0.984 are more noteworthy than Freundlich and Temkin models (0.980, 0.703). The adsorption limit with respect to MB got from the Langmuir models observed to be higher at 293 K (196.1 mg/g). The most extreme adsorption limit of (196.1mg/g) got in this work is more noteworthy than the esteem (3.75×10^{-5} mol/g =11.98 mg/g) announced by Wang and Li, 2006 .

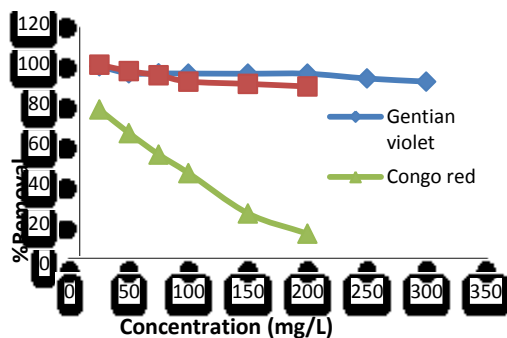


Figure 10: Effect of initial concentration of dyes on the removal efficiency of GV, MB and CR onto MCM-41

Table 2: Isotherm model parameters for the adsorption of Gentian violet, Methylene blue and Congo red onto MCM-41 at different temperatures

Type of dyes	qe. exp. (mg/g)	Temp (K)	Langmuir				Freundlich			Temkin		
			q_{max} (mg/g)	K_L (L/g)	R^2	R_L	K_f (mg ¹⁻ⁿ g ⁻¹ Ln)	$1/n$	R^2	b (J/mol)	K_t (L/g)	R^2
GV	273.8	293	303.1	0.224	0.982	0.1	42.72	0.568	0.954	42.77	2.56	0.843
GV	269.5	313	294.1	0.245	0.993	0.093	49.19	0.439	0.934	53.91	4.18	0.942
GV	261.7	333	285.7	0.252	0.997	0.090	56.91	0.468	0.937	55.33	4.39	0.982
MB	177.7	293	196.1	0.232	0.921	0.097	50.74	0.332	0.937	50.79	1.23	0.903
CR	46.7	293	40.16	0.586	0.984	0.041	10.28	0.385	0.980	327.7	4.02	0.703

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4. Conclusion

Nano porous MCM-41 was prepared for the first time from Iraqi rice husk and used as adsorbent for the removal of GV, MB and CR from synthetic wastewater. It was found that it has higher potential for the adsorption of basic dyes (GV,MB) and lesser for acidic dyes (CR) from aqueous solution in batch system. Batch experiment showed that the percentage of removal of GV, MB and CR increases with increase in the contact time, MCM-41 dosage, pH higher than 5 for GV, higher than 4 for MB and less than 7 for CR and decreases with increase initial GV concentrations. The adsorption isotherms studies for GV,CR demonstrated that the adsorption processes can be well fitted by the Langmuir isotherm model with a higher correlation coefficient (0.997 ,0.984) and MB can well fitted by Freundlich isotherm model with correlation coefficient (0.937).The removal percentage by using uncalcined MCM-41 gives a good removal of dyes.

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