Novel Mesoporous Silicas and its Characterizations for Oil Adsorption from Produced Water Injected in Water Injection Projects using Fixed Bed Column Processes

BY

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Aim of the work

- A novel direct single step synthesis of silica skeleton.
- Determination of chemical and physical characteristics of prepared compounds.
- the adsorption of oil as a standard method is used to evaluate the capacity of the MCM-41 to eliminate organic molecules from water.
- The objective of this study is to control, through an experimental evaluation, the fixed-bed adsorption on MCM-41, and to develop on this basis a model can predict the performances and the characteristics of the bed according to the operating conditions (initial concentration, flow rates and bed depth) .
- Study the kinetic and thermodynamic parameter in batch process.
- Application of stand column to stimulate the field conditions.

INTRODUCTION

- **What is produced water ?**
- **What is Produced Water Volume?**
- **Why Worry About Produced Water?**
- **What is produced Water Management ?**
- **What are technologies of produced water Treatment?**

What is Produced Water?

"Produced water" it is the water flows from reservoir to the surface with oil and gas production.

- Contains many chemical constituents
  - **Salt content** (salinity, total dissolved solids [TDS], electrical conductivity)
  - **Oil and grease** (Composite of many hydrocarbons and other organic materials)
  - **Toxic inorganic and organic** compounds or chemical additives
  - **NORM**

Why Worry About Produced Water?

- The total cost of managing large volumes of produced water includes;
  - The cost of constructing treatment and disposal facilities
  - The operation cost (chemical additives and utilities)
  - The managing cost of any residuals or byproducts
  - Permitting, monitoring, and reporting costs
  - Transportation costs
- Improper management can harm the environment
  - Expensive clean up
  - Bad publicity for company

Produced Water Volume

- Largest volume waste stream from oil and gas production
  - Worldwide estimate – 77 billion bbl/year (2003 SPE paper)
  - U.S. - 15-20 billion bbl/year
    - ~ 1 billion bbl/year offshore Gulf of Mexico

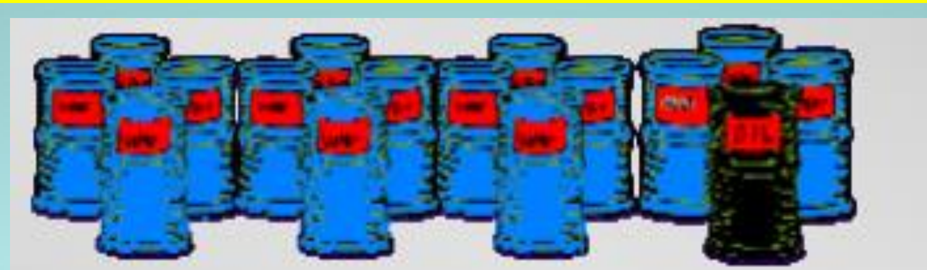
Globally

For Every Barrel of Oil Produced
3 Barrels of Water Are Co-produced

Average Global Produced Water Volumes Increased by 20% in Last Two Years (DOE J. Vale)

- 3:1 Water /Oil Ratio Globally

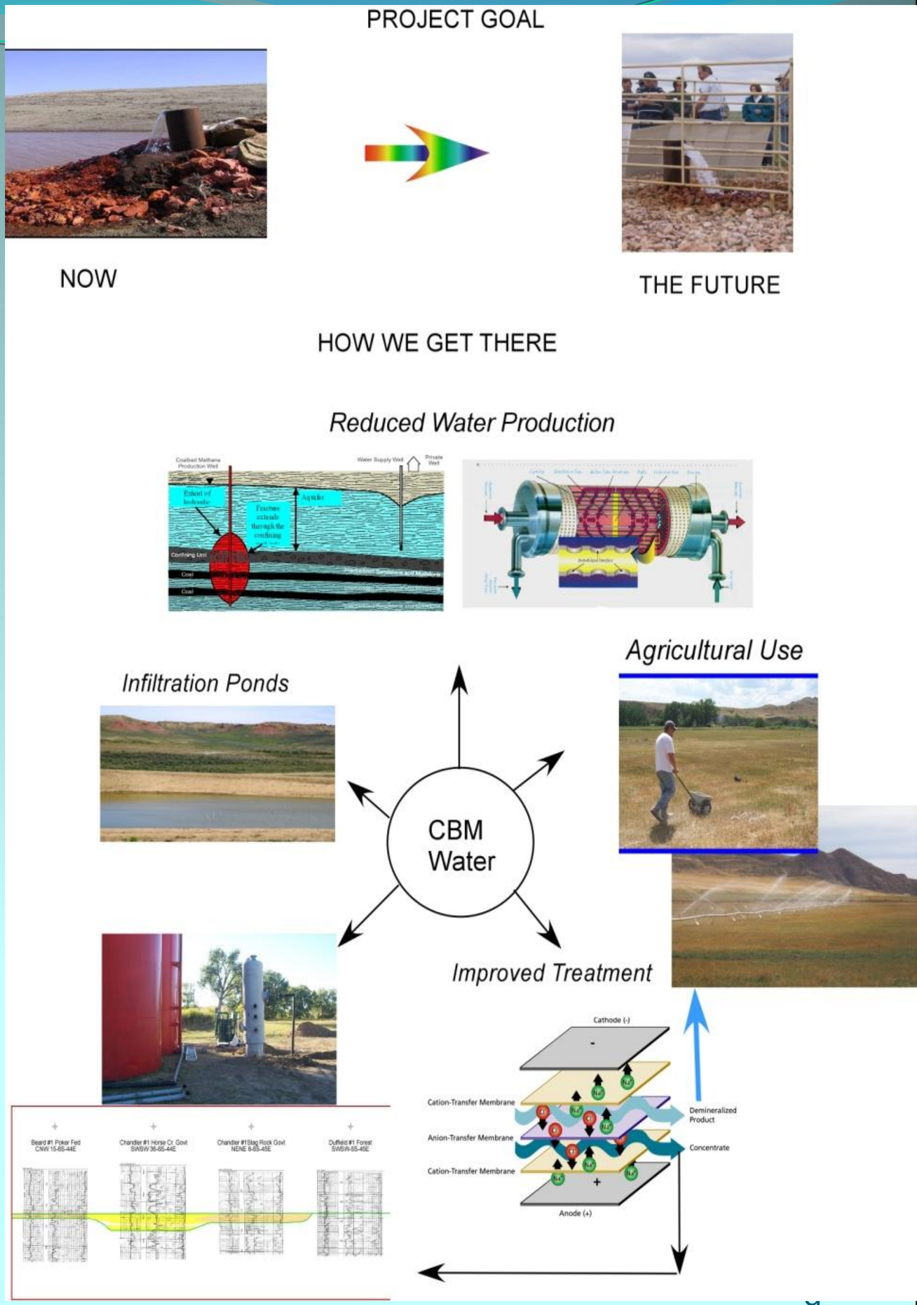
- 10:1 Water/Oil Ratio for Mature Assets



Treatment of Produced Water

Offshore Discharge Regulations

Produced Water Management



Water Management Practices

- ✓ ***Minimise*** the volumes to Surface
- ✓ ***Maximise*** re-use of water by injecting into hydrocarbon producing formation
- ✓ ***Reduce*** footprint and cost
- ✓ ***Use beneficially*** all resources
- ✓ ***Safeguard*** open waters & aquifers

Wastewater Treatment Technologies

- Gravity separation
- Plate coalescence
- Enhanced coalescence
- Enhanced gravity separation
- **Adsorption/Filtration**
- Flotation separation
- Membrane filtration
- Electrodialysis (ED)
- Freeze-thaw/evaporation
- Biological treatment

Materials and Methods

Sample preparation

- Produced water contaminated with oil droplets (oily produced water, OPW) sample was kindly obtained from the local Egyptian oilfield.
- The OPW used in these experiments are being brought from oilfield exposed to the atmosphere

Results and Disscusion

Oily produced water analysis

- IC
- HLPC
- Turbidity meter

Table (1) Extended analysis for brinewater sample

Total Dissolved Solids	244927.7mg/l	**pH**	7.2@ 25 °C
Conductivity	23.2 x10-2mohs/cm@2.7°C	**Density**	1.15770g/m@ 60F
Resistivity	0.04310ohm-m @24.5 °C	**Specific gravity**	1.15885
Salinity	244691.7mg/l	**Hardness**	18883.1mg/l

Constituents	**mg/L**	**Constituents**	**mg/L**
Lithium	5.60	***Fluoride***	2.20
Sodium	87175.00	***Chloride***	148298.00
Potassium	569.62	***Bromide***	119.00
Magnesium	1390.66	***Nitrate***	48.00
Calcium	4585.51	***Hydroxide***	Nil
Iron	5.30	***Carbonate***	Nil
Copper	Nil	***Bicarbonate***	231.80
Barium	Nil	***Sulfate***	2497.00
Strontium	Nil		

Experiments

- Catalyst Preparation
- Batch test
- Kinetic Study
- Column adsorption model

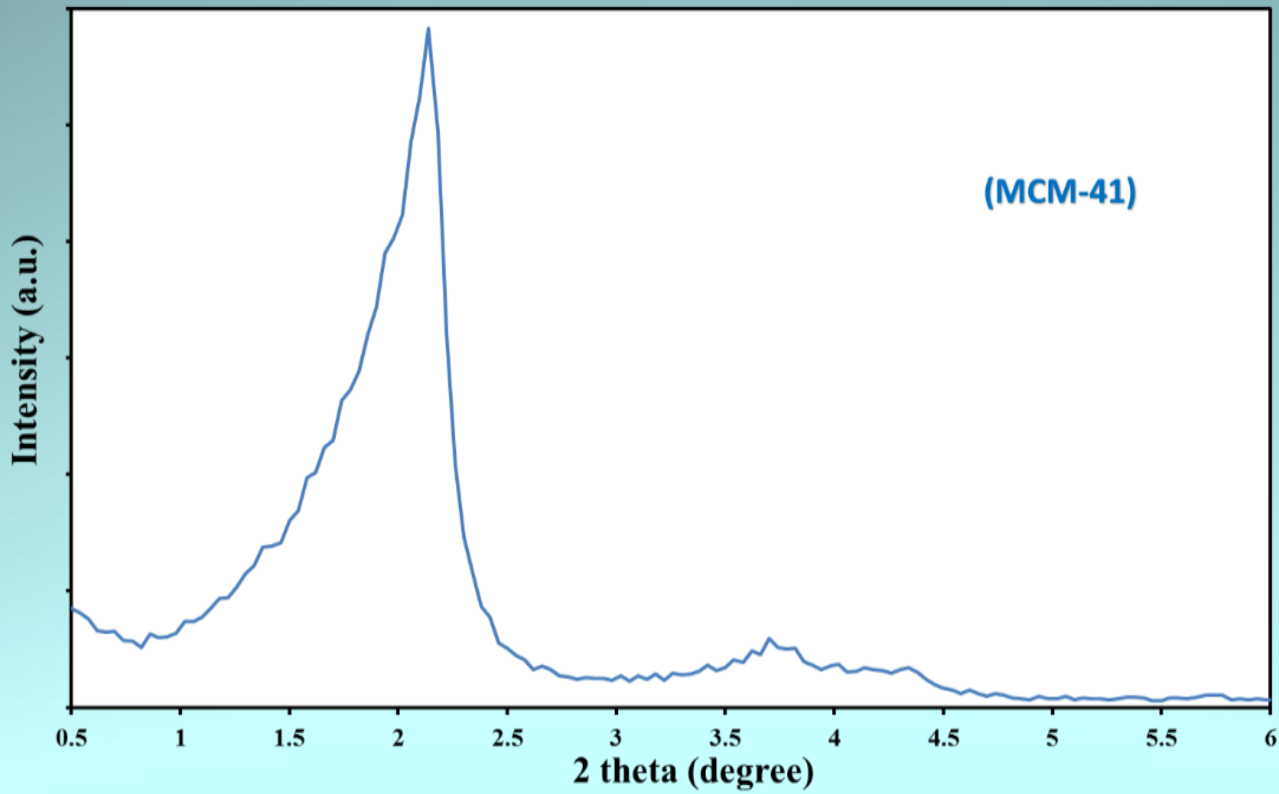
Catalysts preparation

- MCM-41 was prepared by a direct precipitation synthesis method using cationic surfactant cetyltrimethylammonium bromide (CTAB) as a template and tetraethylorthosilicate (TEOS) as a silicon source in basic conditions. Typically, at 30 °C, 16.2 g of CTAB was dissolved into a solution containing 145 mL of deionized water, 8.21 mL of TEOS and 32 mL of 30% NH_3 was then added drop wise and stirred vigorously for 12 h for hydrolysis of TEOS. The product obtained was filtered and dried under vacuum at 40 °C night over. The samples were annealed at 550 °C for 4h to remove the surfactant.

Catalyst characterization

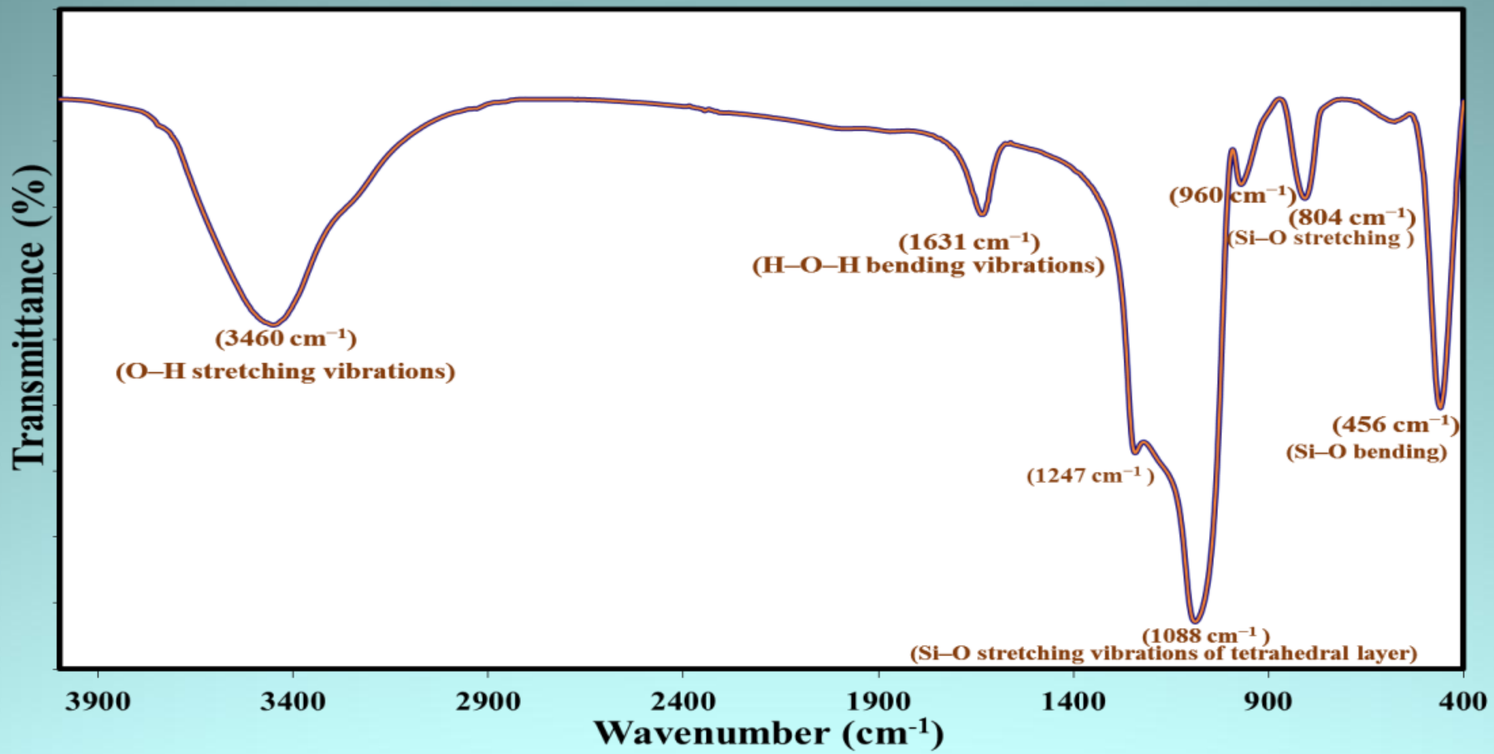
- The X-ray diffraction
- HRTEM
- FTIR spectrum
- Raman spectra
- surface area

X-ray diffraction



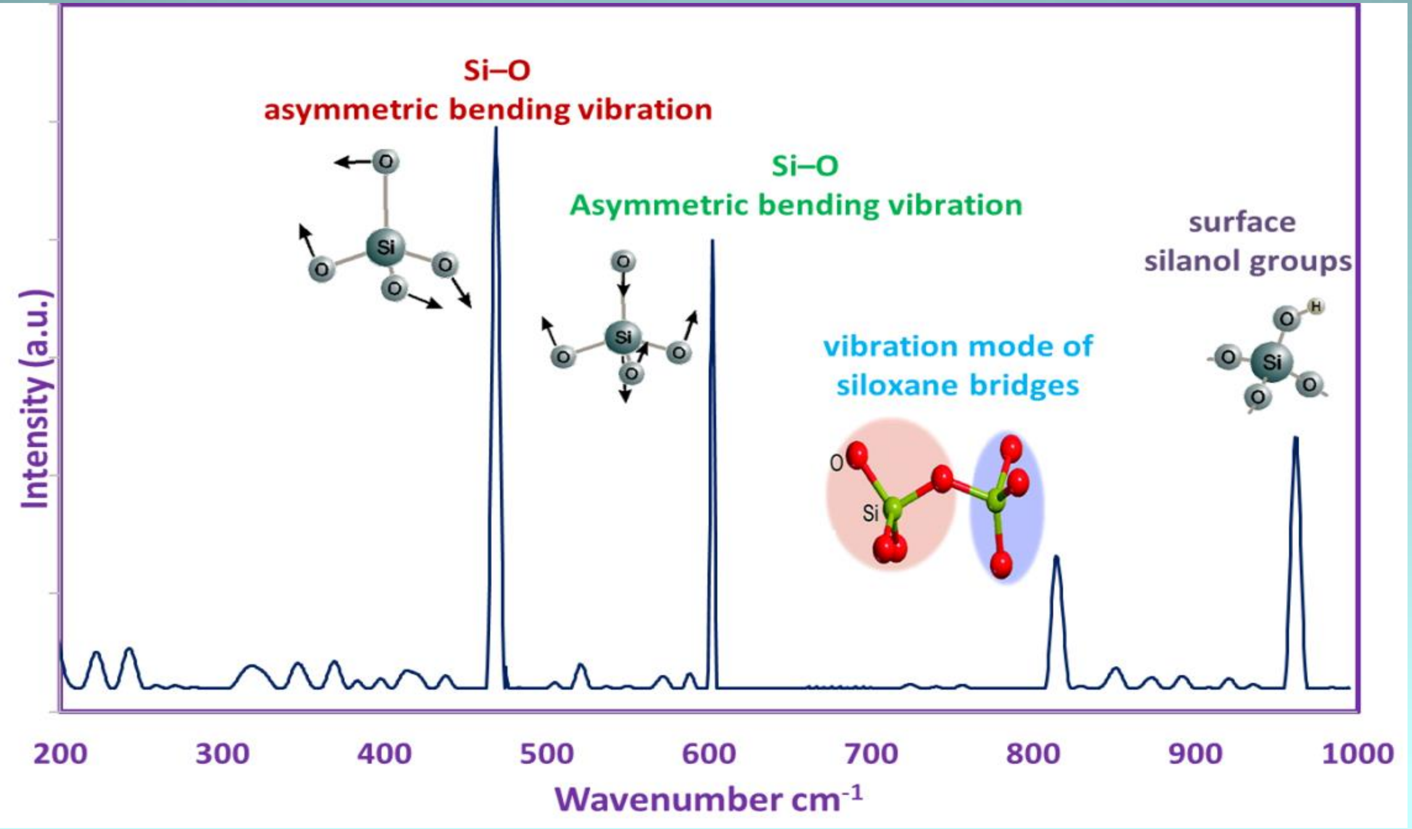
The low angle XRD patterns of mesoporous silica MCM-41

FT-IR Spectra



FTIR Spectrum of prepared MCM-41

Raman analysis

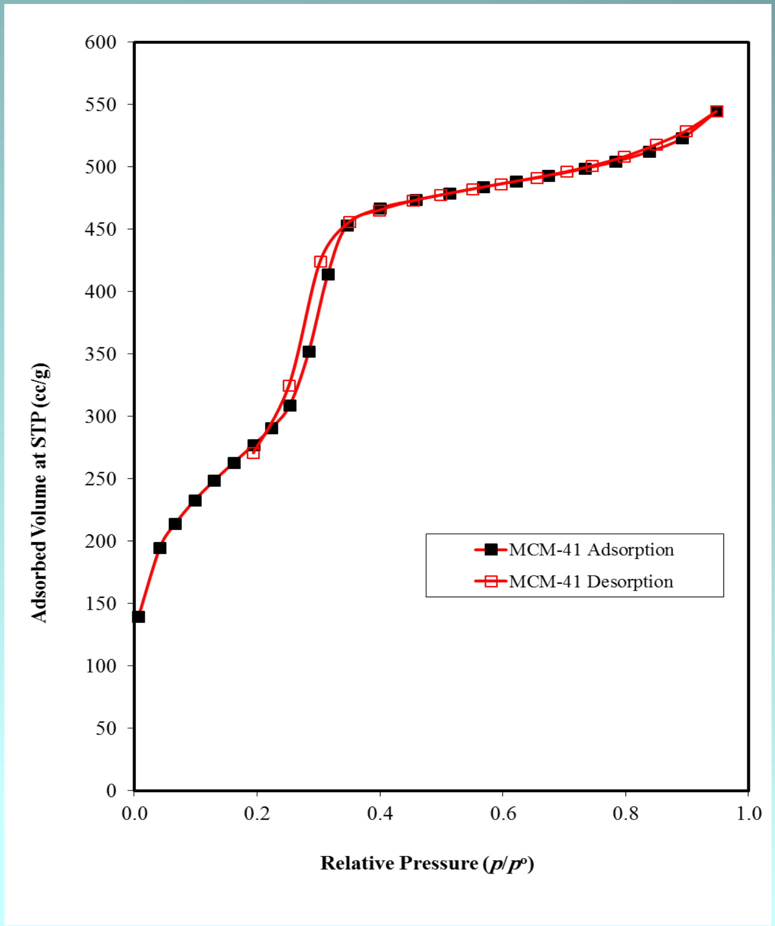


Raman Spectrum of prepared MCM-41

Surface structure properties

Data of BET surface area

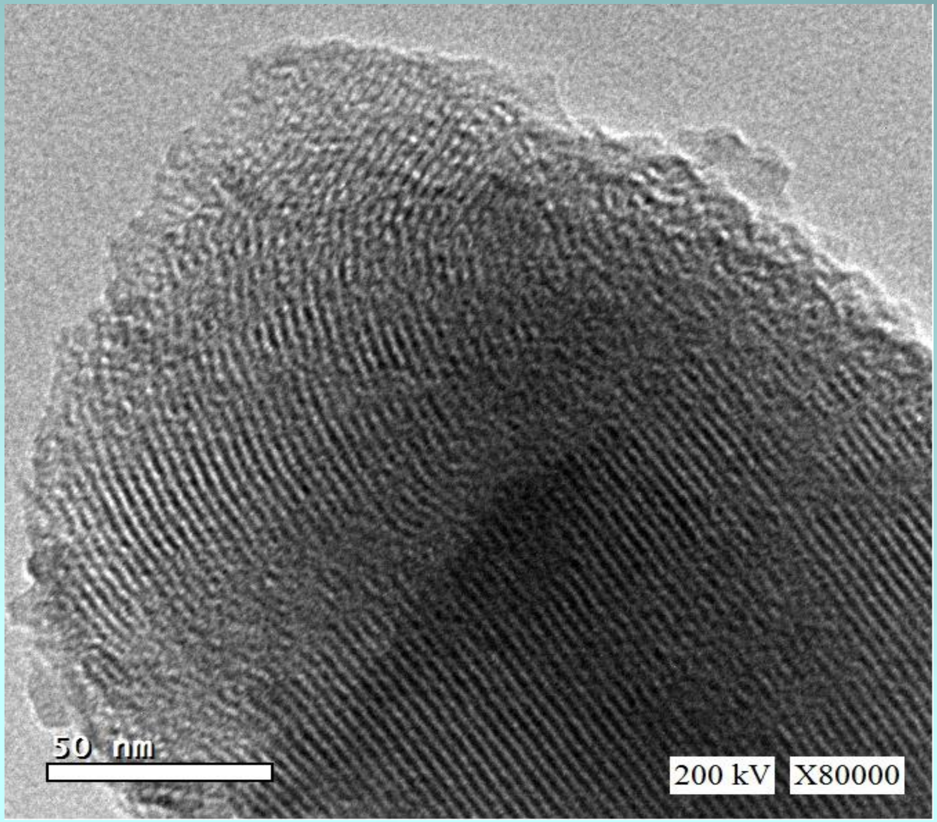
Sample	$C_{constant}$	$S_{BET}(m^2/gm)$	$V_m(cc/gm)$
MCM-41	98.7	1022.6	0.99



N2 adsorption–desorption isotherm for MCM-41

Transmission Electron Microscope (TEM)

As evidenced by HRTEM image shown, MCM-41 possesses an order mesoporous structure. As revealed, a regular hexagonal array of uniform channels is exhibited indicating a highly ordered pore structure of MCM-41.



HRTEM image of prepared MCM-41

Isothermal study

- Langmuir
- Freundlich

The Langmuir equation

$$Ceq/Qeq = 1/Qmb + Ceq/Qm$$

The Freundlich isotherm

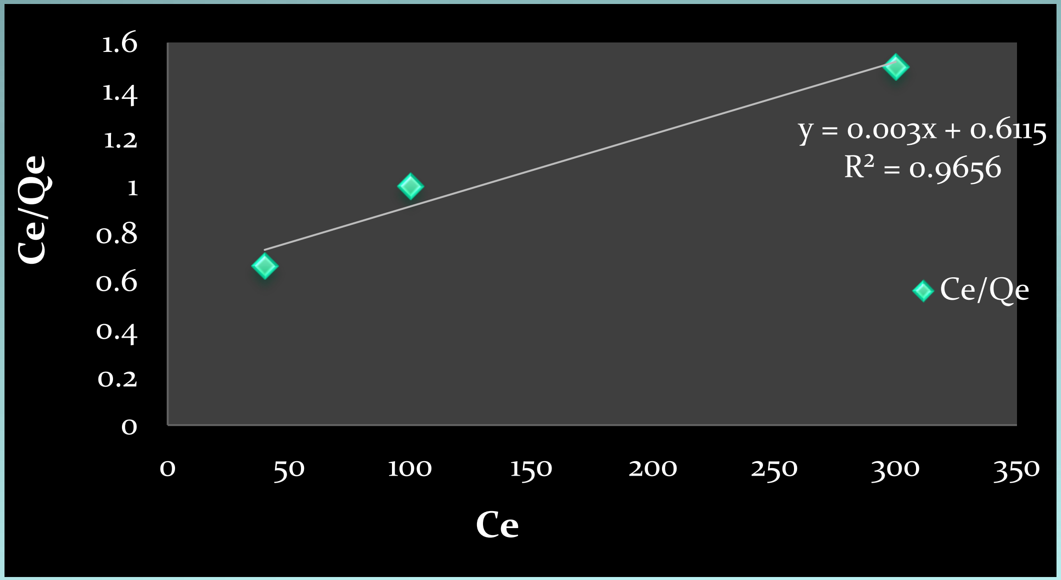
$$\log Qe = \log Kf + \frac{1}{n} \log Ce$$

Where Ceq is the equilibrium concentration of oil in solution (mg/L), Qeq is the amount of oil adsorbed; Qm and b is Langmuir constants.

Qe is the amount of oil adsorbed (mg/g), *Ce* is the equilibrium concentration of oil in solution (mg/L), and *K*f and n are constant integrates

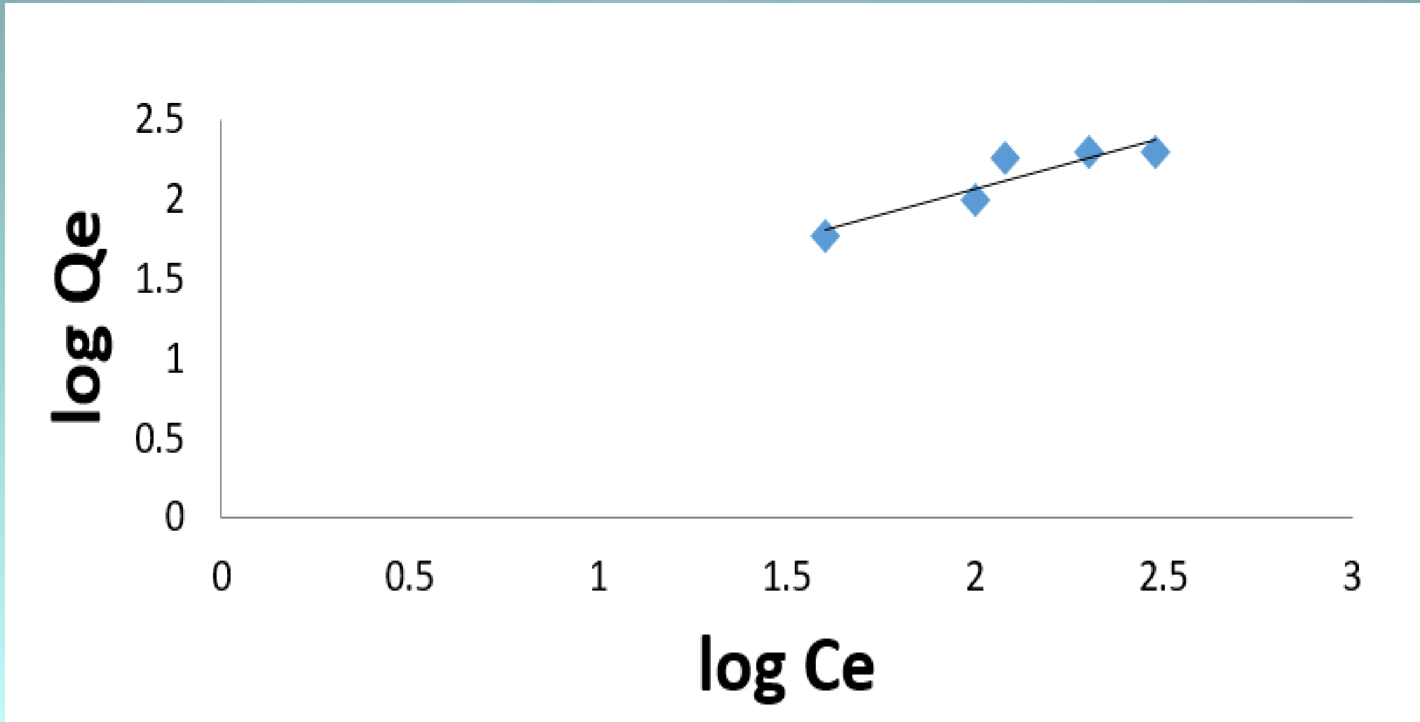
Langmuir			Freundlich		
K	*Qe*	R^2	*n*	*K*	R^2
0.004951	930.297	0.982669	1.549759		0.924122

Langmuir isotherm



Langmuir Isotherm for the adsorption of oil onto silica

Freundlich isotherm

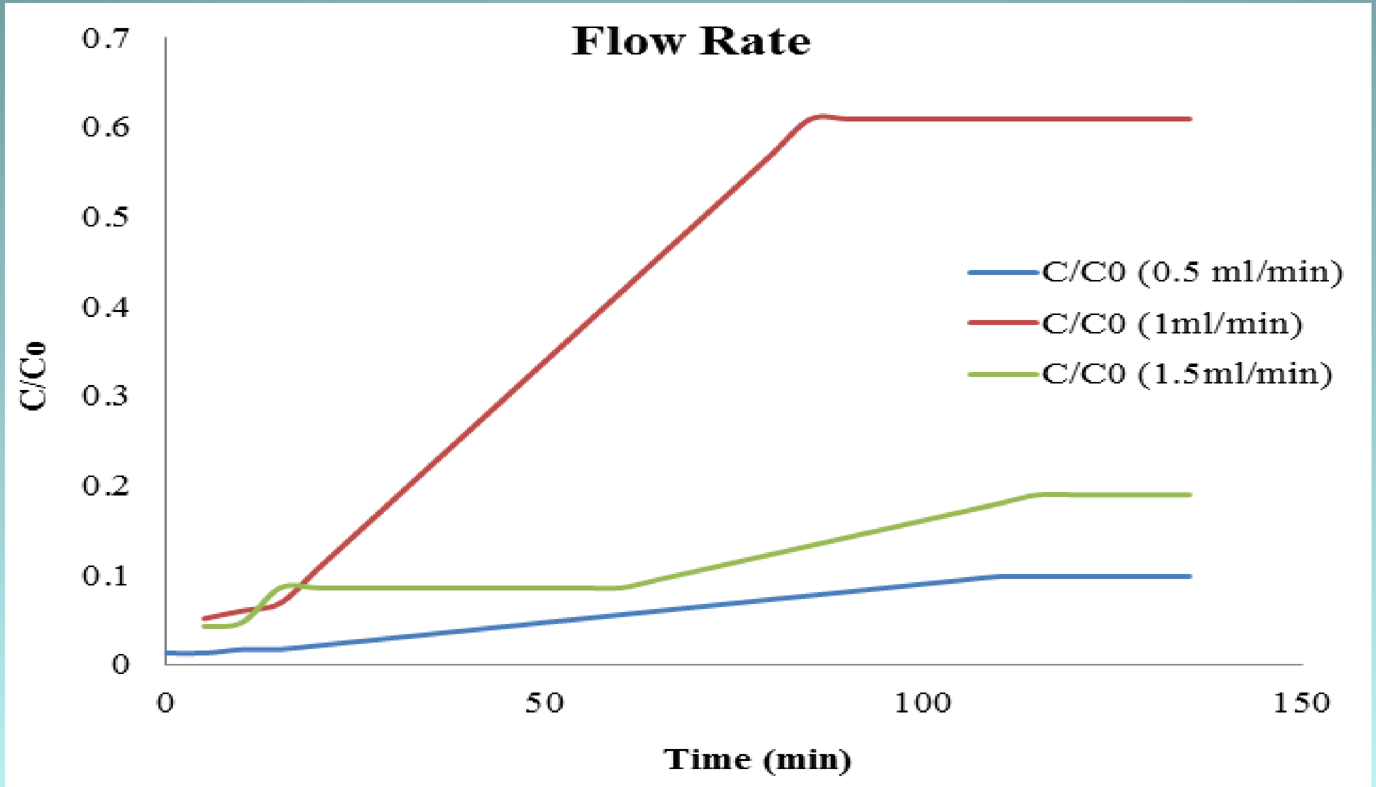


The Freundlich isotherm for the adsorption of oil onto silica

Adsorption Columns technique

Column Adsorption Studies

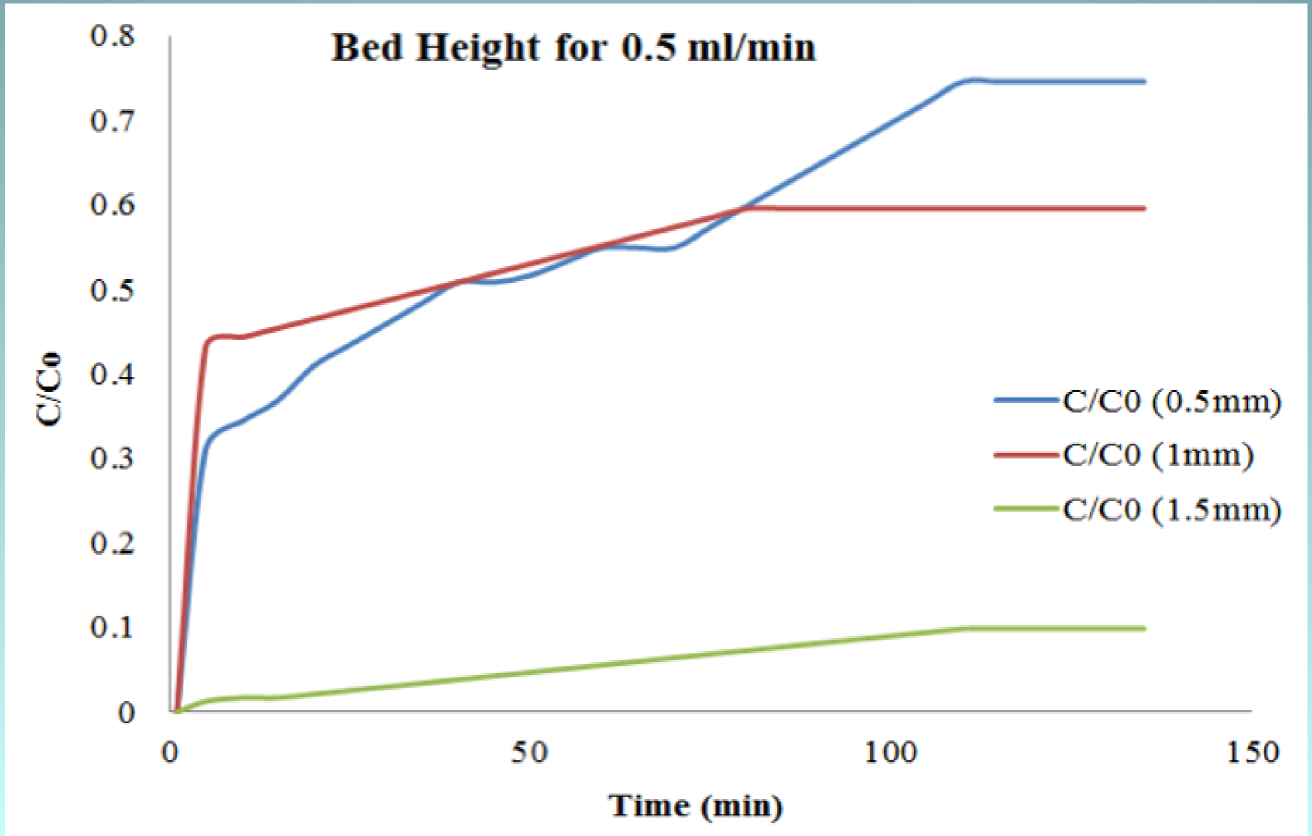
Effect of flow rate



Flow rate of oil adsorption on MCM-41 versus time

Column Adsorption Studies

Effect of bed height



Effect of the bed height for adsorption of oil on MCM-41

Breakthrough Models

Thomas model

$$\ln\left(\frac{C_0}{C_t}-1\right)=\frac{k_{Th}q_e x}{Q}-k_{Th}C_0 t$$

Yoon-Nelson model

$$\ln\frac{C_t}{C_0-C_t}=k_{YN}t-\tau k_{YN} \quad .$$

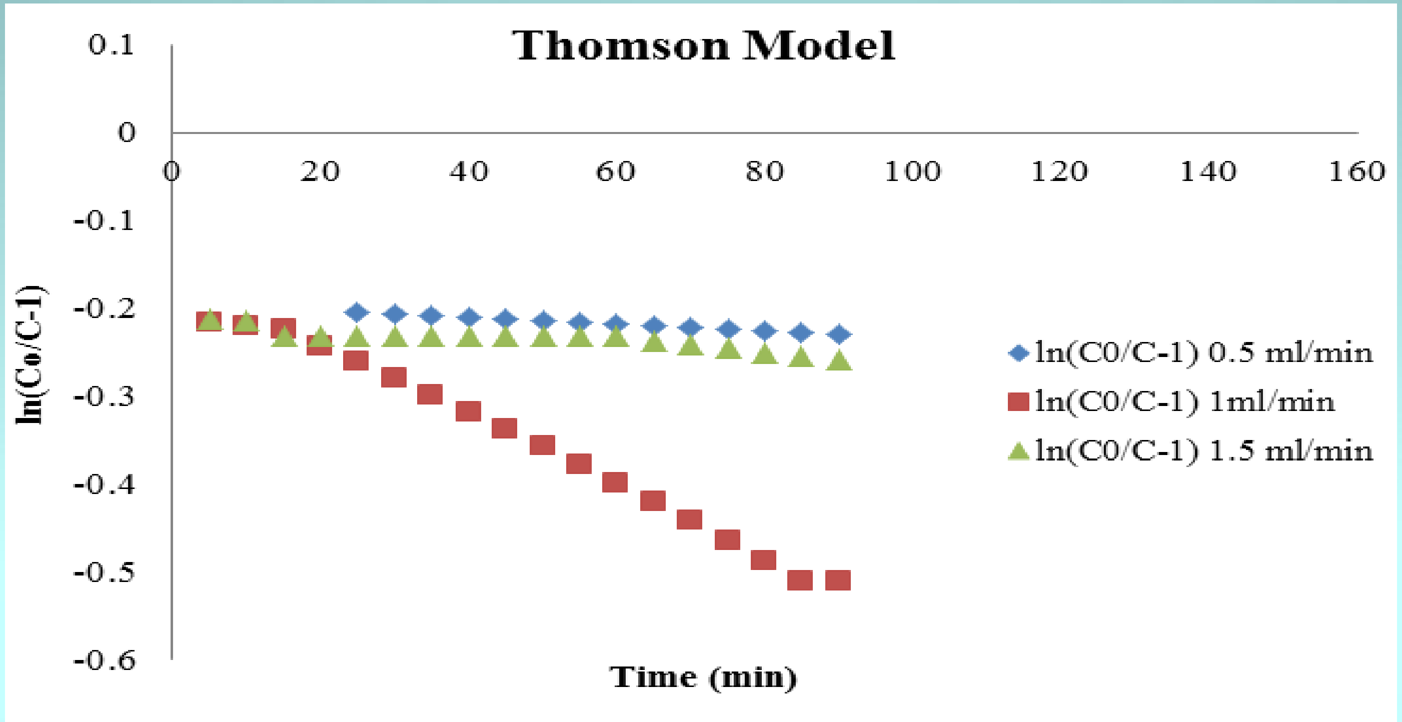
Where k_{Th} (mL/min.mg) is the Thomas model constant, qe (mg/g) is the predicted adsorption capacity, x is mass of adsorbent (g), Q is influent flow rate (mL/min), C_0 is initial solution concentration (mg/L), and Ct is effluent solution concentration (mg/L). The linear form of Thomas model is expressed as Equation (2).

Where k_{YN} (L/min) is the rate constant and τ (min) is thetime required for 50% adsorbate breakthrough. The linear form of Yoon-Nelson model is expressed as Equation (4)

Kinetic study of Thomas model

Table (4) Thomson model parameters

Flow (mL min^{-1})	k_{Th}	R^2	q (mg g^{-1})	*SSE (%)*
0.5	0.000175	0.999994	1113.795	0.001
1	0.00171	0.99585	100.7273	0.002
1.5	0.00017	0.88319	1259.224	0.006



Conclusion

Conclusions

- A novel mesoporous MCM-41 for oil removal from produced water on a continuous fixed bed study was synthesized by facile, simple and cost effective method
- The structure and surface morphology of prepared sample has been studied and the results reveal the formation of a pure hexagonal mesoporous structure with a high surface area of 1022 m^2/g.
- The effects of flow rate (0.5, 1 and 1.5 mL/min) and bed height (0.5, 1 and 1.5 mm)on the breakthrough characteristics of the adsorption system at constant the initial oil concentration(1000mg/L),were determined.

Conclusions

- The maximum removal(70.26%) was achieved for aflow rate of 0.5 mL/min and a bed height of 1.5 mm.
- Two models Thomas and Yoon–Nelson were applied to predict the breakthrough curves and to determine the characteristic parameters useful for column design.
- It was clear that the Thomas model fitted well the adsorption data with a correlation coefficient (R^2) at different conditions.
- From the R^2values,we suggested that the Thomas model was suitable for explaining the chemisorption of oil on MCM-41.

Conclusions

- The model employed shows that the MCM-41 was suitable for adsorption of oil using fixed bed adsorption.
- We found that the new modified MCM-41 was useful in water treatment and future remediation processes.


Thank You!