Summer Internship Program

Analysis and Modeling of Adsorptive denitrogenation of Light Gas oil using Fixed Bed Column: An approach to improve Hydrotreating Technology

Submitted by
Vaidish Sumaria
B.Tech. Chemical Engineering (CE+RP)
SAP. ID.: 500023599
Enroll. No.: R900212042

Mentored by:
Dr. Ajay Dalai
Canada Research Chair of Bio-energy and Environmentally Friendly Chemical Processing
University of Saskatchewan

Research Background

- Crude oil is the feedstock from which refineries produce a wide range of petroleum products required by consumers in the transportation, residential, commercial and industrial sectors.
- Due to the increasing demand for gasoline and diesel fuels, the exploitation of heavy oil and bitumen from various deposits is quickly becoming a vital option for meeting the present and future energy requirements.
- Oil sands are primarily a mixture of bitumen, sand, water, and clay.
- The susceptibility of catalysts capable of refining petroleum feedstock, to organic nitrogen bearing compounds has long been recognized and studied.
- Over the years, numerous non-catalytic processes have been investigated for the removal of nitrogen bearing compounds. Transition metal salts such as CuCl2.2H2O have also been utilized due to their ability to extract nitrogen compounds of the basic and those of the heterocyclic nature from synthetic crude oils by complex formation.
- These aforementioned methods tend to be fairly effective in the removal of basic nitrogen compounds as well as sulphur compounds; however, none of them are efficient enough for the selective removal of non-basic or neutral nitrogen compounds, an area which has not been extensively explored.

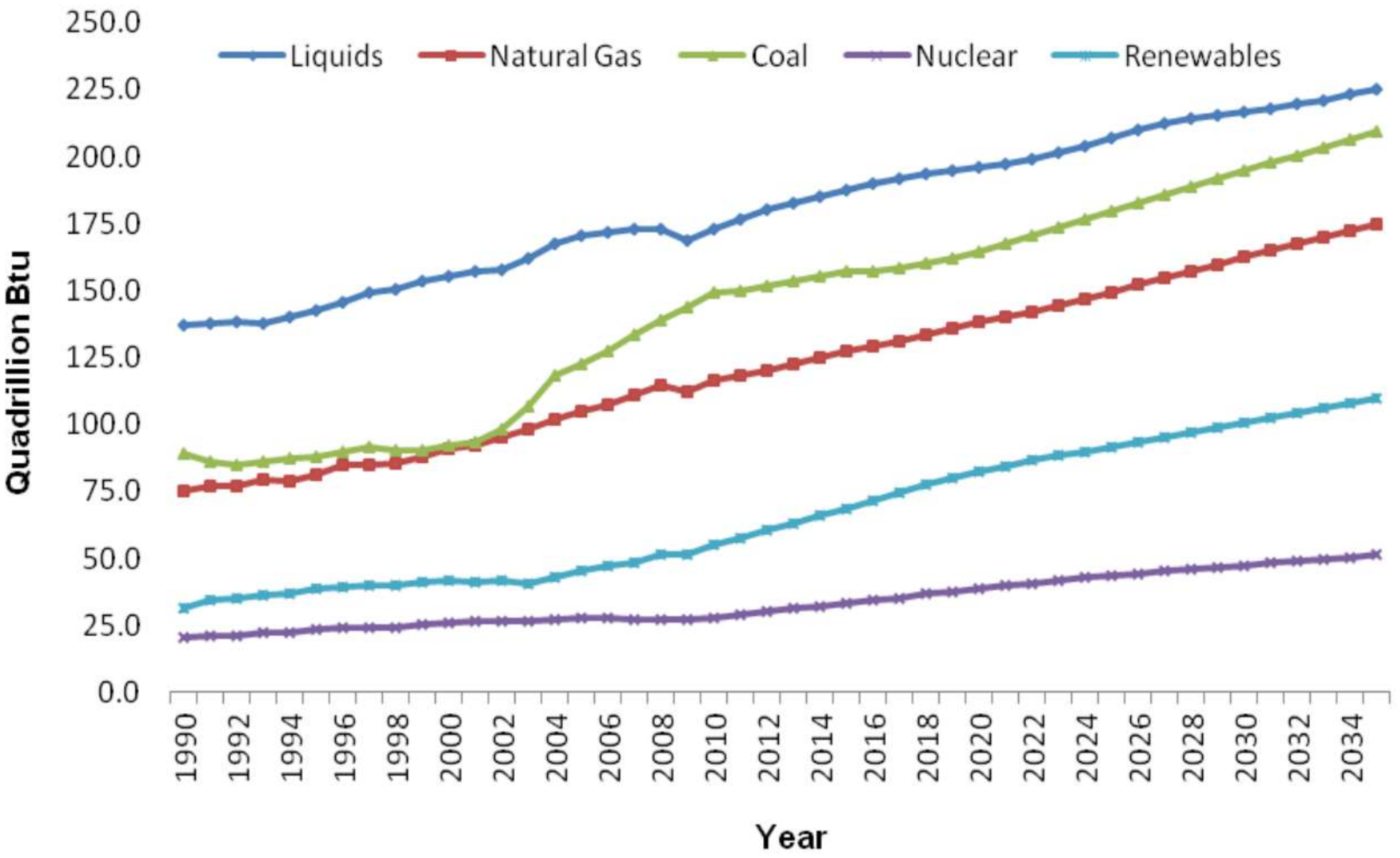


Figure 1: World energy consumption (Adapted from U.S. Energy Information Administration, 2011

Objective

- To explore the synthesis of a novel polymer, poly (glycidyl methacrylate) incorporated with the organic compound tetranitrofluorenone (PGMA-TENF).
- Analyze the selectivity targeting the nitrogen species present in bitumen derived light gas oil extracted from the Athabasca Oil Sands.
- Analysing and modelling the adsorptive denitrogenation of the light gas oil using a fixed bed column.

Knowledge Gaps:

- Synthesis and optimization of functionalized polymer such as poly(glycidyl methacrylate) (PGMA) incorporated with organic compound tetranitrofluorenone for selective removal of nitrogen bearing species from bitumen derived light gas oil, to the best of our knowledge, has never been investigated.
- Fixed bed adsorption column studies for functionalized polymers and Breakthrough Curve simulation by Thomas model and Yoon-Nelson Model has not been exploited.

Characterization of Oil Sand, Bitumen and Gas Oil

Table 1: Characteristics of conventional crude oil, bitumen, and Light gas oil

	Viscosity [mPa.s]	Density [g/cm^3]	API- Gravity
Conventional Crude Oil	10	-	25-37
Bitumen	>10^5	>1	<10
Light Gas oil	6.615-10.575	0.88-.90	20-25

Table 2: Characterization of various light gas oils derived from Athabasca bitumen (Owusu-Boakye, 2005)

	N (wppm)	BN (wppm)	S (wppm)	C (wt. %)	H (wt. %)	^{13}C NMR	Density (g/cm^3)
HLGO	1773	1211	7149	86.5	12.89	24	.97
VLGO	634	285	26780	85.4	11.92	23.9	.94
ALGO	290	153	15020	85.7	12.66	15.5	.89
BLGO	461	247	17420	85.5	12.6	17.1	

The feed streams shown in Table 2 represent hydrocrack light gas oil (HLGO), vacuum light gas oil (VLGO), atmospheric light gas oil (ALGO), and blended light gas oil (BLGO).

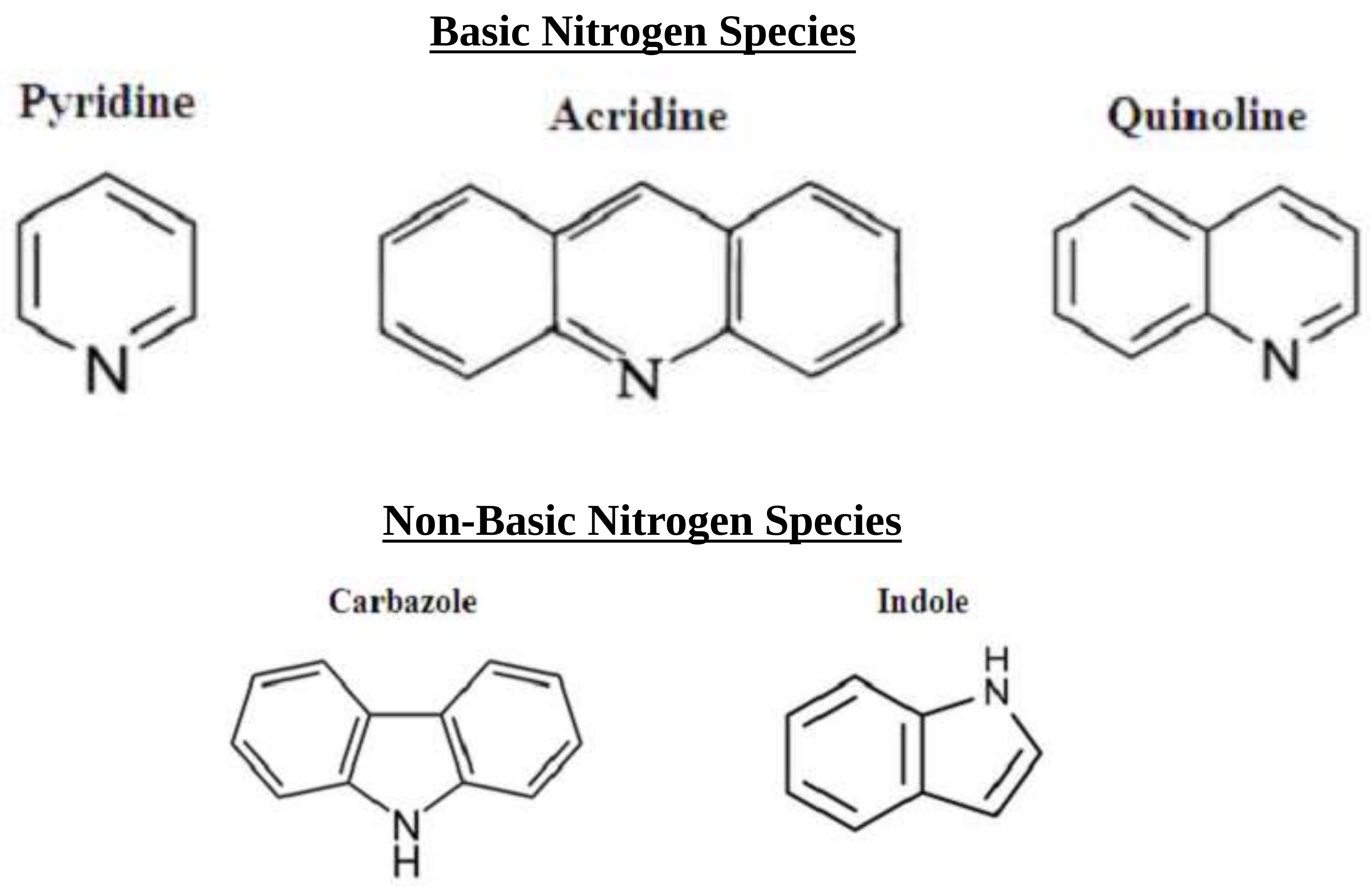


Figure 2: Typical basic and non-basic nitrogen compounds in gas oil (adapted from Wikipedia, 2015).

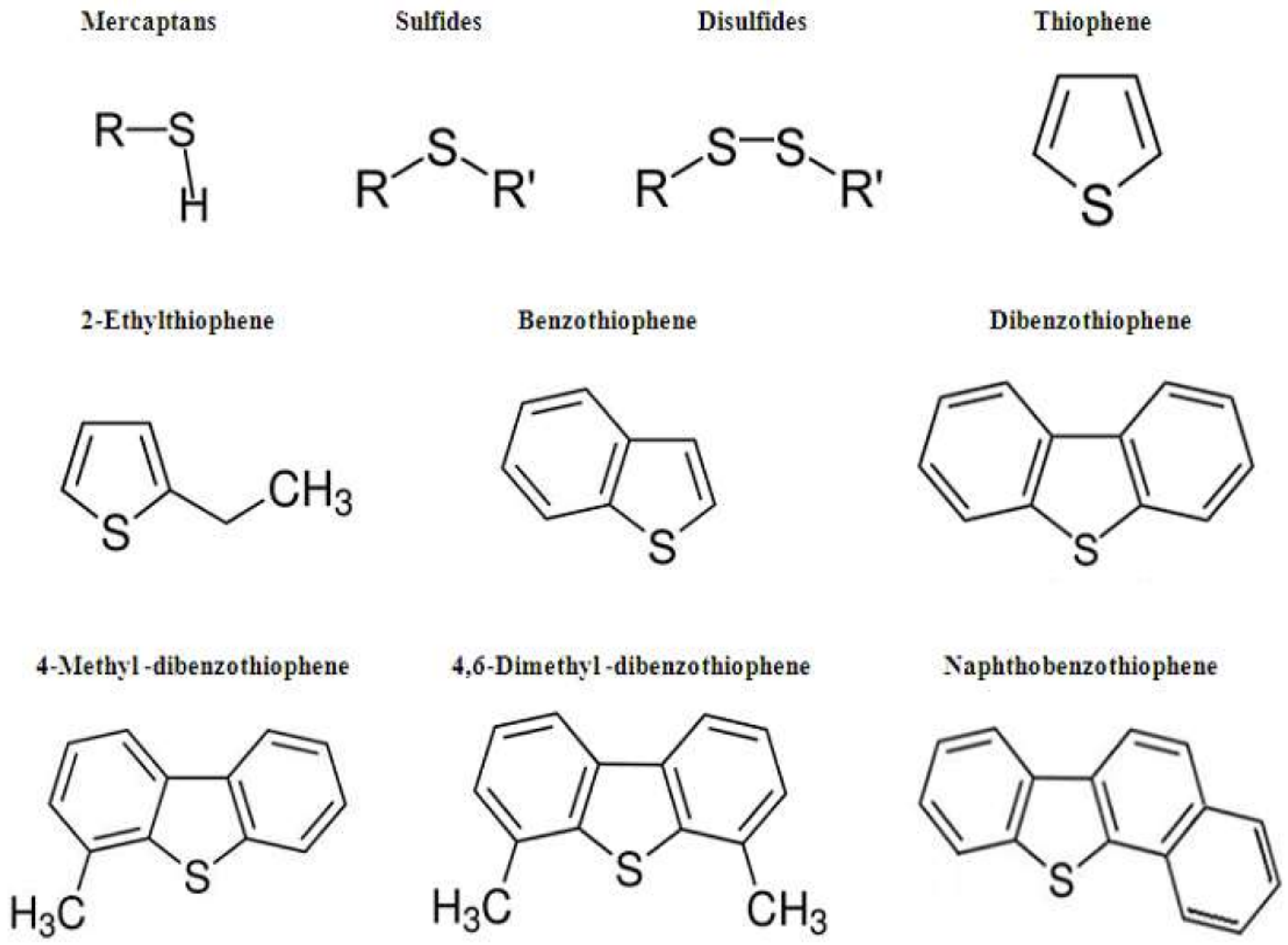


Figure 3: Typical Sulphur Compounds present in Petroleum Feedstock (Adapted from Topsøe et. al., 1996).

Functionalized Polymer for Pretreatment of Gas Oil

Poly(glycidyl methacrylate) Tetranitrofluorenone

(PGMA-TENF)

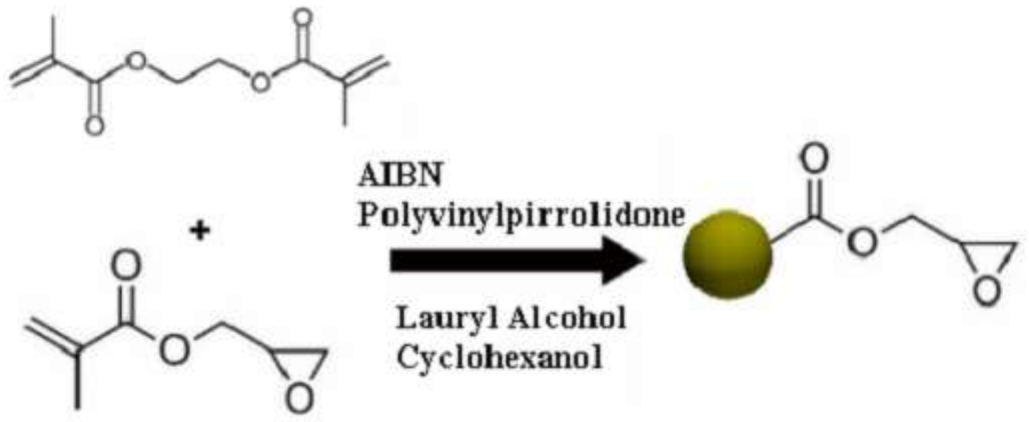


Figure 4: Synthesis of polymer poly(glycidyl methacrylate)

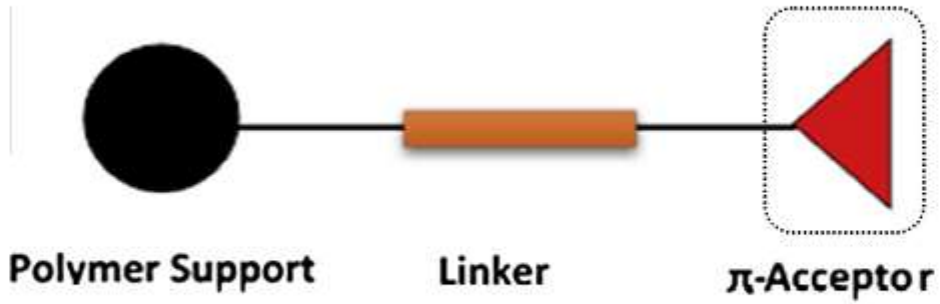


Figure 5: Components of functionalized polymers

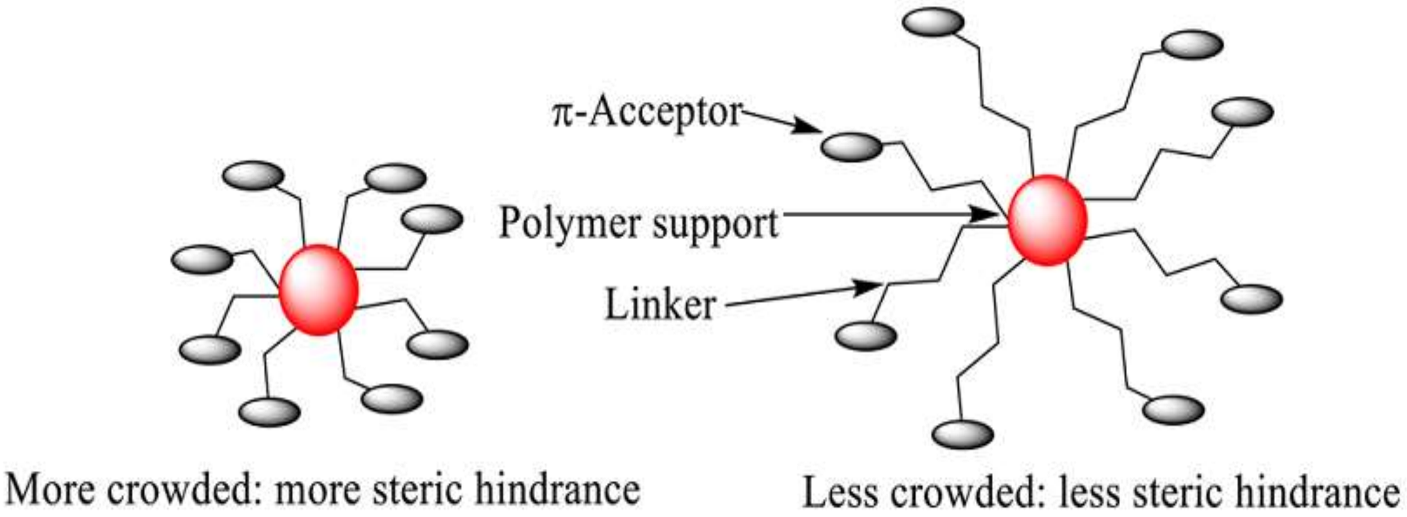
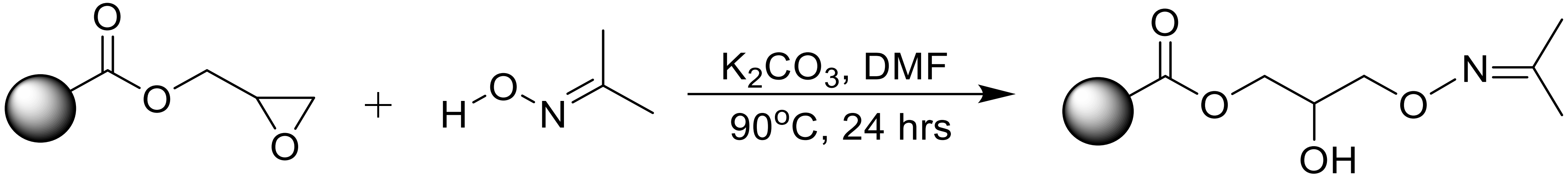


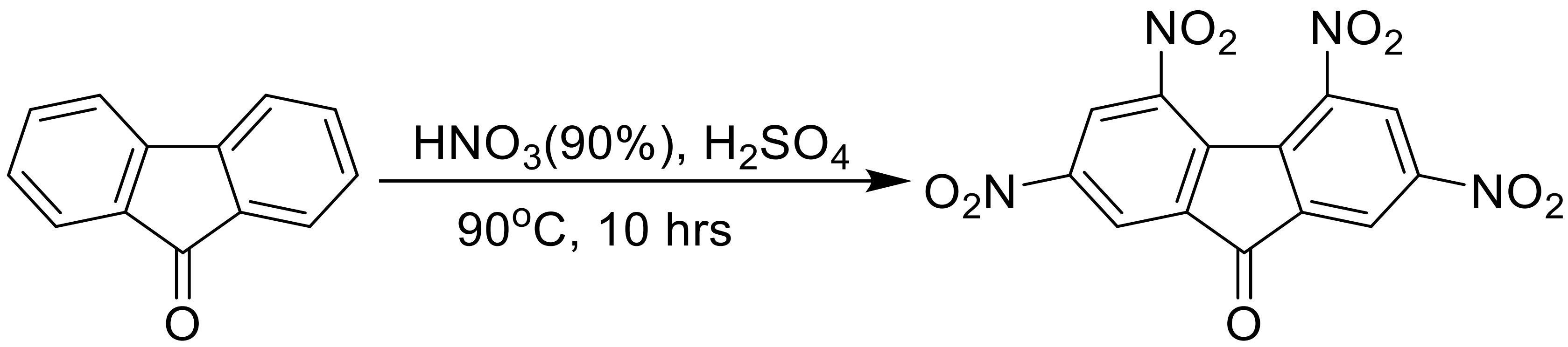
Figure 6: Visual comparison of particles with shorter linkers (left) to ones with longer linkers (right)

Step 2: Substitution of Epoxy Ring with Acetone Oxime



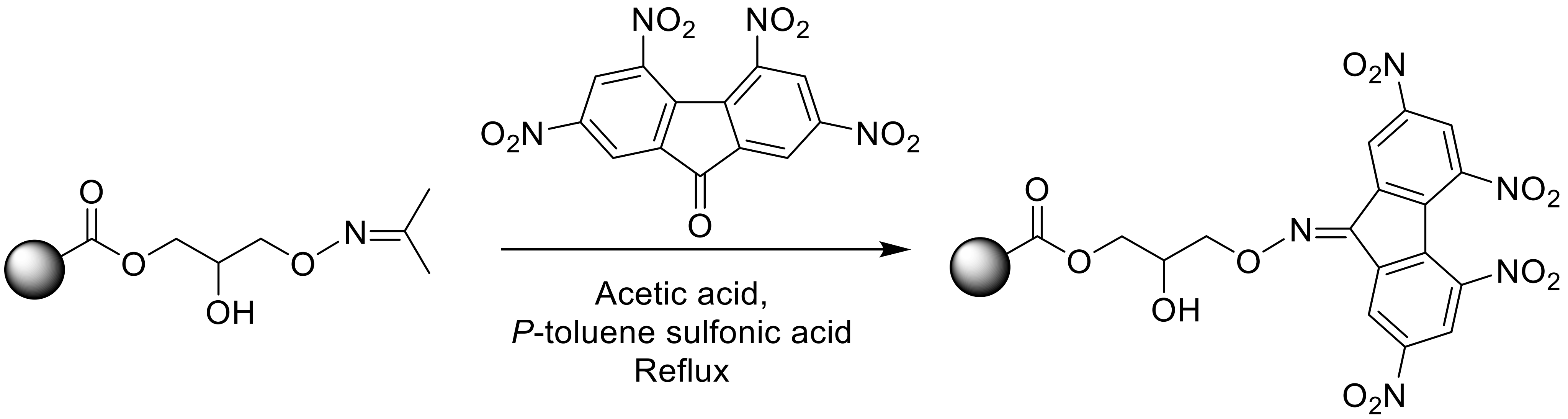
Scheme 2: Substitution of epoxy ring with acetone oxime.

Step 3: Synthesis of Tetranitrofluorenone (TENF)



Scheme 3: Synthesis of 2, 4, 5, 7- tetranitro-9-flourenone (TENF)

Step 4: Coupling of Tetranitrofluorenone (TENF) On Poly(glycidyl methacrylate)



Scheme 4: Immobilization of TENF on PGMA

FIXED BED STUDIES

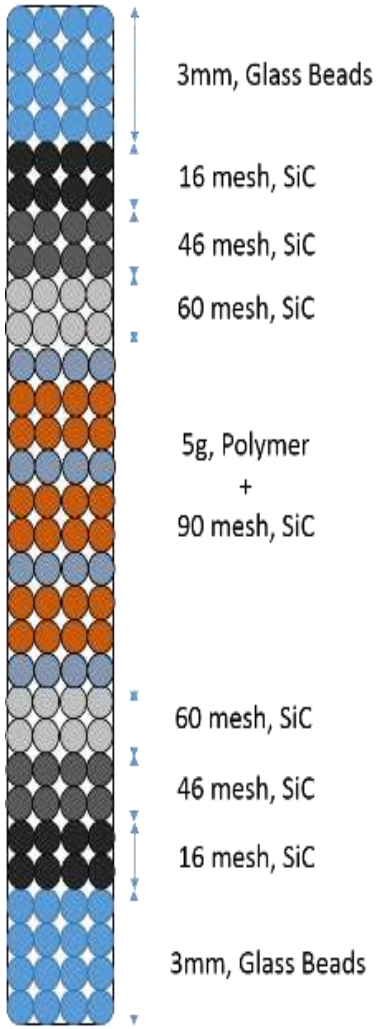


Figure 7: Fixed Bed Column Loading Specification

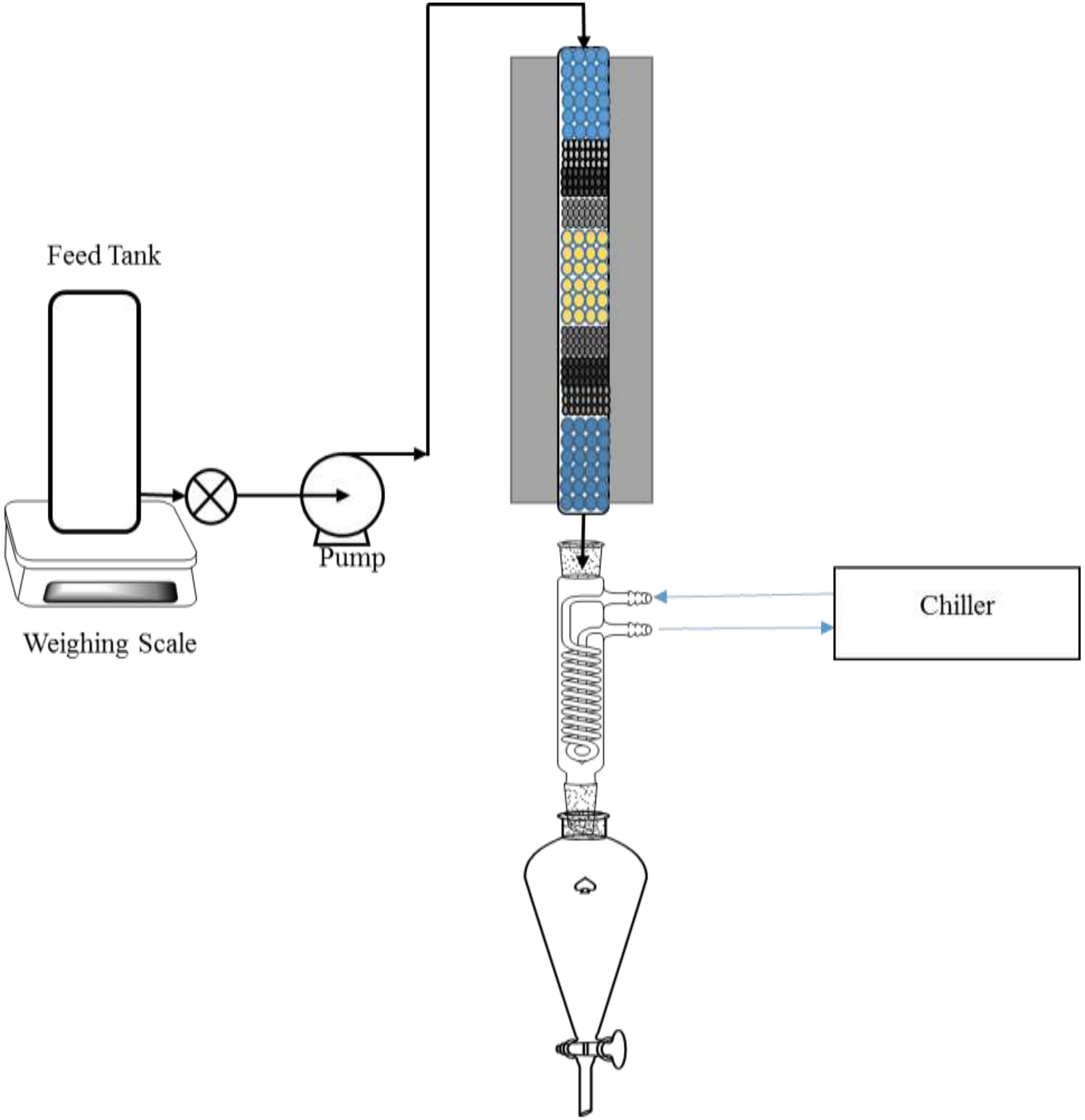


Figure 8: Experimental setup for the adsorption studies.

Fixed Bed Column Specifications

- The fixed bed column was made of Stainless steel with 46 cm long and 0.9 cm internal diameter.
- In order to have a uniform flow of the feed through the bed i.e. to avoid channelling of the feed, the column is packed with glass beads and SiC particles of different sizes.

	Height in the column (cm)	Volume in the Column (cm^3)
3mm Glass Beads	3	1.9
16 mesh SiC	1	0.64
46 mesh SiC	1	0.64
60 mesh SiC	1	0.6
90 mesh SiC	4	2.54
Polymer	28	18

Experimental Procedure

- Light gas oil is fed to the column from the top at a constant flow rate using a peristaltic pump.
- The concentration of the Nitrogen and Sulfur containing compounds in the samples is found using Antek NS combustion analyser.
- Conversion (N) %= (Conc. Of N in feed – Conc. Of N in sample)/ (Conc. Of N in feed) *100
- After the saturation is achieved the breakthrough curve us obtained by plotting the C_t/Co vs. t, where C_t is the concentration of Nitrogen compounds in sample collected at time t and C_o is the Nitrogen compound concentration in the feed.
- The polymer is regenerated by passing Toluene at the same flow rate at which LGO was passed through the bed.
- To remove the residual amount of toluene from the bed, the bed temperature is raised to a temperature equal to the boiling point of toluene i.e. 111^0C and inert gas Argon was passed through the bed, to purge the bed. Purge of argon is done for 5 hours and the heating of bed is done overnight.
- Re-adsorption was performed to evaluate the effect of regeneration.

Results and Calculations

- The adsorption was performed for 3 different flowrates: 0.02 ml/min, 0.26 ml/min and 0.5m ml/min and at two temperatures: Room temperature and 45^{0}C to study the effect of flowrate and temperature on total uptake by the polymer and effect on the breakthrough curve.
- **AD 1: Flow rate= 0.02 ml/min, Temperature: Room Temperature**
- **AD 2: Flow rate= 0.5 ml/min, Temperature: Room Temperature**
- **AD 3: Flow rate= 0.26 ml/min, Temperature: Room Temperature**
- **AD 4: Flow rate= 0.26 ml/min, Temperature: 45^{0}C**

Thomas Model

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{k_{TH} q_o m}{Q} - k_{TH} C_o\, t$$

Where, Ct = effluent concentration at time t (mg/L)

Co= influent Concentration (of the feed) (mg/ L)

k_{TH} = Thomas rate constant (L/ (ml.min))

q_o = equilibrium uptake per gram of the adsorbent (ml/g)

m = amount of adsorbent in the column

Q= Flow rate (L/min)

Therefore: slope of the modelling curve = - kth. Co

Intercept = (kth. q_o. m)/ Q

From which kth and q_o can be found.

Yoon-Nelson Model:

$$\ln\left(\frac{C_o}{C_o - C_t}\right) = k_{YN}t - k_{YN}\tau$$

Where C_t = effluent concentration at time t (ml/L)

C_o= influent Concentration (of the feed) (ml/ L)

k_{YN}= Yoon Nelson Rate constant

τ=Time required for 50% adsorbate breakthrough

t= time

AD 1: Flow rate= 0.02 ml/min, Temperature: Room Temperature

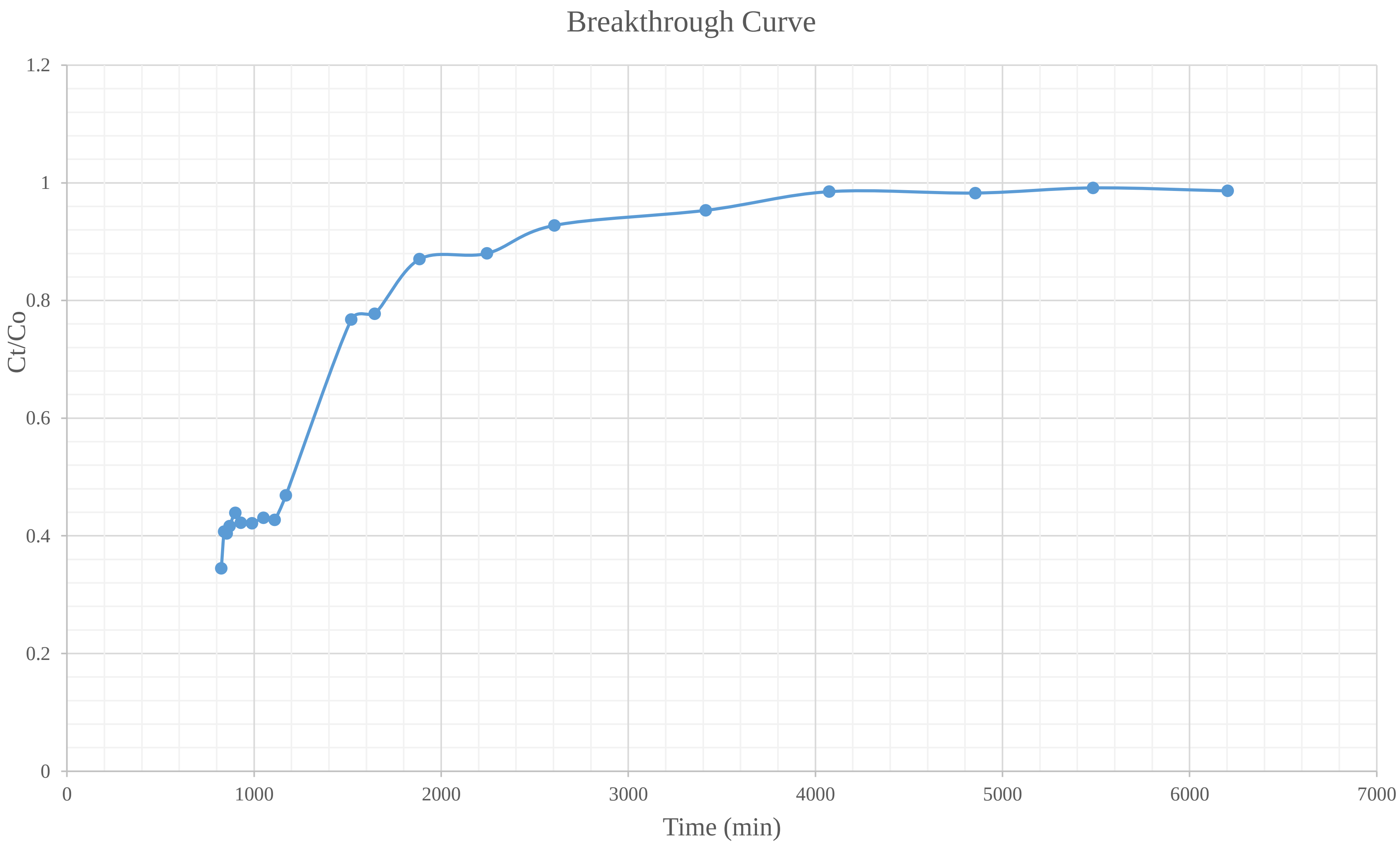


Figure 9: Breakthrough curve for adsorption samples of AD1: Flow rate 0.02 ml/min, Temperature: Room Temp.

Figure 10: Thomas Modelling Curve for adsorption samples of AD1: Flow rate 0.02 ml/min, Temperature: Room Temp.

$$\ln\left(\frac{C_o}{C_t} - 1\right) = 1.6002 - 0.0015\,t$$

Q= 0.00002 l/min

m=5g

C_o= 1786.161 mg/L

Therefore,

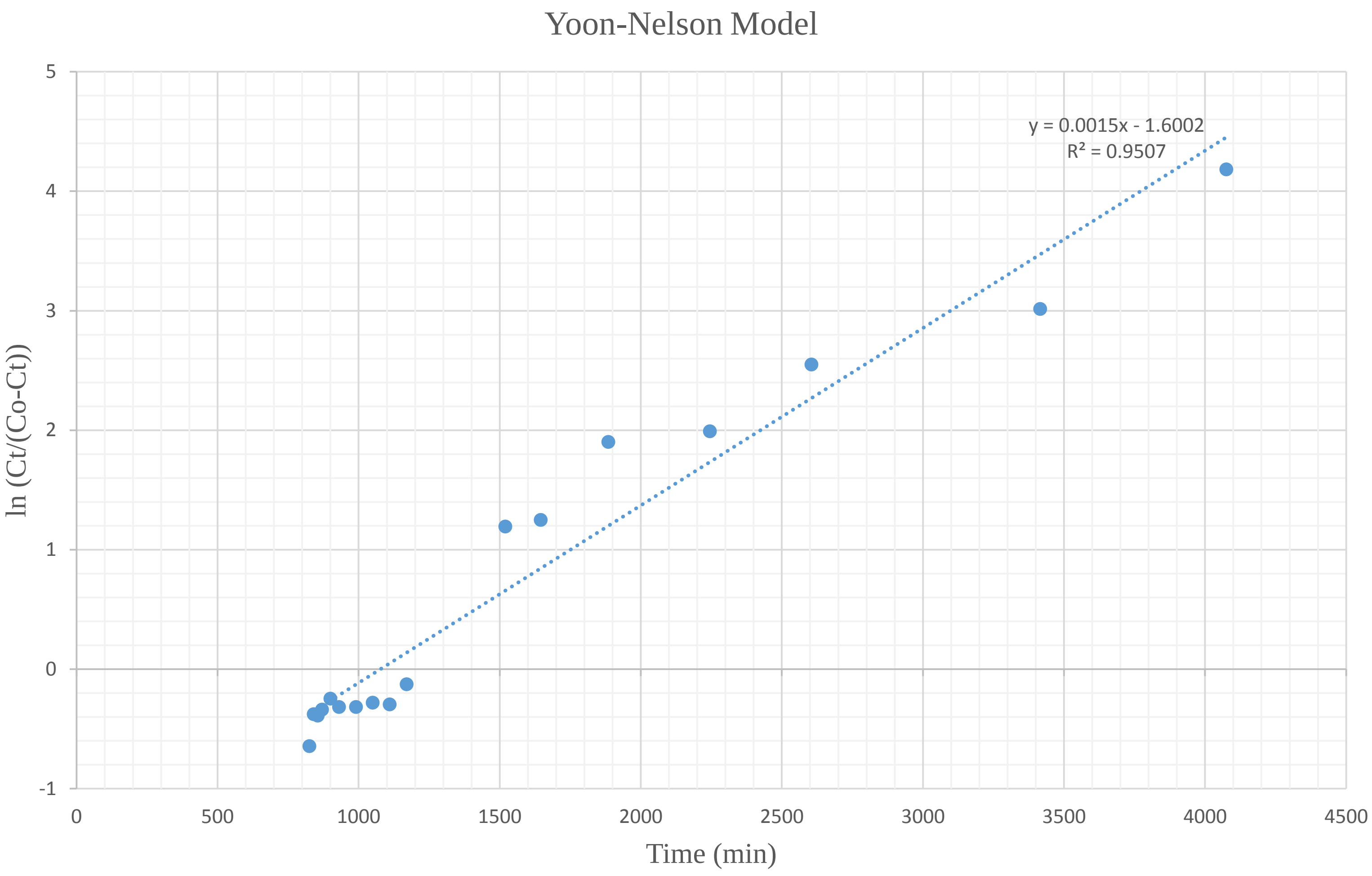
$k_{TH}C_o$ = 0.0015 min^{-1}

$(k_{TH}q_o m)/Q$ = 1.6002

$k_{TH}q_o$ = 1.6002*Q/m = 6.4008E-6

k_{TH}= 8.3979E-07 L/ (mg. min)

q_o= 7.6129 mg/g



$$\ln\left(\frac{C_o}{C_o - C_t}\right) = 0.0015t - 1.6002$$

$k_{YN} = 0.0015\ min^{-1}$

$k_{YN} . \tau = 1.6002$

$\tau = 1066.8\ min$

Figure 11: Yoon Nelson Model for adsorption samples of AD1: Flow rate 0.02 ml/min, Temperature: Room Temp.

AD 2: Flow rate= 0.5 ml/min, Temperature: Room Temperature
with Desorption and Re-Adsorption

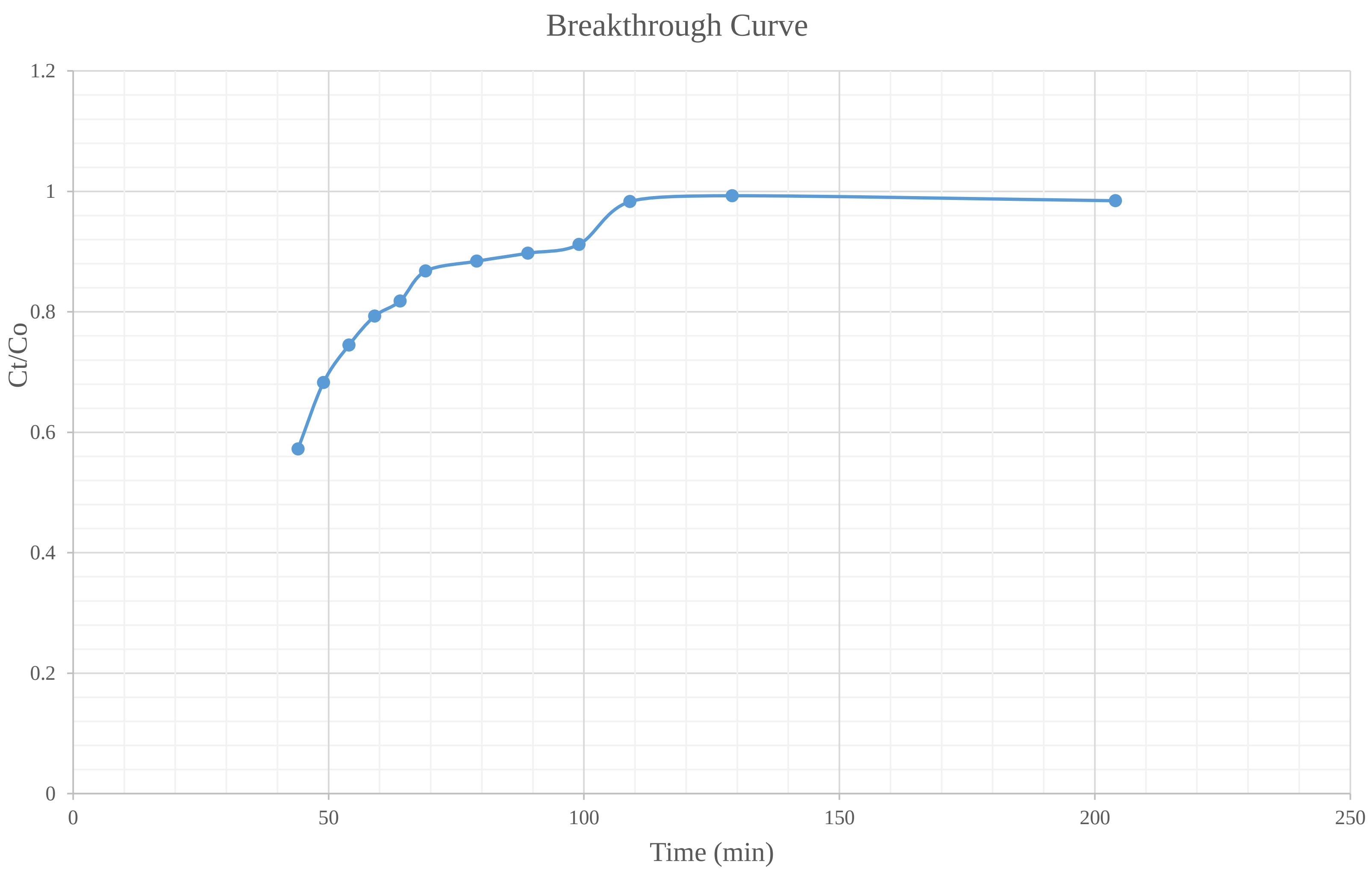


Figure 12: Breakthrough curve for adsorption samples of AD2: Flow rate 0.5 ml/min, Temperature: Room Temp.

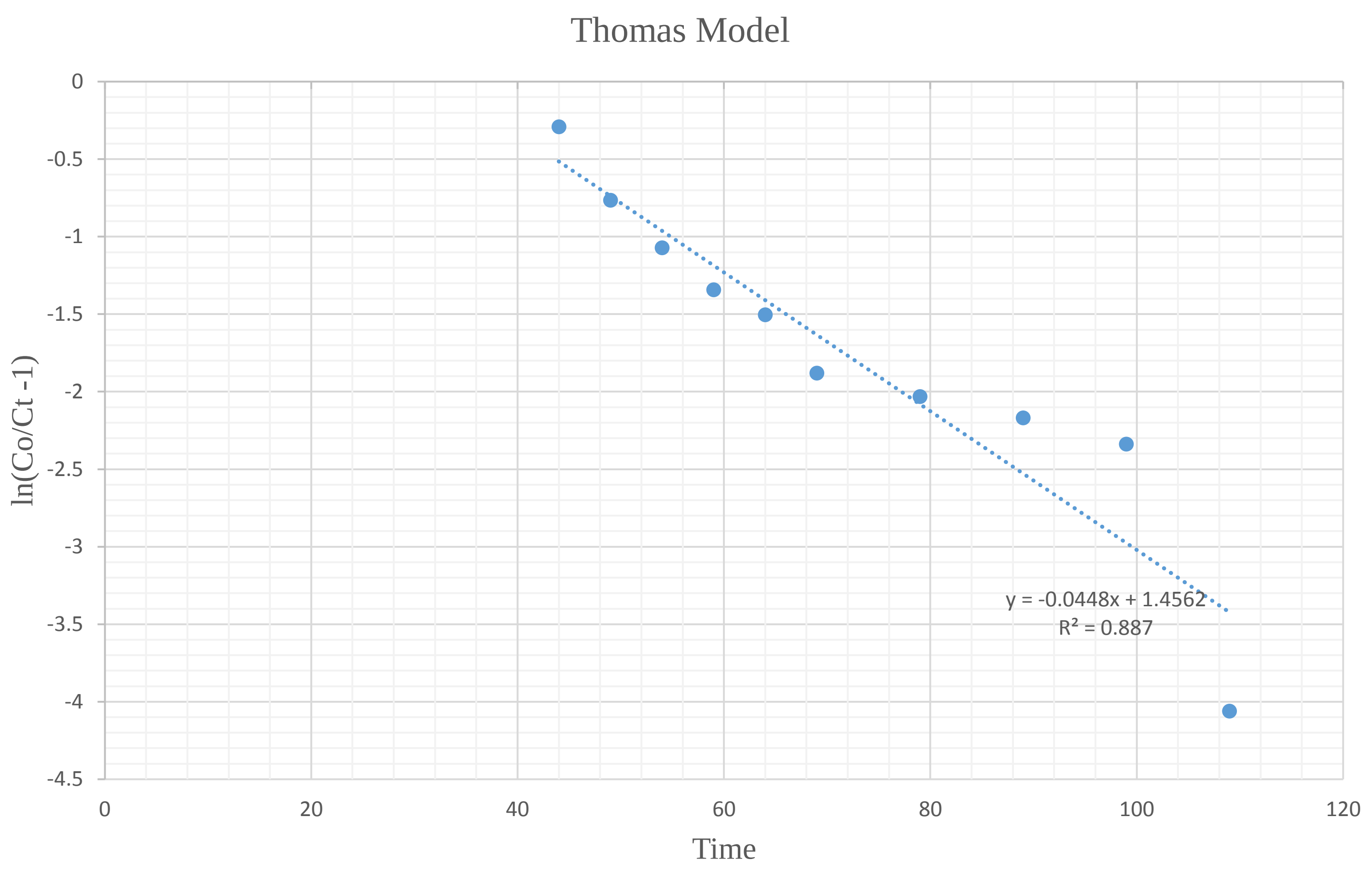


Figure 13: Thomas Modelling Curve for adsorption samples of AD2: Flow rate 0.5 ml/min, Temperature: Room Temp.

$$\ln\left(\frac{C_o}{C_t} - 1\right) = 1.4562 - 0.0448\,t$$

Q= 0.0005 l/min

m=5g

C_o= 1818.252 mg/L

Therefore,

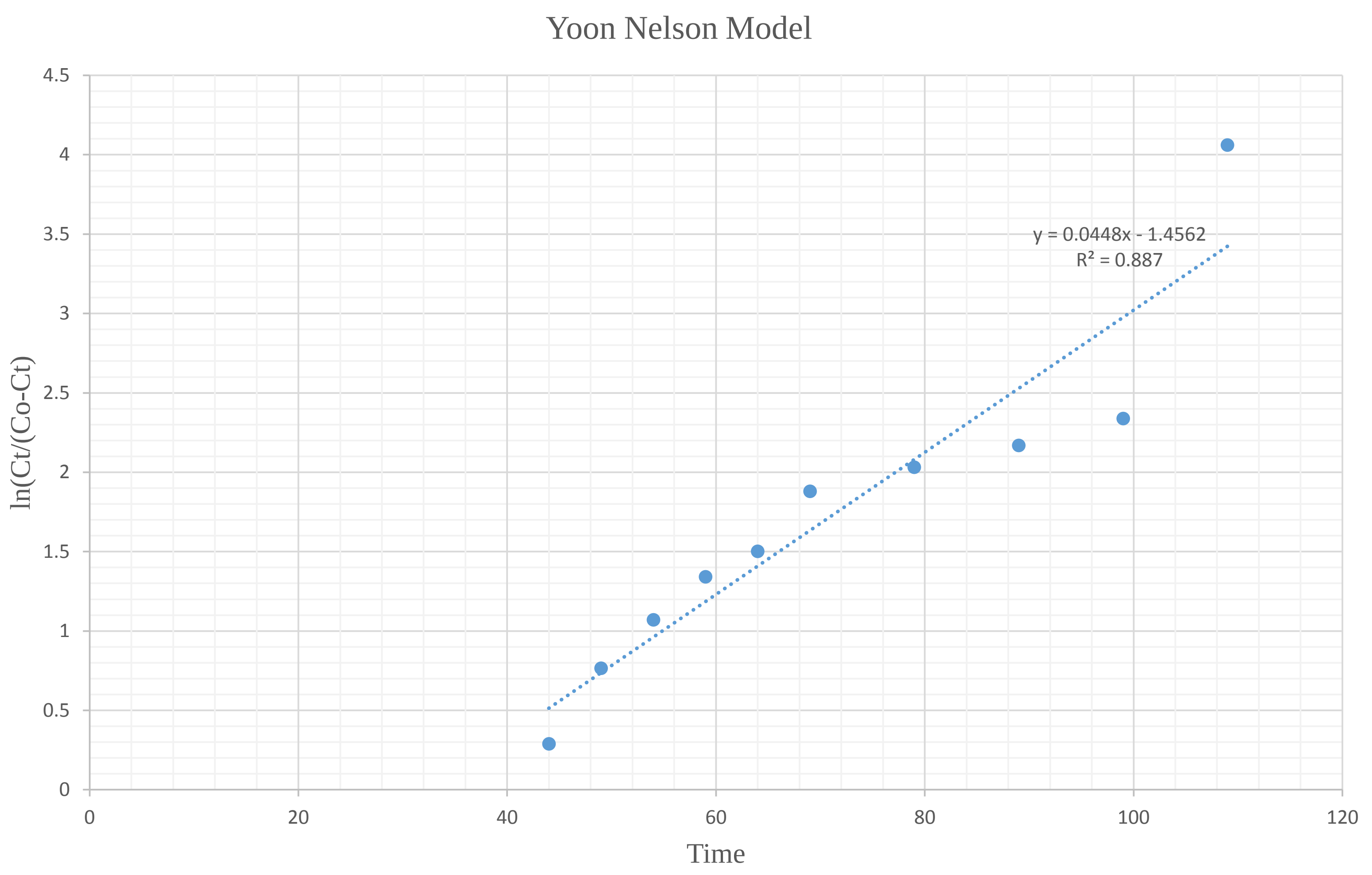
$k_{TH}C_o$ = 0.0448 min^{-1}

$(k_{TH}q_o m)/Q$ = 1.4562

$k_{TH}q_o$ = 1.4562*Q/m = 0.00014562 L/(min. g)

k_{TH}= 2.4639E-05 L/ (mg. min)

q_o= 5.9101 mg/g



$$\ln\left(\frac{C_o}{C_o - C_t}\right) = 0.0448\,t - 1.4562$$

$k_{YN} = 0.0448\ min^{-1}$

$k_{YN}\,.\,\tau = 1.4562$

$\tau = 32.50446\ min$

Figure 14: Yoon Nelson Model for adsorption samples of AD2: Flow rate 0.5 ml/min, Temperature: Room Temp.

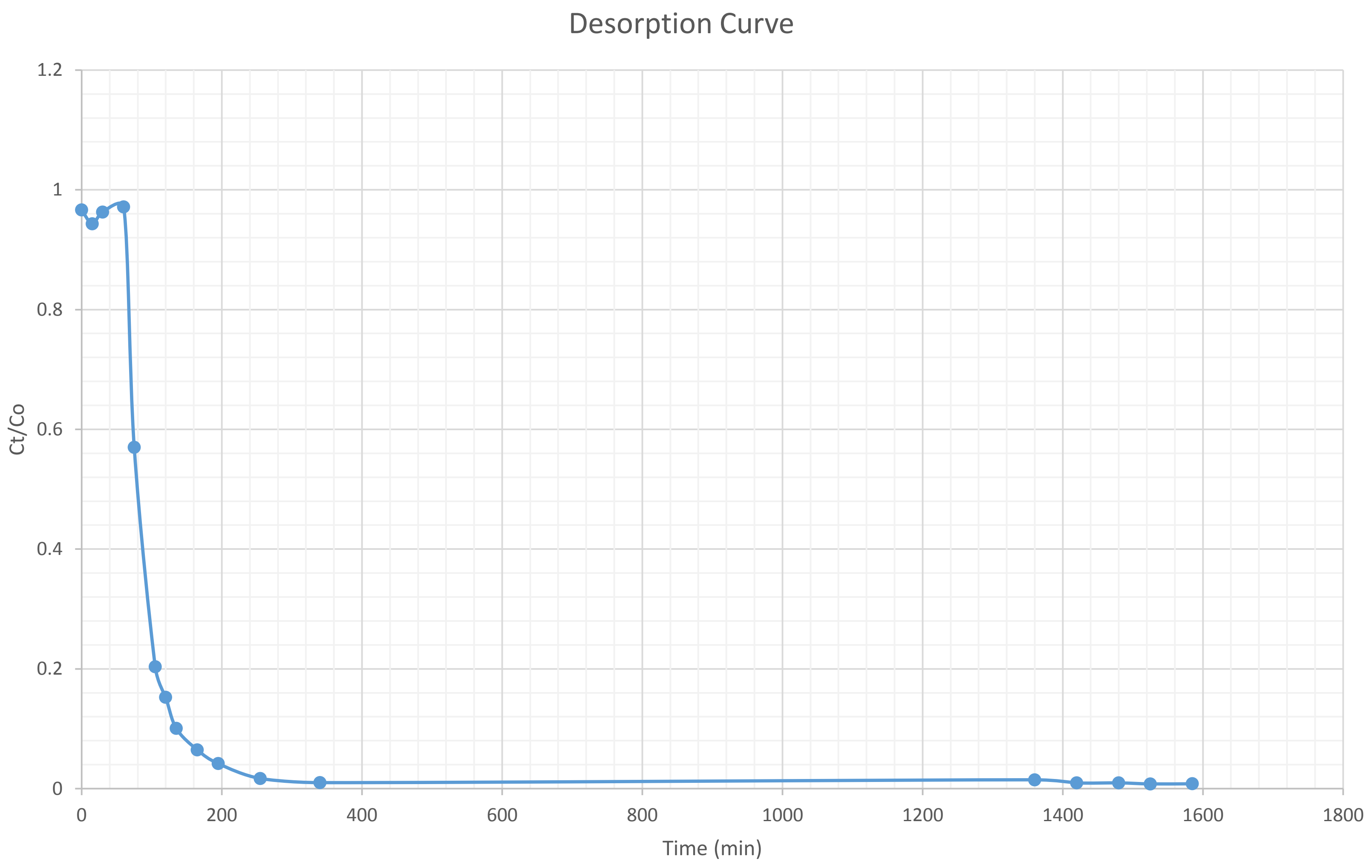


Figure 15: Desorption curve for adsorption samples of AD2: Flow rate 0.5 ml/min, Temperature: Room Temp.

Re-adsorption

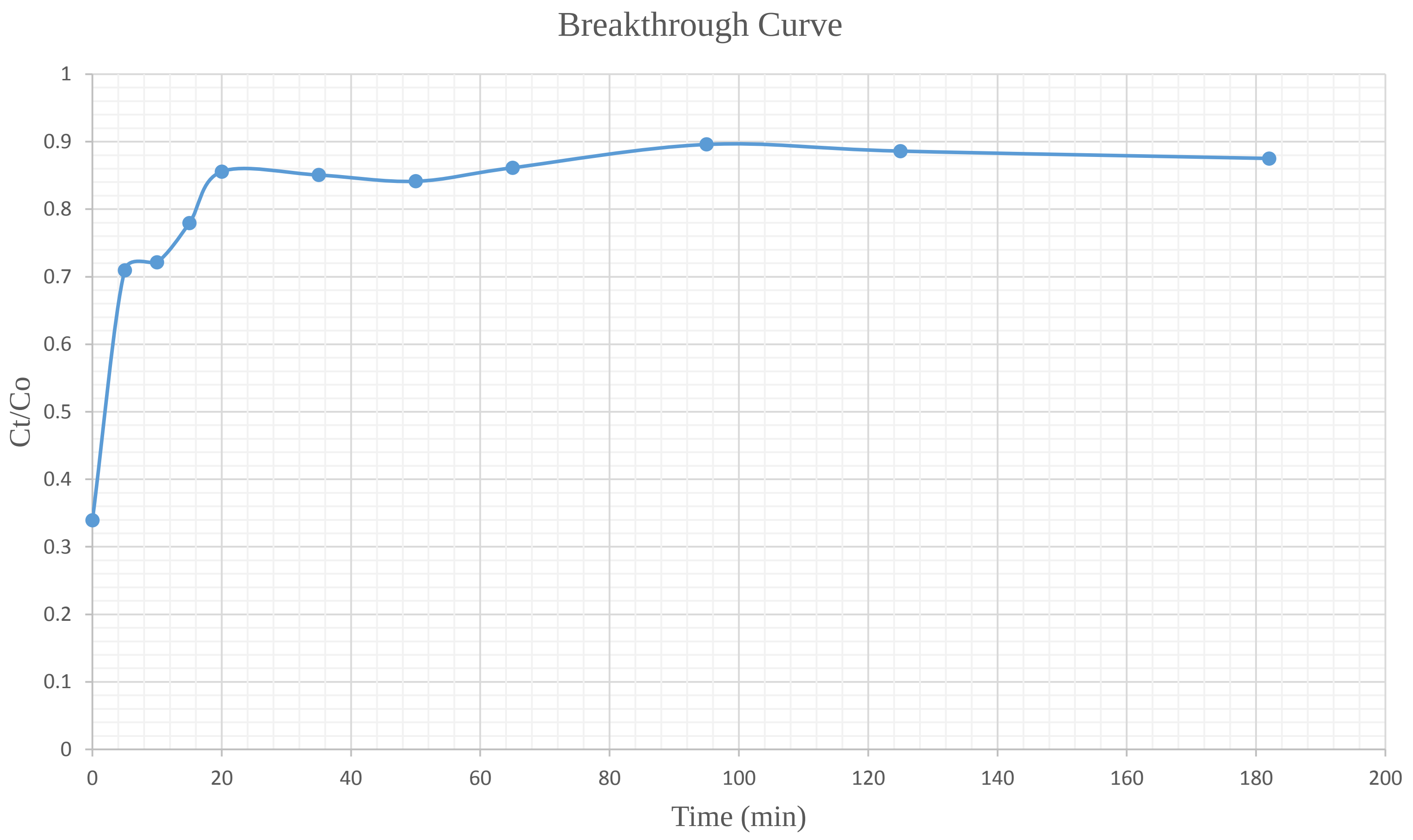


Figure 16: Breakthrough curve for re-adsorption samples of RAD2: Flow rate 0.5 ml/min, Temperature: Room Temp.

AD 3: Flow rate= 0.26 ml/min, Temperature: Room Temperature with Desorption and Re-Adsorption

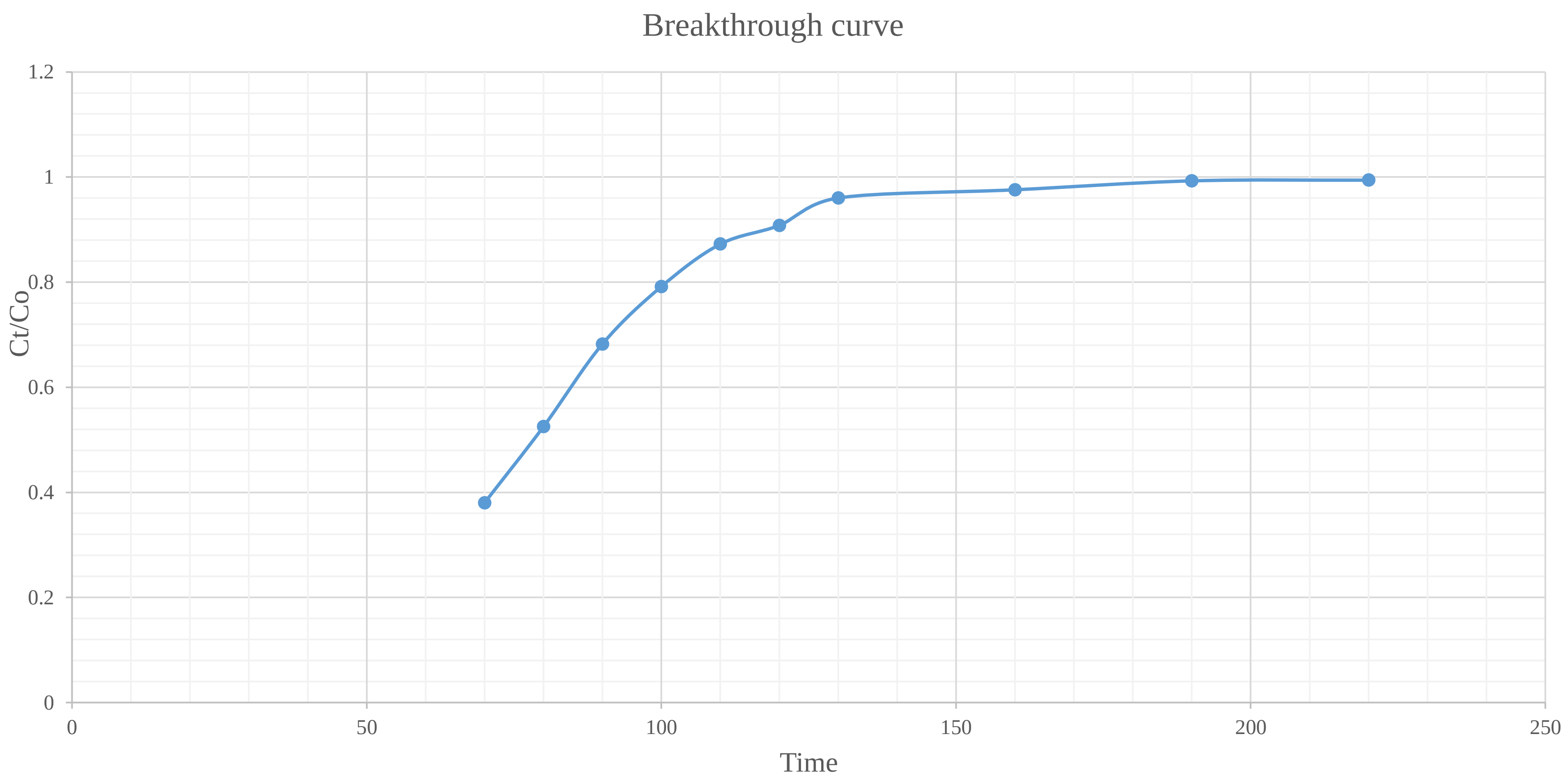


Figure 17: Breakthrough curve for adsorption samples of AD3: Flow rate 0.26 ml/min, Temperature: Room Temp.

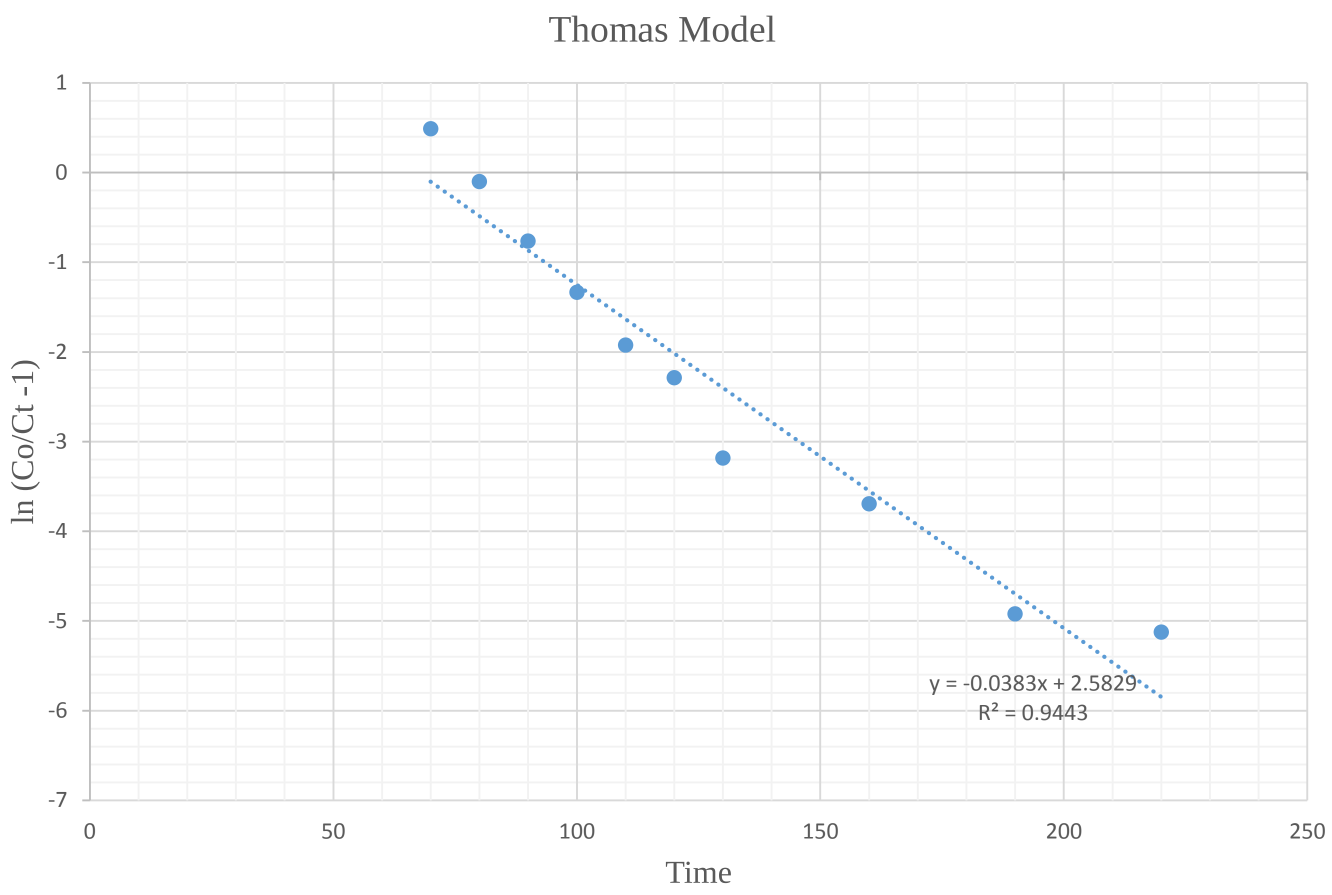


Figure 18: Thomas Modelling Curve for adsorption samples of AD3: Flow rate 0.26 ml/min, Temperature: Room Temp.

$$\ln\left(\frac{C_o}{C_t} - 1\right) = 2.5829 - 0.0383\,t$$

Q= 0.00026 l/min

m=5g

C_o= 1682.864 mg/L

Therefore,

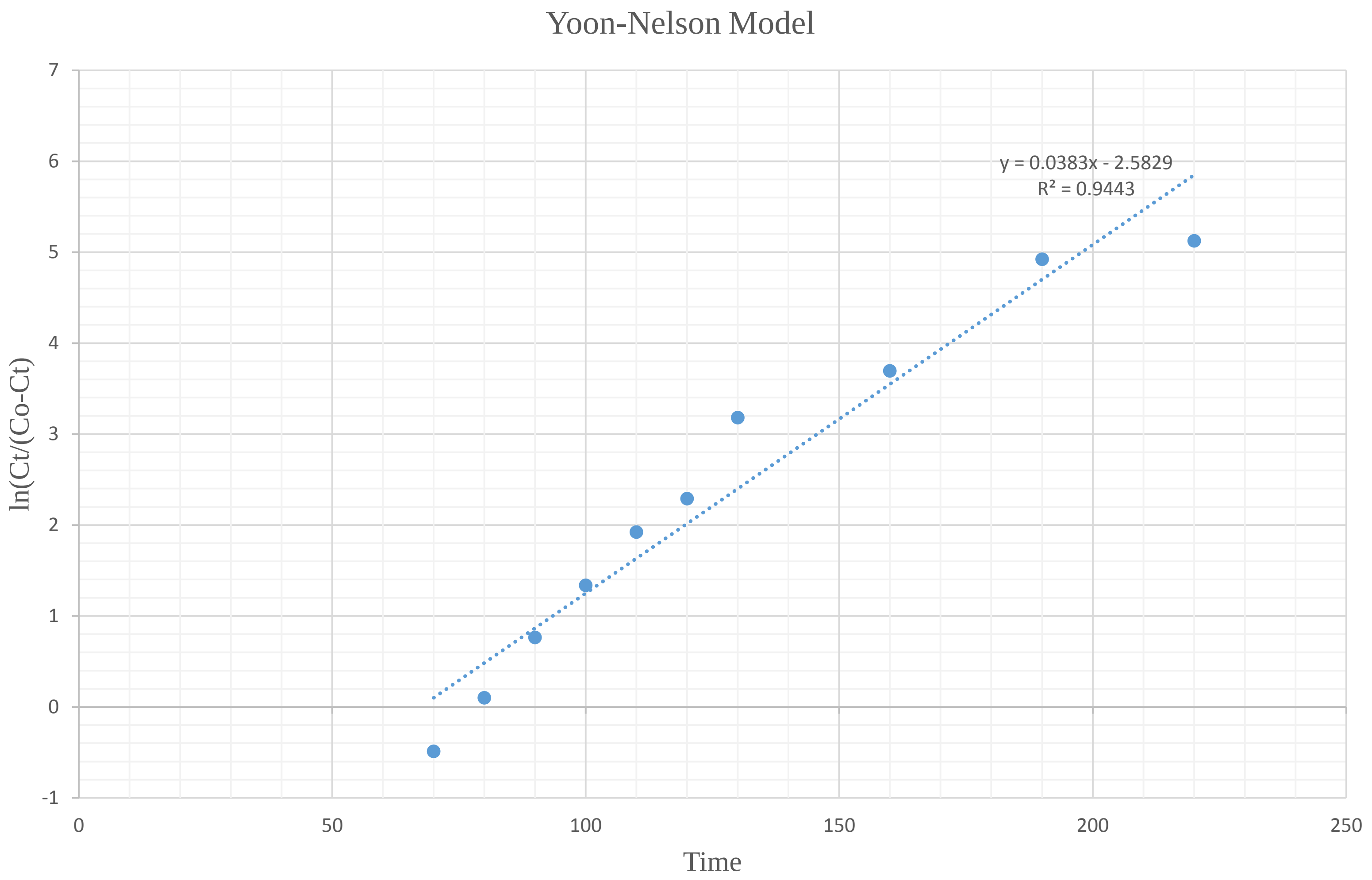
$k_{TH}C_o$ = 0.0383 min^{-1}

$(k_{TH}q_om)/Q$ = 2.5829

$k_{TH}q_o$ = 2.5829*Q/m = 0.000134311 L/(min. g)

k_{TH}= 2.27588E-05 L/ (mg. min)

q_o= 5.901482504 mg/g



$$\ln\left(\frac{C_o}{C_o - C_t}\right) = 0.0383t - 2.5829$$

$k_{YN} = 0.0383\ min^{-1}$

$k_{YN}\,.\,\tau = 2.5829$

$\tau = 67.44\ min$

Figure 19: Yoon Nelson Modelling Curve for adsorption samples of AD3: Flow rate 0.26 ml/min, Temperature: Room Temp.

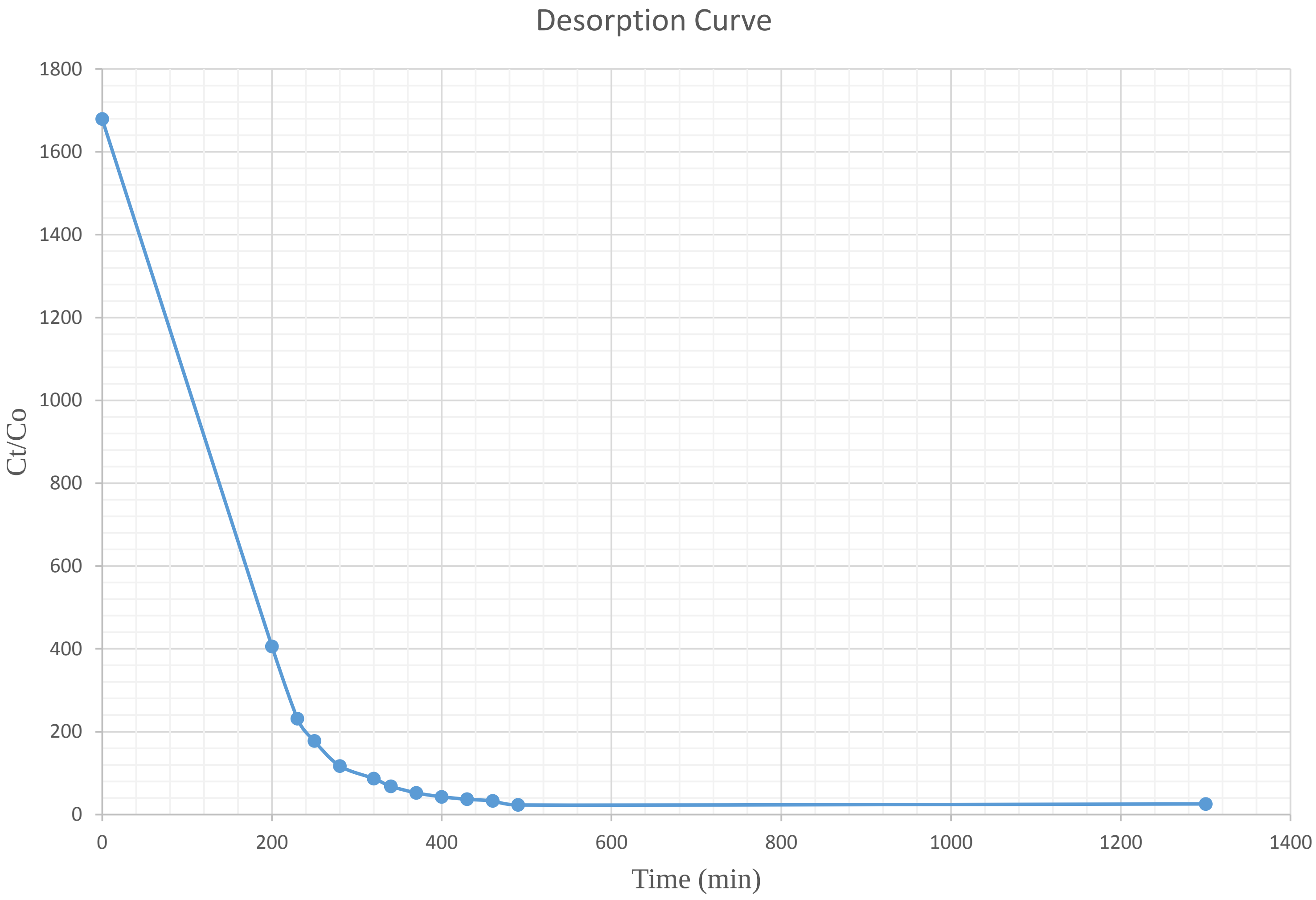


Figure 20: Desorption curve for adsorption samples of AD3: Flow rate 0.26 ml/min, Temperature: Room Temp.

Re-adsorption:

There was too much discrepancy in the results due to instrumental error. According to the results the bed was saturated within 15 min of flow of LGO.

AD 4: Flow rate= 0.26 ml/min, Temperature: $45^{0}C$

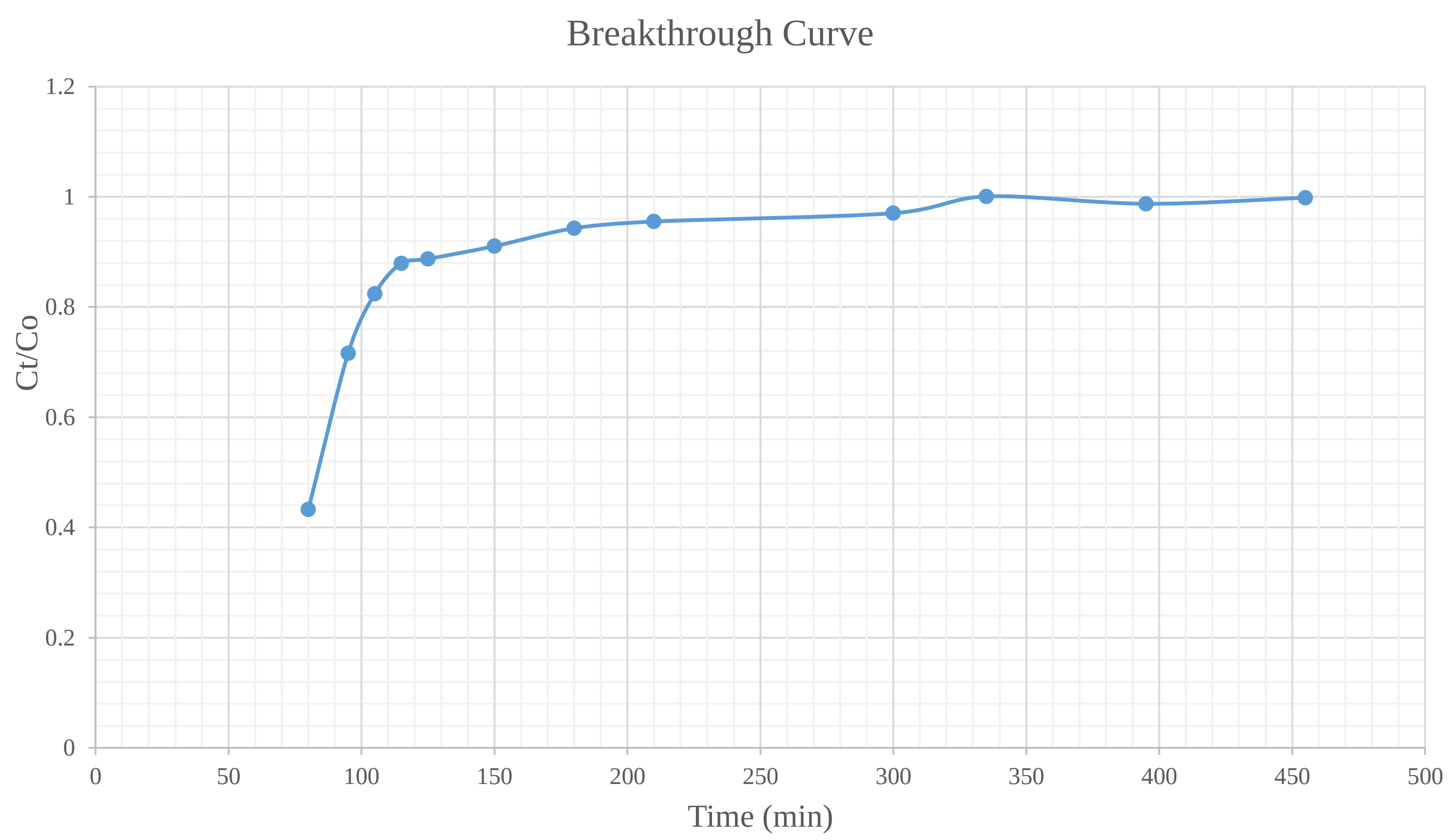


Figure 21: Breakthrough curve for adsorption samples of AD 4: Flow rate 0.26 ml/min, Temperature: 45 degree C

Conclusion

- An extensive laboratory investigation was conducted to evaluate the PGMA-ON-TENF fixed-bed column performance for nitrogen species removal from light gas oil samples obtained from synthetic crude.
- The effect of flow rate and temperature on the breakthrough curves was investigated.
- The column experimental data was analysed using Thomas and Nelson-Yoon adsorption models.
- The adsorbed amount of Nitrogen compounds decreased as temperature increased from 293 K to 318K (as expected as: adsorption is generally an exothermic process).
- The re-adsorption (on the regenerated polymer) was not a complete success which could be because the regeneration was done at room temperature.
- Also only toluene was used as the solvent for desorption thus other solvents can also investigated.