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ORIGINAL ARTICLE

MESOPOROUS MCM-41 SYNTHESISED FROM INDUSTRIAL WASTE RICE HUSK ASH AS A WATER STERILIZER

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Abstract:

Mesoporous MCM-41 was produced from rice husk ash generated by a biomass fired power plant. Above 96 % of amorphous silica was extracted from rice husk ash by acid leaching. The R-MCM-41 was synthesized using sodium silicate prepared from rice husk ash and CTAB as an organic template. The mixture was stirred at room temperature for 24 h and then calcined at 550 °C for 4 h. The results from the XRD indicated the well-defined crystallinity of the synthesized MCM-41. The diameters determined from the Scanning Electron Micrographs of fine silica particles and the MCM-41 particles were approximately 50 µm and 0.3-0.5 µm, respectively. The BET surface area of the R-MCM-41 particles determined from nitrogen adsorption isotherm was about 1102 m^2g^{-1}

KEYWORDS:

Rice husk ash (RHA) Mesoporous silica materials (MCM-41) treatment of water

INTRODUCTION:

Since the discovery at Mobile Oil Corporation in 1992 Mesoporous materials have become an alternative source to make chemical process green and environmentally benevolent. Mesoporous MCM-41 material can be synthesized using various silica precursors. However, major drawback of these precursors is their towering starting costs of the raw materials which results in high production cost. To prevail over these difficulties, the best substituting silica source is the rice husk ash (RHA) which is the waste product of rice mills. This generates an enormous amount of fly ash and thus well-organized disposal of RHA is a worldwide concern. The major chemical constituents of RHA is SiO_2 (93-97 wt %),The incorporation of aluminum species into the framework of MCM-41 makes the sample exhibiting moderate acidity, and which is important characteristic property of catalyst and adsorption. Route of synthesis of MCM-41from RHA involves the blend of sodium hydroxide with RHA, to form soluble sodium silicate (Supernatant solution) during the blending process. Usually, template used for the synthesis of MCM-41 is Cetyl Trimethyl Ammonium Bromide (CTAB), interaction between the organic surfactant and the inorganic template is dictated by the synthesis reagent feature in influencing the physical and chemical properties of the synthesized mesoporous materials. MCM-41 consists of hexagonal arrays of uniform pore size. Synthesized MCM-41 have extensive application in basic sciences, petrochemical sciences, energy conservation, chemical sensor, waste water treatment, air purification because of their high surface area and large pore size and volume.

This paper reports a green and novel synthesis route for MCM-41 mesoporous silica material. The chemical and physical properties of synthesized MCM-41 material were characterized by means of crystallinity, porosity and surface study and were then compared with MCM-41 synthesized chemically. Subsequently, understanding the usability and surface characterization, their adsorption activity was

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investigated for the purification of waste water with the emphasis on the ammonia, organic pollutants like hydro chlorofluorocarbons, petroleum products, heavy metal removal from water. There are increasing demands for healthier environment, with the emphasis on high-quality drinking water and on the removal of contaminants from industrial, agricultural and municipal wastewaters.Most technologies using MCM-41 for water purification are based on their unique cation-exchange behavior through which dissolved cations are removed from water by exchanging with cations on MCM-41 exchange sites. The most common cation in waters affecting human and animal health is NH_4^+. Ammonia removal is very important to prevent oxygen depletion, algae bloom and due to its extreme toxicity and harmful effects on disinfections of water supplies. Nitric oxides, Nitrates and Ammonia/Ammonium are very soluble in water and can quickly end up in ground and drinking water.MCM-41 showed the best results for ammonia removal. Heavy metals are well known for toxicity and their disposal is a significant industrial waste problem.MCM-41 proved to be very efficient for the removal of transition metals, like Cu^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+}, Mn^{2+}, CO^{2+}, etc.,

(A) MATERIALS AND METHODS:

Source materials : Rice Husk Ash :

The Rice husk was obtained from rice mill Nanded, Maharashtra (India).The Chemical composition of fly ash used in the present study are given in Table 1. The amounts of the main components of ash viz. both amorphous (mainly SiO_2, Al_2O_3)

Table-1: CHEMICAL COMPOSITION OF AS COLLECTED RHA

Sr. No.	Compound	Content (wt%)
1	SiO_2	97.15
2	Al_2O_3	1.85
3.	Na_2O	0.36
4.	MgO	0.26
5.	Other	0.28

(B) CHEMICALS:

Other chemical used are Sodium Hydroxide Fisher Scientific, the surfactant solution Cetyl trimethyl ammonium bromide (CTAB), Spectrochem, Ethyl acetate, Sulfuric acid, de-ionized water. All chemicals were AR grade hence they were used without further purification.

SYNTHESIS OF R-MCM-41:

i) Preparation of RHA

The RHA was prepared based on the method described in literature with some modifications. Rice husk was first treated with 3.0 M HCl acid solution at 100˚C and then washed with water to remove the excess acid on the surface. Further it is dried overnight at 90˚C and then calcined at 550˚C for 6 hr to obtain RHA.

ii) Synthesis of R-MCM-41

RHA was first mixed with 3.75 M NaOH solution and stirred overnight to extract the silicate from the ash. CTAB was dissolved in water to obtain a clear solution. The two solutions were then mixed and stirred for 1 hr. The mixture had the molar composition of 1.0 SiO_2 : 3.0 NaOH : 0.25 CTAB: 180 H_2O. The

pH value of the mixture was adjusted to 10.2 by adding 3.0 M HCl solution. The mixture was then heated in microwave oven at 100˚C for 30min for crystallization. Later, the solid was recovered by centrifuge. The solid was dried in oven overnight at 100˚C and calcined at 550˚C for 6 hr. The sample was named as A-MCM-41. For conventional oven heating, the mixture was heated in oven at 100˚C for 18 hr for crystallization. . Later, the solid was recovered by centrifuge. The solid was dried in oven overnight at 100˚C and calcined at 550˚C for 6 hr. The sample was named as B-MCM-41.

(C) CHARACTERIZATION:

1. pH values were measured with a EUTECH digital pH meter
2. Infrared (FT-IR) spectra were recorded on a FT-IR spectrometer (ATR eco ZnSe) using dry KBr as standard reference in the range of 500-4000 cm^{-1}.
3. X-ray diffraction patterns of the collected CFA and synthesized materials were recorded on a Cu/30 kV/15mA MiniFlex2 goniometer with a wave length of 1.540 A0. The powder XRD patterns of synthesized samples were obtained using Cu Kα radiation on a Rigakau monolayer meter. The samples were scanned for 2θ from 20 to 200.
4. Specific BET surface area was calculated using Surface area Analyzer Model SAA-2000 for all synthesized samples.

1. FT-IR ANALYSIS OF RHA (AS COLLECTED AND CALCINED)

FTIR spectra shown in the Fig. 1 provide valuable information about the basic characteristics of the molecule, namely, the nature of atoms, their spatial arrangement and their chemical linkage forces. Infrared spectroscopy has been extensively used for identifying the various functional groups of the support, as well as identifying the various functional groups of the active component. The mid infrared region of the spectrum contains the fundamental frame work vibration of $Si(Al)O_4$ grouping. The absorption band in between the wave numbers 980-1320cm^{-1} in IR spectrum of RHA and treated RHA represent the presence of substituted Al atoms in the tetrahedral forms of silica frame work.

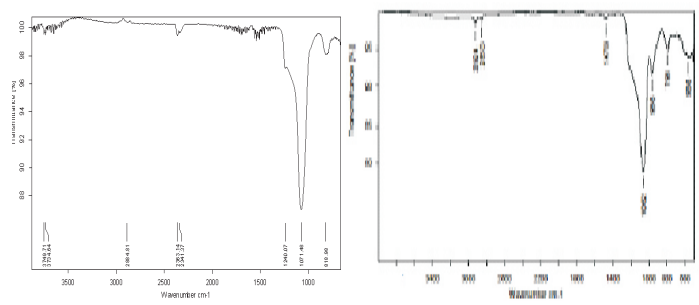

Fig.1: FT-IR spectra of RHA (a) As collected (b) Calcined at 600^0C

2. FT-IR ANALYSIS OF SYNTHESIZED MATERIAL:

FT-IR spectra of as synthesized MCM-41 from RHA is shown in Fig.2. From FT-IR spectra, the absorption bands around 2921 and 2851 cm^{-1} correspond to n-C-H and d-C-H vibrations of the surfactant molecules, such bands disappeared in the calcined sample indicating the total removal of organic material during calcinations. The broad band around 3392.65 cm-1 as observed due to surface silanols and O-H stretching frequency of adsorbed water molecule. Moreover the peaks in the range of 1500-1600 cm^{-1} are because of the deformation mode of surface hydroxyl group. A peak at 1070.63 cm^{-1} and 964.44 cm^{-1} corresponds to the asymmetric and symmetric Si-O groups, respectively. The peaks in the range 1010-1079 cm-1 are assigned to M-O-M bonding, the bands from 960 to 990 cm^{-1} appeared due to Si-O-M (M=metal ions) vibrations in metal incorporated silanols. The shift in the lattice vibration bands to lower wave numbers is due to the substitution of silicon by other metal ions.

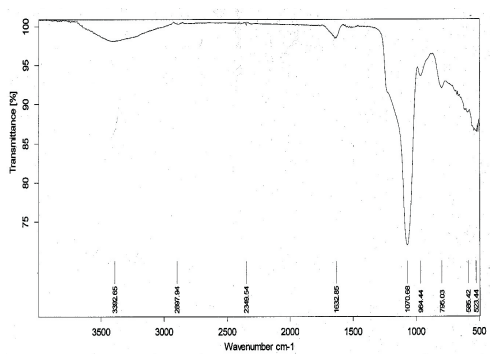

Fig.2: FT-IR spectra of synthesized MCM-41 from RHA

3. THE XRD PATTERN OF SYNTHESIZED MATERIAL:

The X-ray pattern of the synthesized mesoporous silica material is an highly periodic silica phases which is normally reflected by the distinct XRD signatures at low 2 angles from 20 to 200 as shown in Fig.3. Sharp signal in XRD spectra indicates the presence of long range order of uniform hexagonal phase in the mesoporous materials. The well defined reflections from [100] plane are a prime characteristics of the hexagonal lattice symmetry of the R-MCM-41 structure. The observation of three higher angle reflections other than d100 indicates that the product is likely to possess the symmetrical hexagonal pore structure typical of R-MCM-41. X-ray diffraction data therefore indicates that the supernatant of the RHA can be successfully used in the synthesis gel to prepare mesoporous materials.

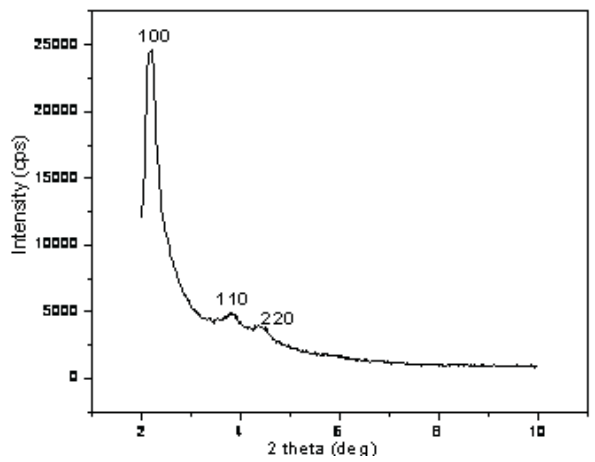

Fig. 3 : XRD pattern of synthesized material

4. N2-ADSORPTION DESORPTION ANALYSIS OF SYNTHESIZED MCM-41 MATERIAL:

Nitrogen physisorption probes the textural properties of materials i.e. surface area, pore volume, pore size and pore geometry. At very low relative pressures (p/p0) a very large amount of nitrogen becomes physisorbed which assigns to condensation of nitrogen inside and outside on the surface of MCM-41.As the surface area is very high this corresponds monolayer adsorption. Upon monolayer adsorption multilayer of nitrogen starts to develop at higher relative pressures. Also in this case both the external surface area and mesopores contributes to the physisorption process. The collected data from the N2 adsorption desorption graph is used to calculate the surface of the material using BET method.From the data it is confirmed that the maximum calculated surface area amounts to 1102m^2/g For the MCM-41.

From the above discussion it is confirmed that the synthesized product is R-MCM-41.Further the synthesized material is modified for our projected work.

The modified samples were R-MCM-41 (Si/Al=3 or Si/Al=8)

(D) RESULT AND DISCUSSION:

Water purifications are based exceptionally on the cation-exchange behavior of mesoporous material R-MCM-41 through which dissolved cations are isolated from water by exchanging with cations on MCM-41 exchange sites. MCM-41 with high exchange capacities can effortlessly strip the hydration shell of a water-cation complex. Inside the MCM-41 sample pore apertures water molecules and charge balancing mono- and divalent cations, such as Ca^{++}, Na^{+} and Mg^{++} can be found. The negative charge of the framework, caused by the replacement of Si^{4+} with Al^{3+}, is compensated by these small cations. Larger cations are partially or completely barred by the sample pore size, whereas smaller species can be exchanged from wastewater.The Si/Al ratio is accountable for the thermal and hydrothermal stability, moreover their acidic nature and comparative hydrophobicity of MCM-41. A low Si/Al ratio is indicative of an increased number of terminal Al-OH surface functional groups at the solid-water interface. It consequently leads to a metal removal from unhygienic waters.

(E) TREATMENT OF WASTE WATER USING MCM-41 ADSORBENTS MADE FROM RHA:

This section describes the adsorption behavior of the R-MCM-41synthesized from RHA, with respect to the immobilization of poisonous elements and heavy metals usually present in process effluents having more ion exchange adsorptive property compare to that synthesized chemically. The aim of present study is to minimize the extent of pollution of potable and irrigation water in the surroundings of Godavari River Basin at Nanded (Maharashtra, India) due to nearby Industrial waste water. Usually, waste water cleaning equipment does not meet all the conventions in waste water treatment, hence more effective methods for waste water treatment has become a pressing issue. Thus, in our research work inorganic ion exchanger R-MCM-41 adsorbents prepared from RHA waste residues were used to improve water excellence and it is suggested that these materials are to be evaluated as substitute for viable resin based adsorbents.

(F) EXPERIMENTAL:

Waste water treatment using R-MCM-41:

Treatment of waste water by using the Batch ion exchange method with synthesized Si-Al-MCM-41 (Si/Al =3) and Si-Al-MCM-41 (Si/Al = 8) is used in this section. In order to optimize the degree of removal of contamination during the application of the adsorbent material for waste water treatment, we have studied the Effect of functionalized R-MCM-41.

For present study the samples of water in the surroundings of Godavari River Basin at Nanded (Maharashtra, India) and two side bore well water of different locations nearby the river were collected and analyzed for the various parameters like pH, EC, COD, TDS, hardness and bacterial count. Then water samples were treated with R-MCM-41 material by routine ion exchange method and again analyzed for the comparison. pH of each sample was determined by using EUTECH digital-pH Analyzer while electric conductivity was measured by ELICO CM 183 EC–TDS Analyzer. All the reagents used in this investigation were of analytical grade. Laboratory incubator was used for maintaining different incubation temperatures. De-ionized water was used for reagent preparation and dilution etc.

A fixed amount of solid to liquid ratio of adsorbent and simulated effluent were used to determine the type of R-MCM-41(Si/Al=3 or Si/Al=8) required for optimum removal of metals from the solution. To the 20 ml of contaminated water (1g/20mL) amount of R-MCM-41(Si/Al =3or Si/Al =8) were added and kept for the reflex at the temperature 850C with continuous magnetic stirring for 4.5 hrs. After the reflex the samples were cooled convectionaly to the room temperature and then filtered mechanically. Adsorbate such as R-MCM-41(Si/Al=3or Si/Al=8) synthesized from RHA were used in quality enhancement of waste water. The results of pre and post unhygienic water treatment route were tabulated in Table-2. Observations reveals waste water was found to be strongly acidic with prominent levels of poisonous metals.

Table 2 : Relative analysis of different waste water parameters before and after treatment with R-MCM-41(Si/Al =3) and R-MCM-41(Si/Al =8)

Parameters	Collected samples		Treatment with R-MCM-41 (Si/Al =3)		Treatment with R-MCM-41 (Si/Al =8)	
	A	B	D	E	G	H
pH	4.88	6.74	6.69	7.22	6.99	6.96
Turbidity	1670	11	277	8	298	7
EC mcm^{-1}	12032	2011	5011	1201	4912	1085
TDS mgL^{-1}	5358	766	3486	401	3391	413
BOD mgL^{-1}	14537	6	5399	2	5107	2
COD mgL^{-1}	31435	32	9421	19	9336	19
Magnesium mgL^{-1}	318	39	43	21	43	21
Chloride mgL^{-1}	1442	108	574	31	574	31
Sulphates mgL^{-1}	254	26	91	11	89	11

Where,

1. Collected samples are
A = Waste water of Godavari River basin. B= Water sample(A)Besides the river.
2. After treatment with R-MCM-41(Si/Al=3)
D = Waste water of Godavari River basin. E = Water sample(A) Besides the river.
3. After treatment with R-MCM-41(Si/Al=8)
G = Waste water of Godavari River basin. H = Water sample (A)Besides the river.

The pH values of the Waste water of Godavari River basin effluent sample is 4.88 and was below the permissible limits of pH for drinking and Irrigation. Ca^{++} and Mg^{++} ions in the waste water are found to be intense in manner which in turn hardens and affects the pH value of the waste water. After treatment with R-MCM-41 on bore well water and Godavari River basin effluent sample of waste water may considerably reduce Mg^{++} or Ca^{++} amounts.

The pH value of Godavari River basin effluent sample of waste water was enhanced to 6.69 when treated the waste water with R-MCM-41(Si/Al=3) adsorbent and 6.99 when treated with R-MCM-41(Si/Al=8) adsorbent, these values were feasible to the permissible limits and the water can be used for irrigation purpose. The increase in pH values with the R-MCM-41 treatment is endorsed due to the absorption of H^{+} ions by the R-MCM-41. The variations in EC reduces from 12032 to 5011µm cm^{-1}, TDS varies from 5358 to 3391 mg L-1 after treatment with both R-MCM-41 adsorbents.

The pH values of Bore well water 6.74 and was within the permissible limits. Perhaps their electrical conductivity (EC) values are high ranging between 1612-12032 µm cm^{-1} creates harms for agricultural fields. After treatment with R-MCM-41(Si/Al =3 or Si/Al =8) adsorbents the sudden variation in EC and other parameter values were examined.

CONCLUSION:

R-MCM-41(Si/Al =8) used for ion exchange in this work shown good results as compared to the R-MCM-41(Si/Al=3).This may be due to the high adsorptive behavior of the R-MCM-41(Si/Al=8) over R-MCM-41(Si/Al=3) which basically depends on the surface area of the adsorbent. These results shows potential for the use of RHA prepared R-MCM-41(Si/Al=8) over commercially available tools to treat

contaminated ground water and industrial waste effluents, since they possess the high capacity for cation exchange, anion sorption and acid hydrolysis of organic contaminants. The higher aluminum content of R-MCM-41(Si/Al=8) is important factor governing its enhanced performance relative with higher Si/Al ratio. This study demonstrates that converting RHA into mesoporous materials not only eliminates the disposal problem of RHA but also turns a waste material into a value added product. The proposed method provides one of the best ways of recycling RHA.

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