Treatment of a Selected Refinery Wastewater Compound (Benzene) by Chitin and Chitosan

by

Dr Maryam Mohamed

معهد البحرين للتدريب
Bahrain Training Institute

UNIVERSITY OF SURREY

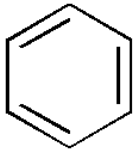
مملكة البحرين
وزارة التربية والتعليم

Outline

- **Introduction**
  - Benzene
  - Treatment Methods for VOCs
  - Treatment Techniques of Oil Refinery Wastewater
- **Aim and objectives**
- **Methodology**
  - Experimental Programme
  - Adsorption Isotherm Models
- **Results**
- **Conclusions**
- **Recommendations**

Introduction

- Benzene is a toxic organic compound



- Scarce of water in GCC countries
- Main sources of benzene wastewaters
- Benzene level ≈ 1–100 mg/l in refinery wastewater

BAPCO Bahrain Petroleum Company

Benzene Regulations & Guidelines

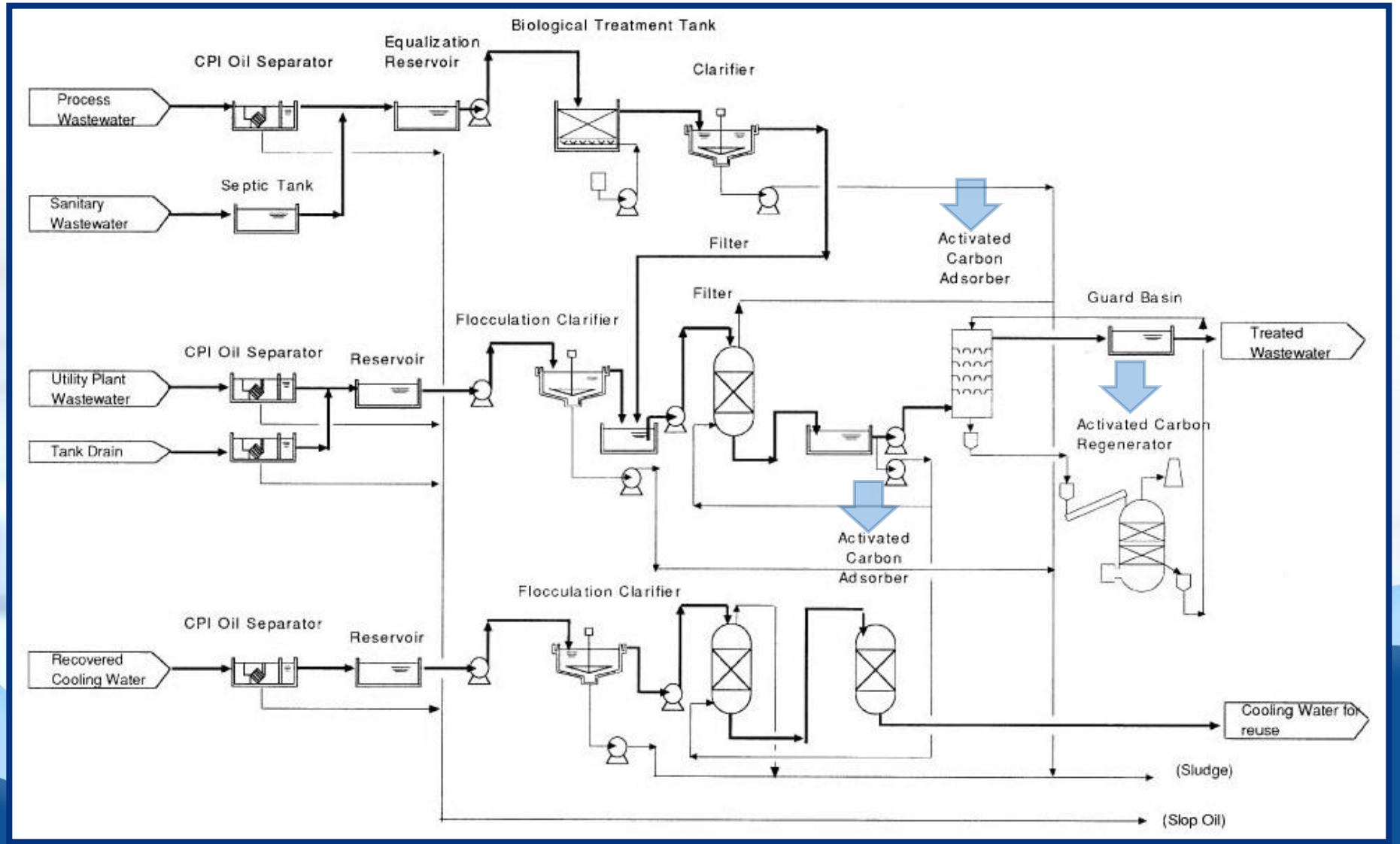
Agency	Regulations and guidelines	Classifications and values
International IARC WHO	Carcinogenicity classification Drinking Water Quality Guidelines	Group 1 0.001 mg/l
National EPA	Designated as hazardous substances in accordance with Section 311(b)(2)(A) of the Clean Water Act	Yes
	National primary drinking water standards MCLG MCL	Zero 0.005 mg/l
	Water quality criteria for human health consumption of: Water + organism Organism only	2.2 µg/l 51 µg/l

Treatment Methods for VOCs

- Chemical, biological and physico-chemical treatment methods
- Removal by the activated carbon adsorbents

Kuwait Battling Oil Spill in the Gulf (Auguest 2017).

Treatment Techniques of Oil Refinery Wastewater



Aim and objectives of the Research

- **Aim**
  - Potential of using chitin and chitosan as adsorbents and the development of “Greener" processes
- **Objectives**
  - Effects of adsorbent dose, initial concentration of benzene, and contact time

Adsorption Isotherm Models

Isotherm Model	Slope	Intercept
Langmuir	$\frac{1}{ab}$	$\frac{1}{a}$
Freundlich	$\frac{1}{n}$	$\ln(K)$
Redlich–Peterson	β	$\ln(a_R)$
Temkin	B_1	$B_1 \ln(K_T)$
Dubinin–Radushkevich	$-B_D R^2 T^2$	$\ln(q_D)$

Kinetic Models

Kinetic Model	Y-axis	X-axis
Pseudo-first order	$\ln[1-U(t)]$	t
Pseudo-second order	t/X	t
Intraparticle diffusion	X/M	$t^{1/2}$

Methodology

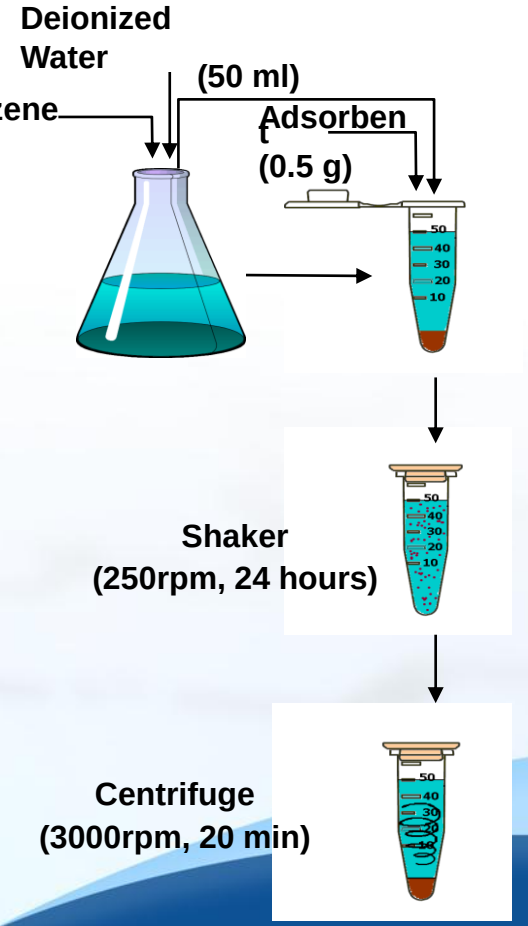
- **Experiments**

(a) (b)

Chitin and chitosan (a) in glass tubes and (b) after mixing with solutions.

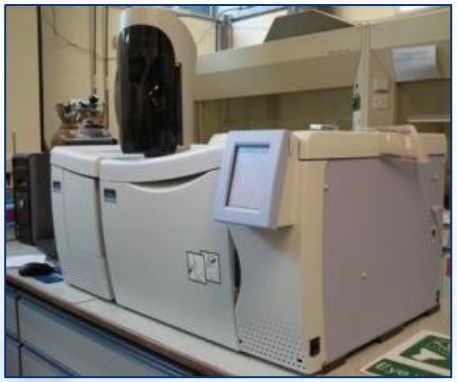
Sample placed in a rotary shaker at 300 rpm for 24 hr.

Suspended particles settle down by placing the samples in centrifuged at 3000 rpm for 20 minutes.

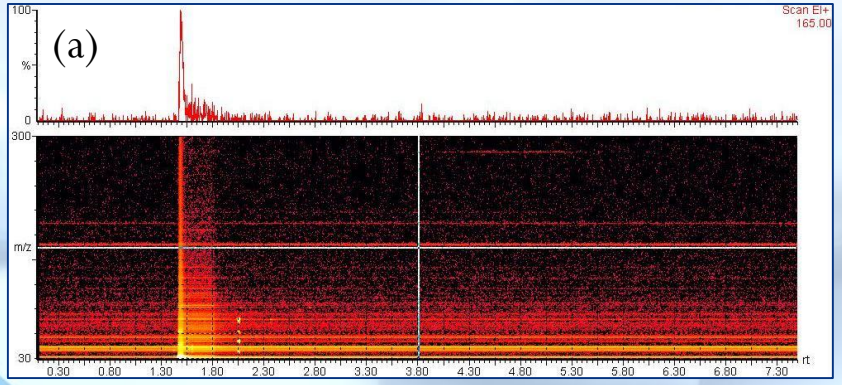


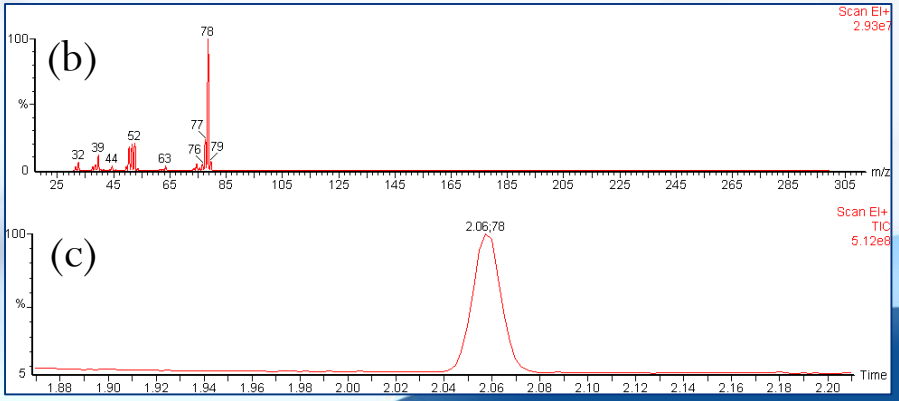
Methodology

- **Experiments**



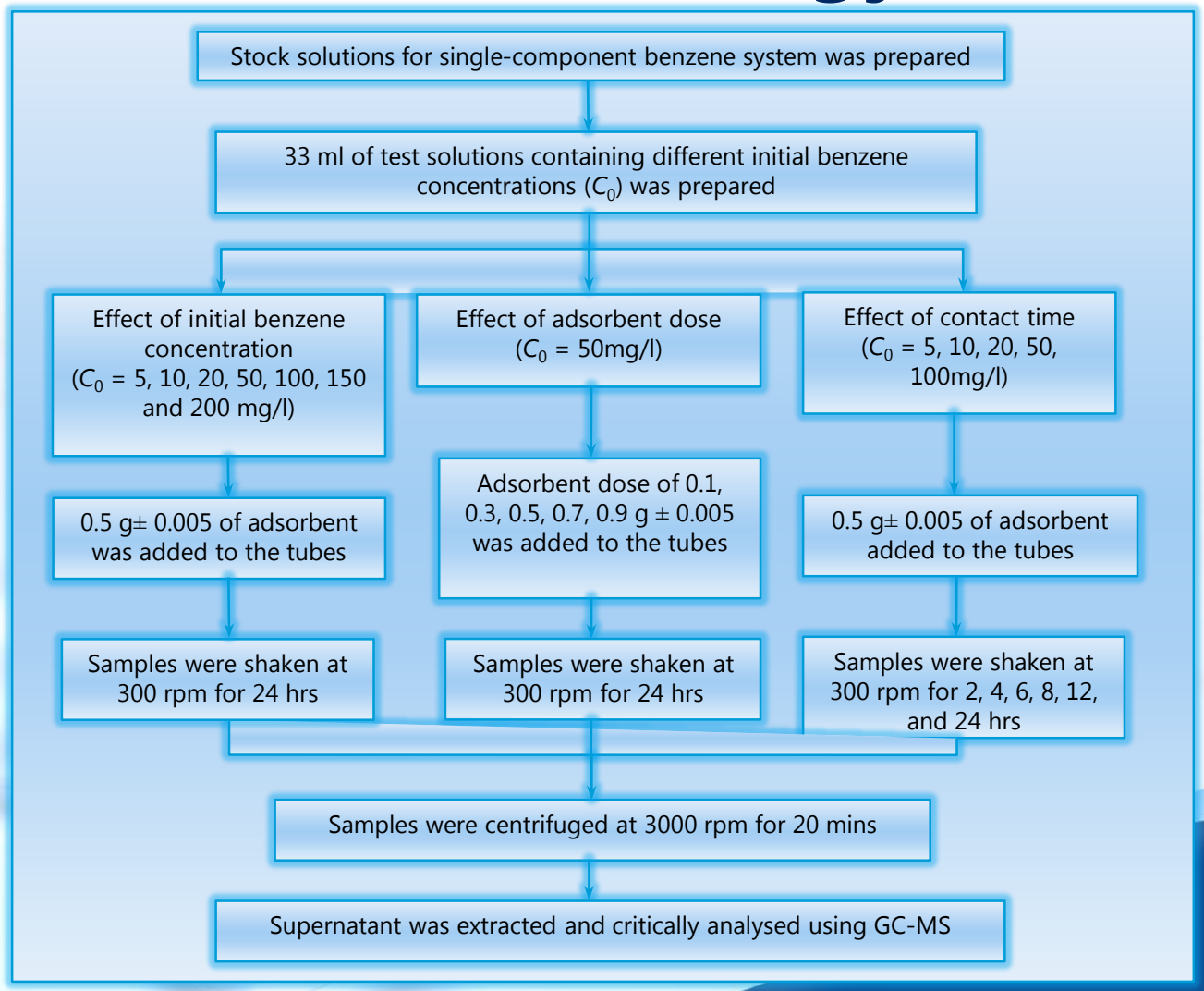
The supernatant was analyzed for the residual concentration of benzene using GC-MS.



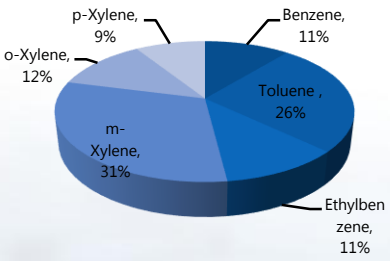


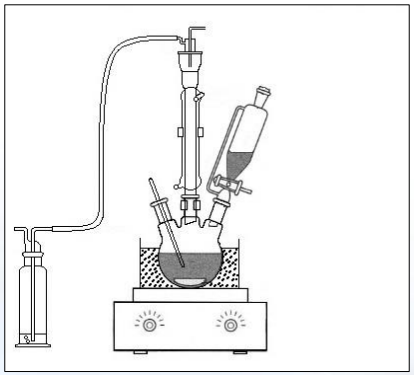
(a), (b) and (c) Chromatogram and spectrum of benzene solution (temperature = 22 ± 1 °C, initial concentration of benzene =100 mg/l, adsorbent dosage = 15 g/l)

Methodology

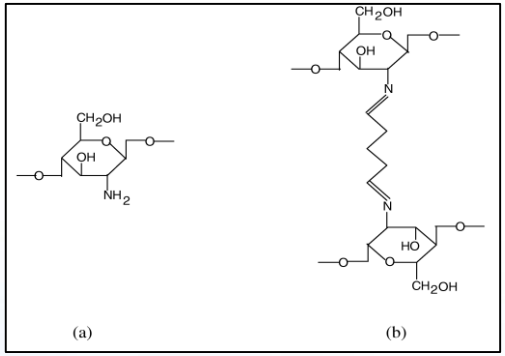


Methodology

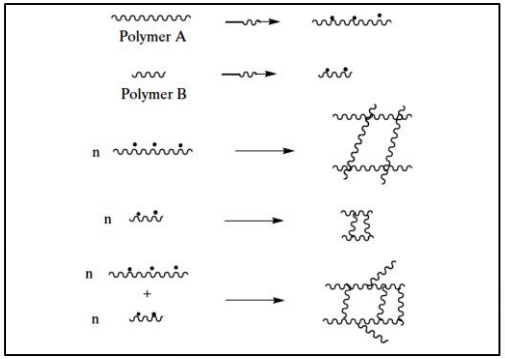




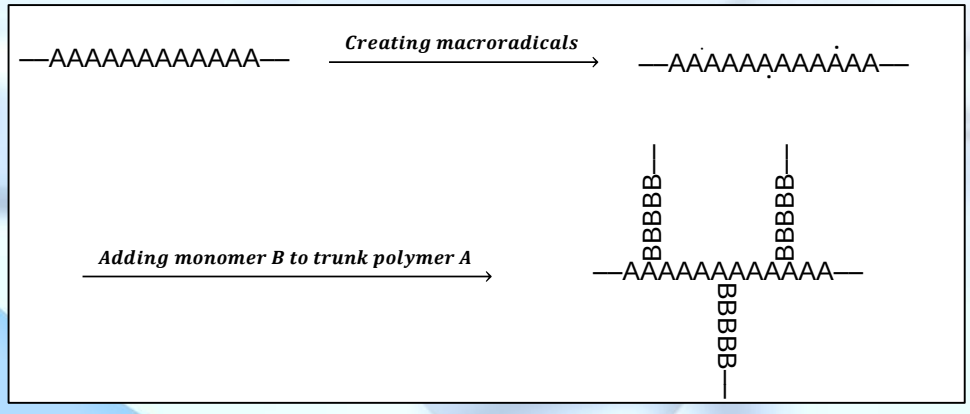
Schematic diagram of experimental set-up of graft copolymerization of crosslinked chitosan microspheres



Structure of raw chitosan and cross-linked chitosan

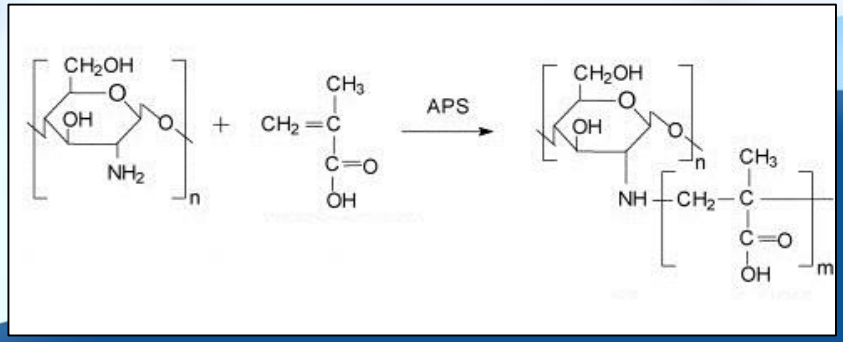


Reactions that may occur in chemical modification by crosslinking

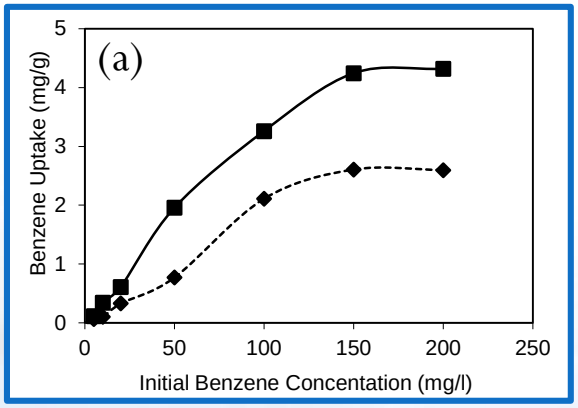


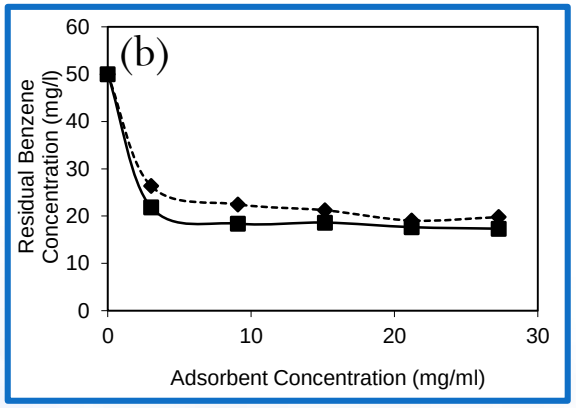
Schematic diagram of "grafting from" mechanism

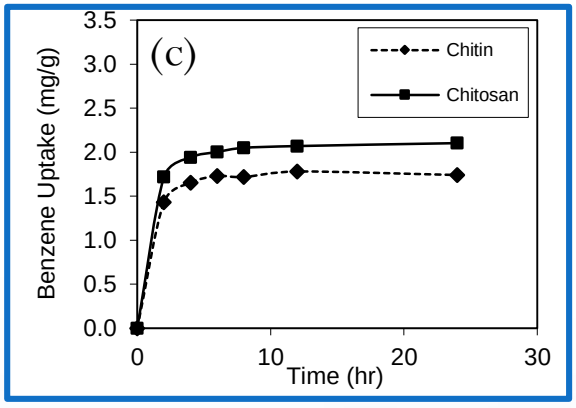
Graft copolymerization of methacrylic acid with chitosan



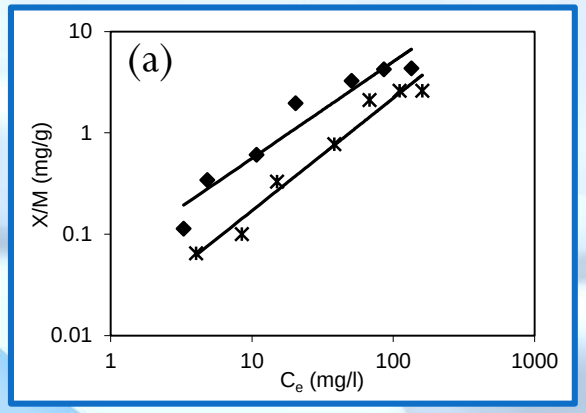
Results

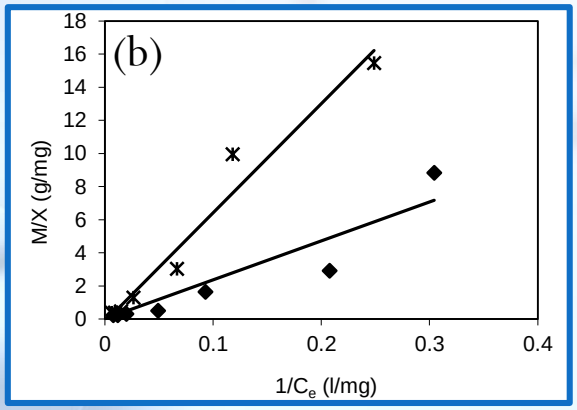


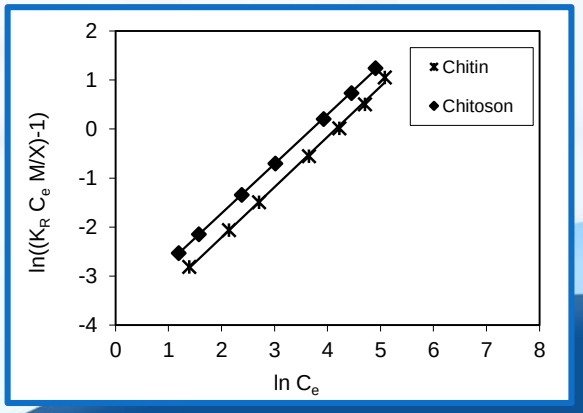




The effects of (a) Initial adsorbate concentration (b) adsorbent dosage and (c) contact time, on benzene removal by chitin and chitosan.

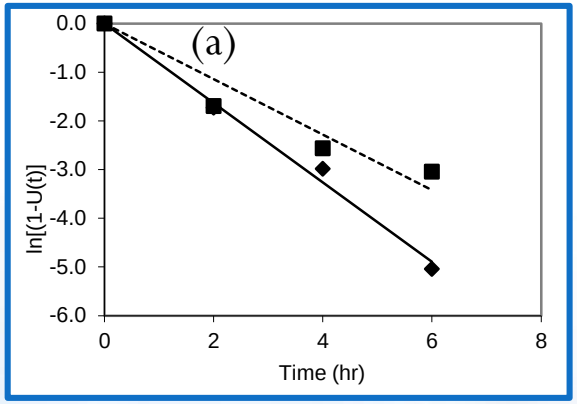


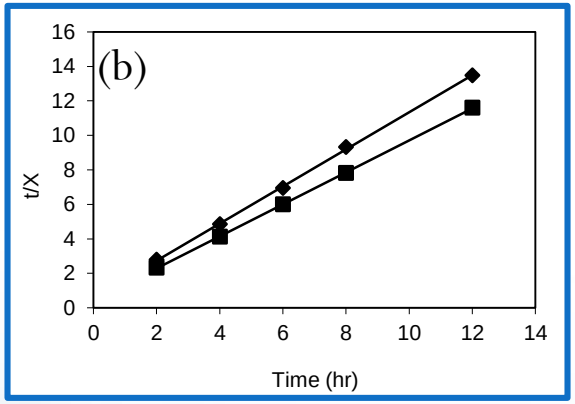


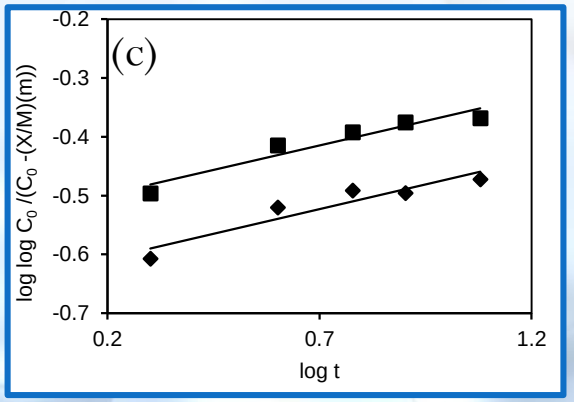


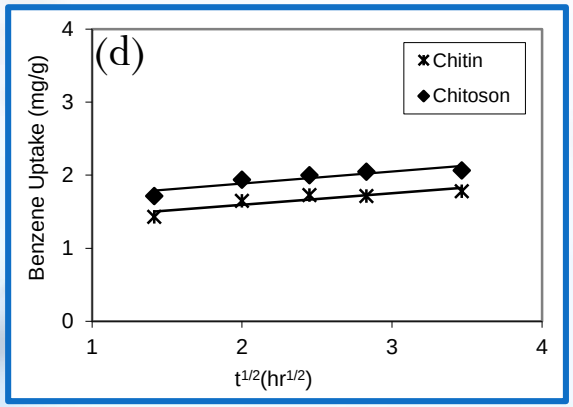
(a) Freundlich and (b) Langmuir isotherm models (room temperature = 22 ± 1 °C; adsorbent dosage = 15 g/l).

Results



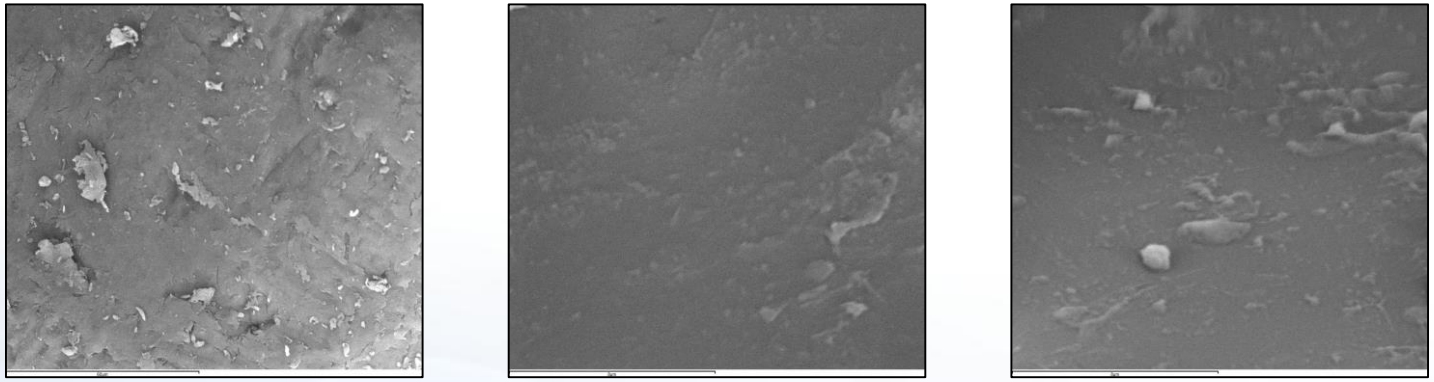






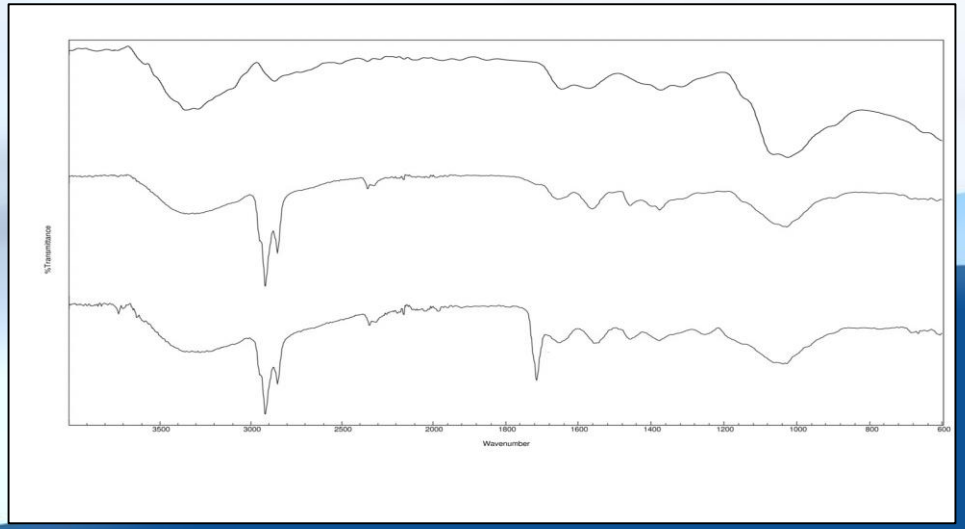
(a) Pseudo-first-order rate equation, (b) Pseudo-second-order rate equation (c) Bangham's equation and (d) Intra-particle diffusion equation, (temperature = 22 ± 1 °C, initial concentration of benzene =50 mg/l, adsorbent dosage = 15 g/l).

Results

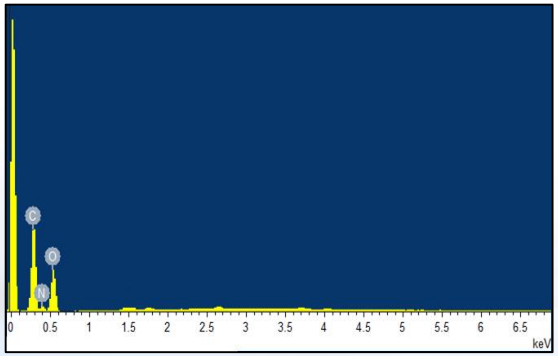


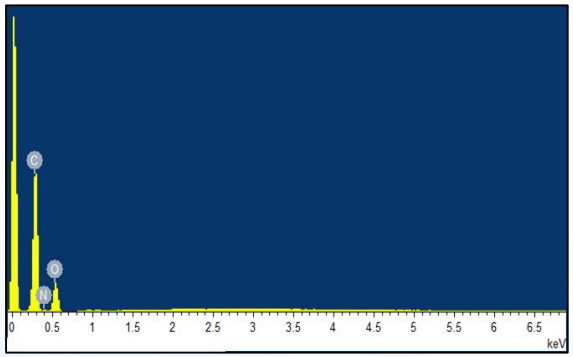
The SEM micrograph (20 kv) of (a) chitosan (b) glutaraldehyde crosslinked with chitosan (c) chitosan modified with poly(methacrylic acid)

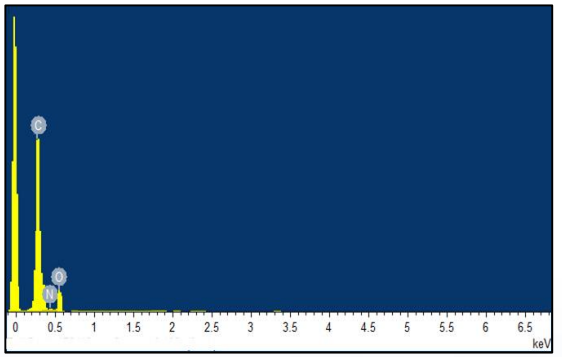
FTIR spectra of (a) chitosan (b) glutaraldehyde cosslinked chitosan and (c) methacrylic acid grafted with cosslinked chitosan



Results

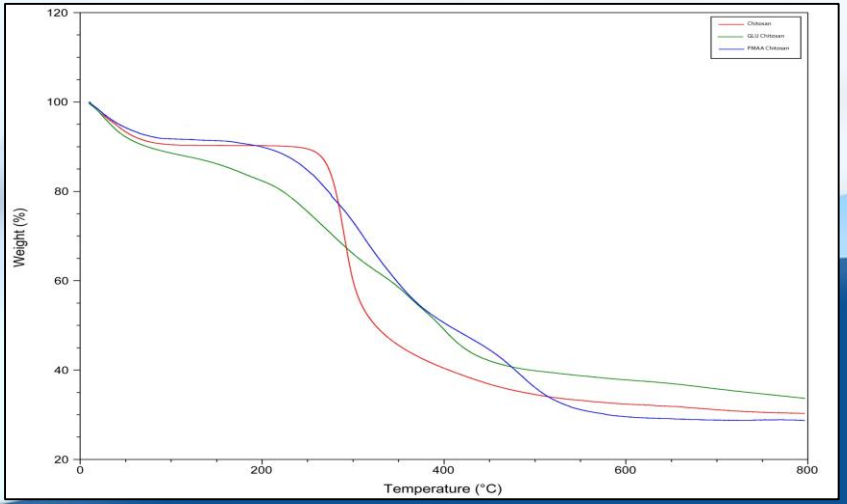




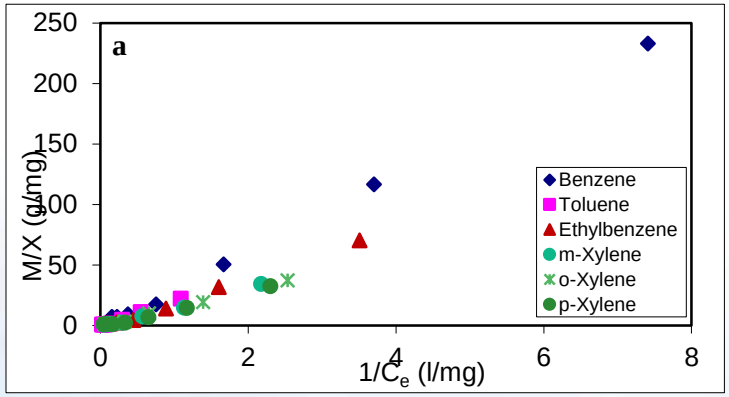


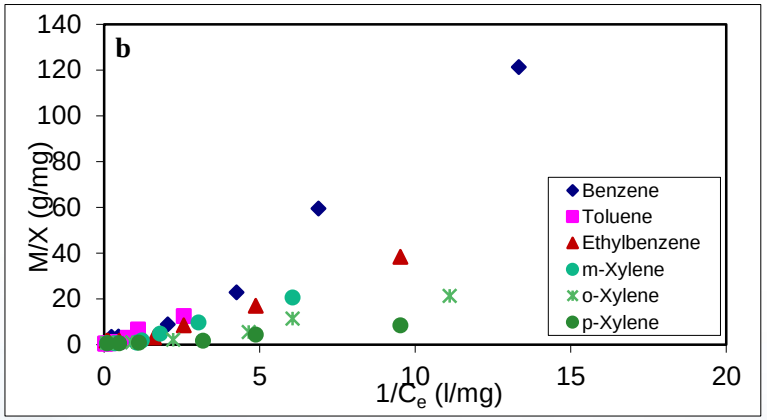
EDX analysis of (a) chitosan (b) of glutaraldehyde crosslinked with chitosan and (c) grafted crosslinked chitosan with poly(methacrylic acid

TGA analysis of chitosan, crosslinked chitosan and crosslinked chitosan grafted with poly(methacrylic acid) under nitrogen gas.

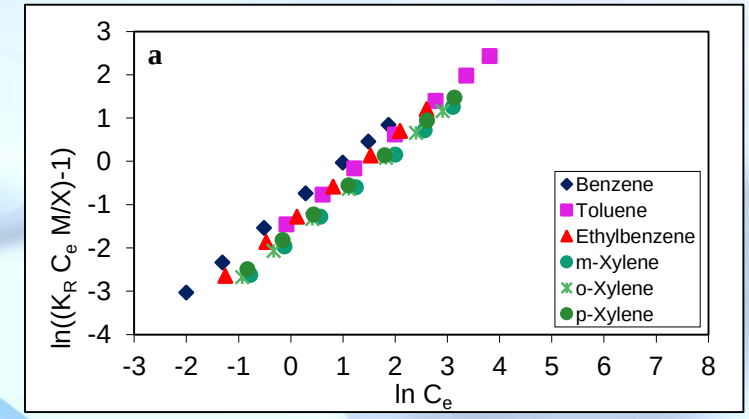


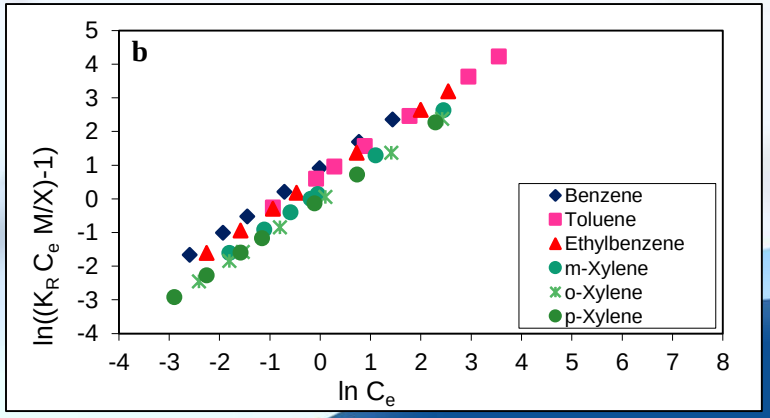
Results





Langmuir isotherms for BTEX sorption by (a) chitosan and (b) modified chitosan at various initial BTEX concentrations (adsorbent dose = 0.5 g; room temperature = 22 ± 1 °C)





Redlich–Peterson isotherms for BTEX sorption by (a) chitosan and (b) modified chitosan at various initial BTEX concentrations (adsorbent dose = 0.5 g; room temperature = 22 ± 1 °C)

Conclusions

- Freundlich isotherm was the best model to fit the equilibrium data.
- Chitosan showed better removal efficiency than chitin.
- Chemically modified chitosan showed the best removal among other adsorbents
- The pseudo-second order rate model described best the adsorption kinetics of benzene for the two selected adsorbents.

Recommendations for Further Research

- Real samples of industrial effluents
- Effects of other competing ions
- Integrated processes

Collaborative research with other GCC countries and UK

Thank You