



COAL FLY ASH UTILIZATION FOR SUSTAINABLE ENVIRONMENT MANAGEMENT: STUDY OF MCM-48 AS A BEST ADSORBENT

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ABSTRACT

We report eco-friendly synthesis of mesoporous molecular sieve of M41S family using coal fly ash available in ample as the thermal power station waste during electricity generation. This contributes to the green synthesis of MCM-48 at a cheaper production cost. Coal fly ash was used to synthesize MCM-48 by alkali fusion followed by hydro-thermal treatment and was characterized using various techniques viz. XRD, SEM, FTIR, N₂ sorption for surface area measurement etc. The synthesis and history dependent parameters were optimized to obtain highly crystalline phase of MCM-48. The synthesized material was tested for the adsorption of waste water contamination.

KEYWORDS: Coal fly ash; MCM-48; hydrothermal synthesis parameter, Activation energy.

1. INTRODUCTION

The removal of toxic organic and inorganic compounds produces an extensive impact on the deterioration of the surface water, ground water and irrigation water environment¹⁻⁶. Depletion of such polluted water in the cultivated land contaminates the soil and creates a great impact on the crop production and its intake by both human and animals causes environmental and health risks.⁷⁻⁹

Most of the contemporary methods of water purification have some drawbacks; one of them is high operational cost. This drawback had lead many researchers to investigate the use of more cost effective and alternative adsorbents¹⁰ like coal fly ash, rice husk¹¹, zeolites like microporous materials as molecular sieves¹² and M41S type mesoporous materials for the removal of organic compounds from wastewater¹³⁻¹⁵ because of their fine textural, structural and chemical properties¹⁶.

In 1992, scientist at Mobil Oil Corporation discovered new family (M41S) of mesoporous materials, (MCM-41, MCM-48 etc.). MCM-48 possesses hexagonal mono dimensional molecular sieves having fairly uniform pores with pore diameter of 20-100Å.

Mesoporous material MCM-48 showed that they have higher adsorption capacity for the removal of ink, dyes and pollutants from wastewater because of its large surface area and nanometer-sized pore sizes¹⁷⁻²⁰.

Very few studies have been reported on MCM-48 synthesized from no-cost raw materials such as CFA (CFA-MCM-48) used in the waste water treatment. Particularly, no attention have been given for the removal of bulky molecules like phenolic compounds^{21,22}, heavy metal ions from industrial waste water.

In view of this our research endeavors the use of CFA collected from the Parali TPS. The reason for choosing this source for our further investigations is:

1) it add value; reduce the cost and effective utilization to protect the environment.

2) Its potential application in synthesis of highly useful porous materials which will be further used in water purification technology,



as industrial catalyst, supporting materials, exchanger, molecular sieves etc.

Thus we have first time studied and reported the use of MCM-48 synthesized from CFA for the removal of bulky molecules like phenolic compounds and its analogues, heavy metal ions from industrial waste water.

Water purifications are based on the characteristic cation-exchange performance of mesoporous materials CFA-MCM-48 through which dissolved cations are eradicated from water by exchanging with cations on their exchange sites. CFA-MCM-48 with elevated exchange capacities can easily streak the hydration shell of a water-cation complex.

The negative charge of the framework, caused by the replacement of Si^{4+} with Al^{3+} , is reimbursed by these small cations. Larger cations are partially or completely expelled by the CFA-MCM-48 pore size, whereas smaller species can be exchanged or adsorbed. The ready exchangeability and moderately mild nature of the charge-balancing cations, delivers them particularly suitable for the removal of unenviable species from wastewaters.

An equally significant parameter of CFA-MCM-48 is the Si/Al ratio. It is accountable for their thermal and hydrothermal stability, as well as their basicity and relative hydrophobicity. A low Si/Al ratio is indicative of an increased number of terminal Al-OH surface functional groups at the solid-water interface which in turn found that the total exchange capacity may depend upon the experimental conditions.

Kinetic experiments were conducted to investigate the rate constants of adsorption for phenolic compounds which are potentially toxic to humans and aquatic life and other contaminants on CFA-MCM-48. The amounts of adsorbates removed by CFA-MCM-48 were also evaluated in these studies.

Nitrophenols are bioplasmic poisonous compounds which pose significant health risks. In addition, they could restrain microorganism growth, crop growth, thus decreasing the self-purifying ability of water²³⁻³⁰. A threshold permissible concentration of phenolic compounds in drinking water is 0.001mg/l and maximum concentration level of 1.0 mg/l in industrial wastewaters for safe release into surface water.

The Maharashtra Industrial Development Corporation (MIDC), Nanded District is one of the major industrial areas in Maharashtra, India, located nearby Nanded town. Industrial waste water from the places nearby MIDC areas is highly contaminated with many phenolic compounds, its analogues and heavy metals. These adsorbates were analyzed and found to be containing hazardous phenolic compounds. This polluted water gets drained and percolated in nearby bore wells and cultivated land which directly affects on its fertility, crop quality and crop production capacity.

Our studies describe the adsorption behavior of CFA-MCM-48 with respect to the immobilization of toxic elements and softening of effluents so as to prevent the infectivity of soil. This will definitely enhance the crop quality and crop production capacity which in turn will help in developing the financial condition of the suffering farmers.

In support of this we have investigated the effectiveness of the CFA-MCM-48 to adsorb phenols, its analogues and heavy metals during the treatment processes. We have also investigated the effect of the contact time during treatment methods.

The adsorption capacity of CFA-MCM-48 for organic and inorganic compounds has been found to be more than ion exchange adsorptive property of chemically synthesized MCM-48. CFA-MCM-48 is thus highly efficient, environmentally friendliness and well-established technique due to its inexpensiveness, effectiveness and the availability of source material in the ample range.

2. SYNTHESIS OF MCM-48 FROM CFA IN ALKALINE MEDIUM:

The MCM-48 phase was hydrothermally synthesized under the molar system **1.0SiO₂: 1.5NaOH: 0.008 (Triton -X): 0.08 EA: 42H₂O** at 130 °C for 4 hrs under stirring condition (300 rpm). After hydrothermal treatment the mixture was cooled and filtered till the effluent shows neutral pH. The collected cake was dried and calcined at 550 °C at a ramp of 50°C keeping heating rate of 1°C/min for durations of calcination 4.5h. After cooling; the samples was characterized for the investigation of optimization. This synthesized material is further known as CFA-MCM-48.

3. RESULTS AND DISCUSSION

The collected fly ash was analyzed by XRD, SEM techniques and also synthesized samples are characterized by techniques such as XRD, N₂-sorption, SEM, FTIR etc. to elucidate their structural features, pore architecture, morphology and surface area.

3.1 CFA-MCM-48 at Optimized conditions

Fig.1 shows the XRD pattern of optimized sample. The formation of three angle reflections 110,200,210 other than d₁₀₀ indicates that the product possesses the symmetrical hexagonal pore structure typical of MCM-48. Fig.2 presents typical micrographs of synthesized CFA-MCM-48 samples. It exhibits uniform spherical shaped particles having small agglomerates with sizes between 30 and 200 nm. Fourier Transformed Infrared (FTIR) spectra of the final CFA-MCM-48 material can capitulate information concerning structural details as given below.

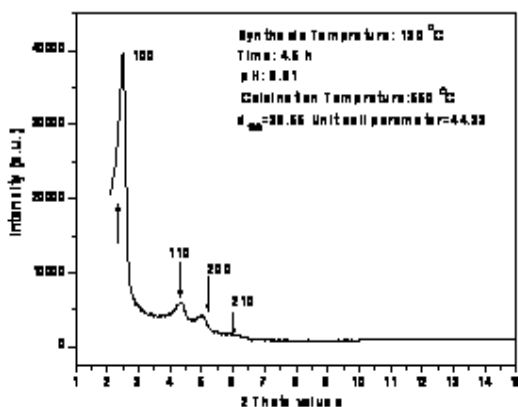


Fig. 1: XRD pattern of MCM-48 (100 % crystalline) at optimized conditions

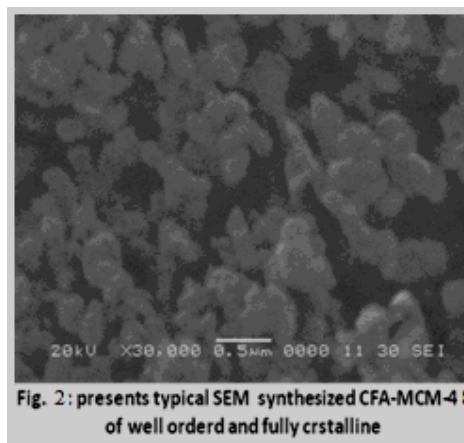


Fig. 2: presents typical SEM synthesized CFA-MCM-48 of well order and fully crystalline

Table:1

Internal tetrahedral	Asymmetric stretch 1250–950cm ⁻¹ , Symmetric stretch 720-650cm ⁻¹
External linkage	Double ring 650–500cm ⁻¹ , Pore opening 300-420cm ⁻¹ Symmetric stretch 750–820cm ⁻¹ , Asymmetric stretch 1050-1150cm ⁻¹

The adsorption/desorption isotherms of N₂ shown in Fig. 3 and the values of specific BET surface area, mean pore diameter of the mesopores, pore volume and wall thickness obtained for fully crystalline CFA-MCM-48 are 1011.6 m²/g, 26.38 Å, 0.879 ml/g and 17.95 Å respectively.

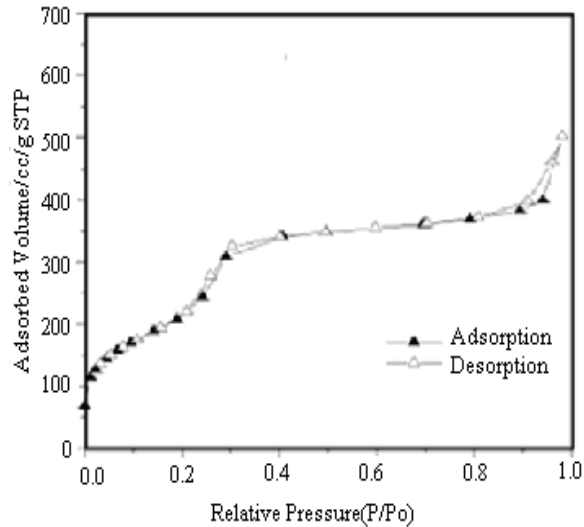


Fig 3: N₂-adsorption-desorption isotherms of CFA-MCM-41

4. WASTE WATER TREATMENT USING CFA-MCM-48

Experimental: Materials and Method :

Waste water samples containing phenolic compounds, its analogues and heavy metals were collected, from the bore well, sewage treatment plant and effluent waste water from nearby MIDC areas of Nanded and CFA-MCM-48 with different Si/Al ratios viz. 9, 6 and 3 were taken from the synthesized samples.

We have taken 100 ml of contaminated bore well water, sewage water and industrial effluent. A fixed amount of 1, 2, 3, 4 and 5 g of CFA-MCM-48 (Si/Al = 9, 6 and 3) was added in 100ml of adsorbate and kept for the reflux at the temperature 353⁰K for different time intervals with a continuous magnetic stirring (300rpm).

After the reflux the sample was allowed to cool by natural convection to the room temperature and filtered before further investigation. Then, the residual concentration of adsorbate was determined using a UV-spectrophotometer (TU1900) at a wavelength of 280 nm.

The percentage removal of adsorbate was calculated according to the equation

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_e} \times 100\%$$

The adsorption amount (Q_e) was calculated according to the equation

$$Q_e = V \times \frac{C_0 - C_e}{C_e} \times 100\%$$

Where,

- Q_e (in mg/g) represents the adsorption amount,
- V (in liter L) is the volume of the adsorbate solution,
- C₀ (in mg/L) is the initial concentration of adsorbate
- C_e (in mg/L) equilibrium liquid-phase concentration of adsorbate and
- m (in gram) is the mass of the adsorbent used in the experiment

This method was subjected to study various parameters like pH, EC, COD, BOD, TDS etc; by examining effect of duration, effect of the type of adsorbent material and effect of adsorbent loading on the removal of contamination.

The effects of duration:

The adsorption tests was carried out at different times i.e. (0.5Hr, 1Hr, 1.5Hr, 2Hr, 2.5Hr and 3Hr.) intervals so as to evaluate the time reliance of adsorption using the simulated effluent. During this a fixed amount i.e. 0.5g/10mL of solid to liquid ratio of adsorbents CFA-MCM-48(Si/Al=9, 6 and 3) and simulated waste water was taken.

Same batch ion exchange method was espoused to treat contaminated water samples before exploration. Table.2, Table.3 and Table.4 depicts the outcome for the effect of contact time on the removal of phenolic compounds from aqueous solution.

It can be seen that the amount of the entire adsorbates adsorbed onto CFA-MCM-48 increases with respect to time.

Table 2 : Adsorption capacity of CFA-MCM-48 (Si/Al=9) for phenol, 2-NP and 4-NP at pH: 2.7

Time (Hrs)	Phenol [Qt (mg/g)]	Phenol Removal(%)	2-NP [Qt (mg/g)]	2-NP Removal (%)	4-NP[Qt (mg/g)]	4-NP Removal(%)
0.5	0.01732	57.7	0.01701	56.7	0.01948	64.9
1	0.02254	75.1	0.02213	73.8	0.02283	76.1
1.5	0.02295	76.5	0.02237	74.6	0.02302	78.8
2	0.02312	77.1	0.02256	75.2	0.02435	81.2
2.5	0.02322	77.4	0.02294	76.5	0.02498	83.3
3	0.02351	78.4	0.02311	77.0	0.02562	85.4

Table 3 : Adsorption capacity of CFA-MCM-48 (Si/Al=6) for phenol, 2-NP and 4-NP at pH : 2.7

Time (Hrs)	Phenol [Qt (mg/g)]	Phenol Removal(%)	2-NP [Qt (mg/g)]	2-NP Removal (%)	4-NP[Qt (mg/g)]	4-NP Removal(%)
0.5	0.01825	60.8	0.01726	57.5	0.02045	68.2
1	0.02310	77.0	0.02259	75.3	0.02588	86.3
1.5	0.02321	77.4	0.02276	75.9	0.02596	86.5
2	0.02346	78.2	0.02299	76.6	0.02603	86.8
2.5	0.02358	78.6	0.02317	77.2	0.02609	87.0
3	0.02367	78.9	0.02356	78.5	0.02614	87.1

Table 4 : Adsorption capacity of CFA-MCM-48 (Si/Al=3) for phenol, 2-NP and 4-NP at pH : 2.7

Time (Hrs)	Phenol [Qt (mg/g)]	Phenol Removal(%)	2-NP [Qt (mg/g)]	2-NP Removal (%)	4-NP[Qt (mg/g)]	4-NP Removal(%)
0.5	0.01836	61.2	0.01783	59.4	0.01951	71.9
1	0.02507	83.6	0.02445	81.5	0.02731	91.0
1.5	0.02563	85.4	0.02486	82.9	0.02752	91.7
2	0.02579	85.9	0.02499	83.3	0.02787	92.9
2.5	0.02593	86.4	0.02517	83.9	0.02801	93.4
3	0.02624	87.5	0.02524	84.1	0.02822	94.1

From the above experimental data it could be noted that within the first hour of agitation, the adsorption was acute. This is because of the large number of vacant sites accessible on the surface of the CFA-MCM-48 were available. As the time of contact between adsorbet and adsorbent increases the percent rate of removal of phenol, 2-NP and 4-NP slightly declines.

It is evident that consequent to a trail off time, there exist a repulsive force between the adsorbates in the bulk phase and the adsorbent due to the non availability of more vacant sites for adsorption onto the CFA-MCM-48.

The adsorption capacity (Qt) is found to increase with the increase in contact time. The adsorption equilibrium reached values are as high as 0.02624, 0.02524 and 0.02822 mg/g for phenol, 2-NP and 4-NP respectively after 3Hrs of agitation. 4-NP was found to adsorb more than phenol due to its lower solubility in aqueous solution. The more non-polar an organic compound, the lesser is its affinity for solvent and the higher is its adsorption affinity by the adsorbent.

The adsorption capacity for phenol was found to be slightly higher than that of 2-NP and this indicates that solubility is not entirely essential in this scheme because if solubility was to be the controlling factor then 2-NP would have had a higher adsorption affinity for CFA-MCM-48 than phenol because of its lower solubility in water than phenol. In addition, the difference in adsorption behavior of phenolic compounds might be due to the diverse affinities for the reactive functional groups in the CFA-MCM-48.

After one hour of contact, about 75.1%, 73.8% and 76.1 % phenol, 2-NP and 4-NP respectively has been removed by CFA-MCM-48(Si/Al=9), 77%, 75.3 % and 86.3 % by CFA-MCM-48 (Si/Al=6) and 83.6 %, 81.5 % and 91.0 % by CFA-MCM-48 (Si/Al=3) correspondingly. Thus we can conclude that smaller is the Si/Al ratio more is the adsorption capacity of adsorbent.

This is because of the fact that more the Aluminium content at the sites of framework structure, it is accessible on the surface of the CFA-MCM-48 which widens the pore size and more adsorption is feasible. This may be due to the creation of negative charge raised on the surface of pore walls by increasing Al⁺⁺⁺ ions. The average pore diameter became fined by the increasing of metal ions incorporation

However, lower Si/Al ratio was obtained in situ of addition of Al by using more quantum of Al source, which is cost effective. This supports statistically that even though the Si/Al ratio varies from 9 to 5 there is a marginal difference in the removal of phenolic compounds from simulated effluent (about 11%). This may be due to the change in the surface area and pore volume of CFA-MCM-48 from 1017m²/g to 926m²/g and pore diameter from 40.9nm to 35.2nm as Si/Al varies from 9 to 3.

Hence, we can confirm that instead of using CFA-MCM-48 with lower Si/Al ratio, if we increase the contact time between adsorbate and adsorbent CFA-MCM-48 (Si/Al=9) results into more removal of phenolic compounds from waste water.

Table 5. elaborates the effect of contact time between the contaminated waste water (effluent) and different adsorbents i.e.CFA-MCM-48 (Si/Al=9, 6 and 3) on various parameters which determines the quality of water. The significant parameters that were to be examined are pH, EC (Electrical Conductivity), TDS (Total Dissolved Solid), BOD(Bio-chemical O₂ Demand), COD (Chemical O₂ Demand), Calcium, Magnesium, Chloride, Sulphates, Arsenic, Lead, and Cadmium in effluent before and after the treatment of CFA-MCM-48 (Si/Al=9, 6 and 3).

Table 5: Effect of duration of ion exchange processes with CFA-MCM-48(Si/Al=9, 6 and 3).

Parameter	Waste water (Effluent)	Duration of ion exchange with CFA-MCM-48 (Si/Al=9) Adsorbent						Duration of ion exchange with CFA-MCM-48 (Si/Al=6) Adsorbent						Duration of ion exchange with CFA-MCM-48 (Si/Al=3) Adsorbent					
		0.5 H	1H	1.5 H	2H	2.5 H	3H	0.5 H	1H	1.5 H	2H	2.5 H	3.H	0.5 H	1H	1.5 H	2H	2.5 H	3.H
pH	2.70	3.01	3.23	3.73	4.61	5.74	5.89	3.22	3.91	4.62	4.97	5.88	5.99	3.96	4.18	4.81	5.23	5.97	6.18
EC mc/m	12792	7362	4063	3225	2074	1288	964	7022	3325	1923	1174	806	777	6431	3012	1678	884	745	703

TDS mg/ L	7733	389 7	192 3	174 8	112 4	993	861	365 2	171 7	142 1	826	735	71 1	347 1	139 9	112 2	763	70 2	69 4
BO D mg/ L	18552	163 38	136 24	112 46	979 3	721 1	683 5	1473 9	121 00	972 8	762 9	571 2	49 32	131 48	101 42	856 1	621 4	41 18	23 80
CO D mg/ L	37781	346 29	314 52	276 34	225 16	178 54	113 77	332 81	291 18	252 14	205 12	143 58	95 41	318 05	236 56	188 93	125 03	62 88	32 01
Pb mg/ L	1.96	1.5 6	0.7 7	0.4 2	0.2 3	0.1 4	0.0 6	1.3 4	0.4 2	0.2 2	0.1 3	0.0 1	0.0 1	1.2 9	0.3 7	0.2 1	0.0 8	0.0 0	0.0 0
Cd mg/ L	2.46	2.0 7	0.8 2	0.5 7	0.3 4	0.1 6	0.0 9	1.9 8	0.3 7	0.1 1	0.0 2	0.0 1	0.0 1	1.8 3	0.3 7	0.0 8	0.0 1	0.0 1	0.0 0
As mg/ L	1.79	1.2 1	0.4 4	0.2 7	0.1 9	0.0 8	0.0 3	1.0 1	0.2 4	0.0 5	0.0 1	0.0 1	0.0 1	0.7 9	0.2 1	0.0 3	0.0 1	0.0 0	0.0 0

The pH of collected effluent waste water samples was 2.7 which was purely acidic. When such acidic water gets percolated in nearby cultivated land, it affects over the crop production and naturally creates a great impact on agriculture industry. Therefore, it is essential to reduce the acidic nature of effluent by treating it with a neutralizing basic material, with still a possibility of unnecessary production of some hazardous salts which contaminates the soil.

The pure silicious MCM-48 has less adsorption capacity compare to CFA-MCM-48 for the treatment of such highly acidic water. The Al in the framework of CFA-MCM-48 produces salts and minimizes the acidic nature of effluent waste water. However on increasing pH of effluent waste water sample, metal ions starts to decompose rapidly and results in more adsorption of heavy metal ions from water.

This can be attributed to the fact that CFA-MCM-48 surface is spanned by charged OH-silanol groups and hydrolysis of this surface –SiOH sites, raises the resultant final pH, during the equilibration of CFA-MCM-48 with the aqueous phase. This is a pH dependent reaction, which leaves the active sites of the CFA-MCM-48 with a negative charge and as such, the CFA-MCM-48 can interact with potential contaminants to remove them from the aqueous phase.

Therefore, pH value of effluent waste water sample was enhanced from 2.7 to 5.89, when treated with CFA-MCM-48 (Si/Al=9) as shown in Table 5. It was also observed from this tabular data that at a given contact time, as Si/Al = 6 and 5, pH value was enhanced from 2.7 to 5.99 and from 2.7 to 6.18 respectively. These values were extraordinarily close to the permissible limits and the water can be used for irrigation purpose.

The variation of the parameters such as EC and TDS, after the treatment with CFA-MCM-48(Si/Al=9, 6 and 3) adsorbents with escalating contact time shows that water excellence improves gradually. Through the observations we found that there is maximum enhancement in the quality of all the parameters of sewage and effluent waste water samples.

The initial EC of the water to be treated were recorded. Then the adsorbent and wastewater was contacted under stirring for various durations with an overhead stirrer. The EC of each sample were recorded. When the adsorbent CFA-MCM-48 (Si/Al=9, 6 and 3) was kept in contact with effluent waste water sample, EC values were reduced by 92.5%, 93.9% and 94.5%. Thus using adsorbent CFA-MCM-48 (Si/Al=6 and 3), we are achieving just 1.5% and 2% more reduction in EC values of an effluent waste water sample. TDS values were reduced from 7733mg/l to 861mg/l, 711mg/l and 694mg/l when effluent waste water sample was treated with CFA- MCM-48 (Si/Al=9, 6 and 3) adsorbent respectively.

When effluent waste water sample was treated with CFA-MCM-48 (Si/Al=9, 6 and 3), BOD values were reduced by 87.1% and COD values were effectively reduced by 91.54%. Thus we can come to

conclusion that as contact time of the adsorbent in the exchange solution gradually increases the pH value reaching to the permissible limits after 180 minutes of contact. From 180 minutes of contact time and onwards all the parameters of the waste water i.e. EC, TDS, BOD, COD values reaches within the limits of their standard values.

Every metal cation, dissolved in water has a hydrated layer, in which the water molecules surrounds the metal ion and as such an aqua complex, $(M(H_2O)_x)^{n+}$, is formed²⁵. The hydrated layer surrounding the cation has a characteristic thickness and stability, which can be expressed in terms of hydration enthalpies.

After 180 minutes of contact almost complete removal of contaminations were observed. Aluminium being more hydrophobic in nature, among all the three adsorbents CFA-MCM-48 (Si/Al=3) shows an acute effect because of more Aluminium content in the active sites of pores in the crystals of an adsorbent.

From the above discussion we can come to the conclusion that during the first hour of contact between adsorbent and any of the three adsorbents, % removal of phenolic compounds and other contaminants was maximum. After first hour of agitation, rate of adsorption was reduced because of the least number of vacant spaces were left for further adsorption. Among the three adsorbents relative effectiveness of adsorption was found to be in order, Effectivity of CFA-MCM-48 (Si/Al=9) < Effectivity of CFA-MCM-48 (Si/Al=6) < Effectivity of CFA-MCM-48(Si/Al=3)

5. CONCLUSION:

Based upon the experimental study it was concluded that pure and well ordered CFA-MCM-48 material could be successfully synthesized from coal fly ash as the silica source instead of commercial expensive silica sources. The parametric variations such as change of synthesis temperature and pH of gel helps to optimize the synthesis conditions. The well ordered mesoporous material CFA-MCM-48 can be synthesized at 130°C for 4h keeping pH of gel 6.91 and calcined at 550°C.

The following conclusions can be drawn from this research work:

1. In an average more than 80% of phenol, 2-NP and 4-NP were adsorbed within the first hour of agitation, after which there was a slow approach to equilibrium. Among them 4-NP has the highest adsorption capacity is observed.
2. The amount of adsorbate adsorbed was found to increase with an increase in contact time and the adsorbent dosage.
4. It was shown the CFA generated from Chandrapur thermal power plant could be successfully utilized as an adsorbent for the removal of phenols and other toxic contaminants from waste water.

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