Adsorption Equilibrium and Kinetic Study for the Removal of Nitrate from Drinking Water Supplies By Chitosan Composite

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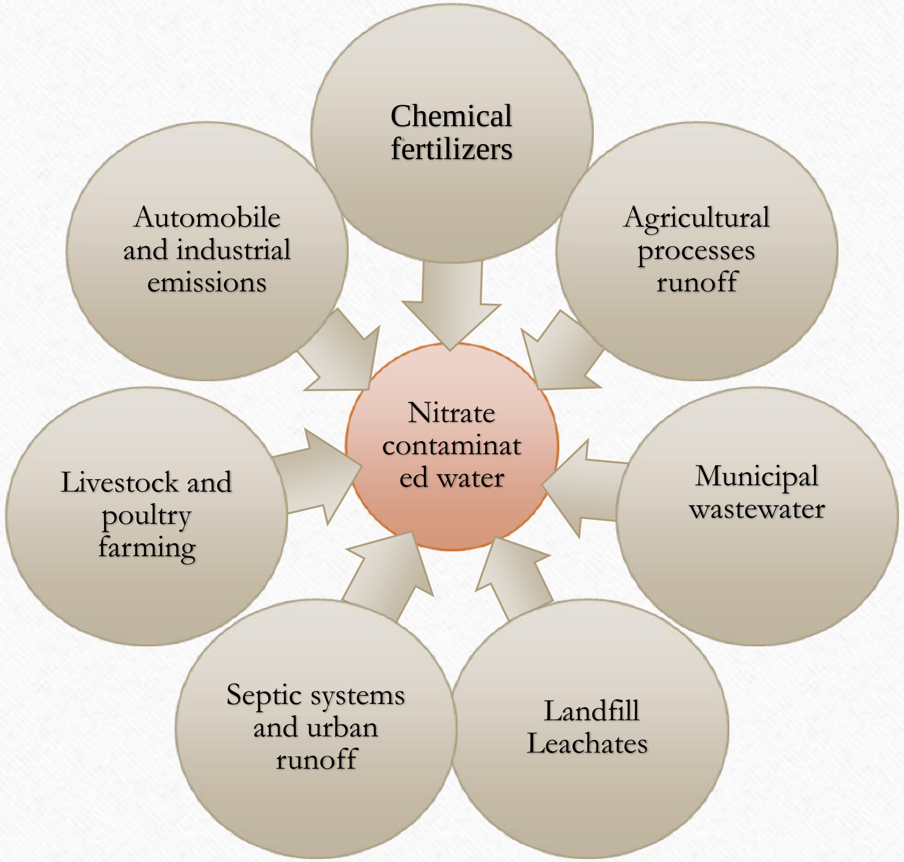
Outline

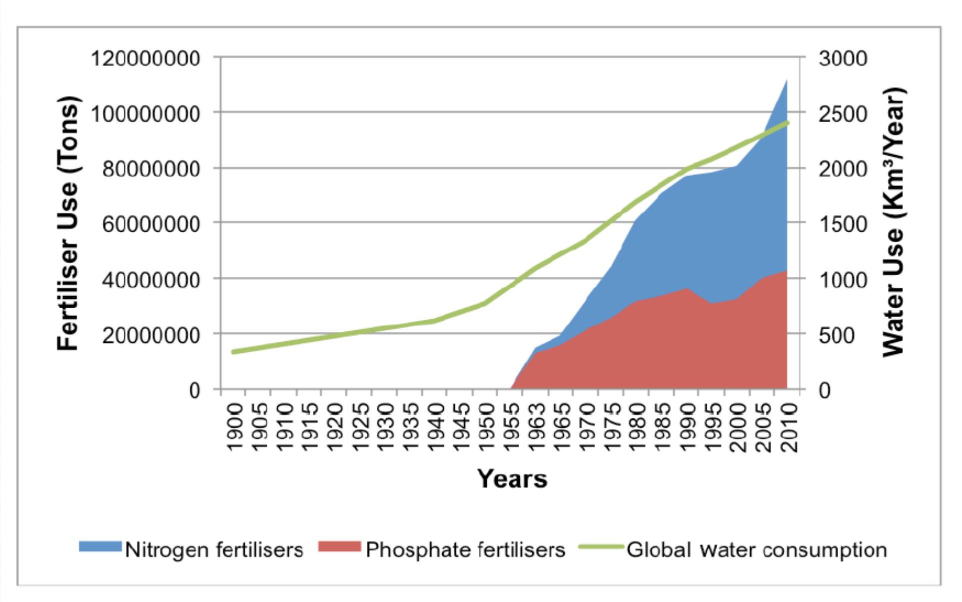
- Introduction
- Objectives
- Experimental
- Results and discussion
- Conclusions

Introduction

- Nitrate is a naturally occurring form of nitrogen and it is part of the nitrogen cycle
- Anthropologic activities cause the imbalances in the nitrogen cycle.



Worldwide fertilizer use and water consumption



Source: https://freshwaterwatch.thewaterhub.org/content/waterpollution

Risks associated with nitrate

1. **Health effects**

   High concentration of nitrate in drinking water leads to:

   - Methemoglobinemia
   - Spontaneous abortions
   - Cancer

2. **Eutrophication**

   - Affects biodiversity

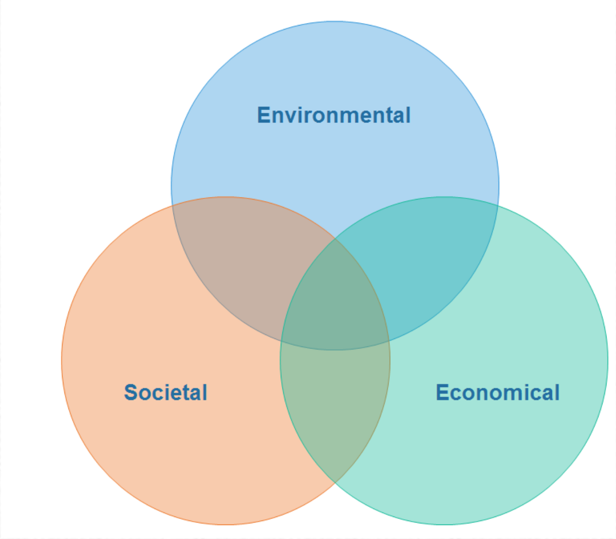
Regulatory limits for nitrate in drinking water

Country/Organization	Max. Acceptable Concentration(MAC)	References
WHO	50 mg/l as NO_3^-	(WHO, 2011)
The USEPA	10 mg NO_3^--N/l	(USEPA, 2009)
European Union	50 mg/l as NO_3^-	European Union (Drinking Water) Regulations, 2014)
Canada	45 mg/l as NO_3^-	(Health Canada, 2012)
Ontario Ministry of the Environment	10 mg NO_3^--N/l	(Ontario Ministry of the Environment, 2006)
Australia	50 mg/l as NO_3^-	(Health Australia, 2004)
Malaysia	50 mg/l as NO_3^-	(Health Malaysia, 2004)
India	45 mg/l as NO_3^-	(Bureau of Indian Stabdards, 2012)

Technologies for Nitrate Removal from Water

Treatment options

- Removal (Physico-chemical)
  - Ion exchange
  - Reverse osmosis
  - Electrodialysis
  - Adsorption



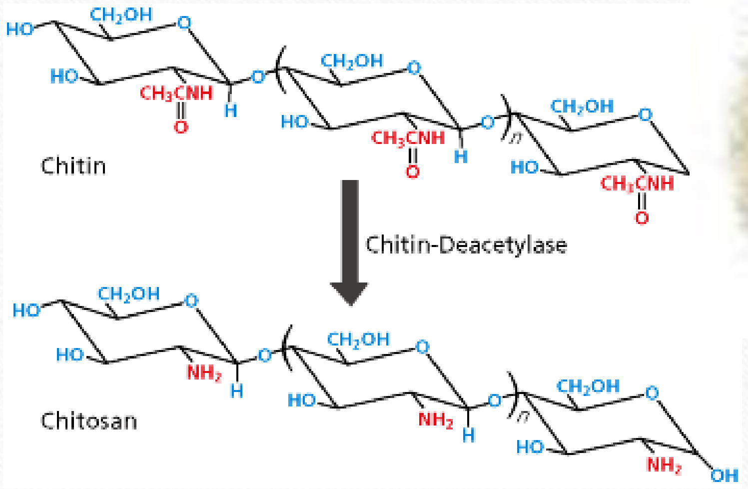
- Reduction
  - Catalytic
  - Chemical
  - Biological

Objectives

- ✓Preparation and characterization of of chitosan/alumina composite for the removal of nitrate from drinking water
- ✓Examine the effect of different parameters on the adsorption of nitrate
- ✓Determine kinetic and equilibrium parameters using batch adsorption experimental data
- ✓Investigate the re-usability of adsorbent by cyclic adsorption-regeneration study

Why Chitosan?

- Chitosan is the *N*-deacetylated derivative of chitin (the 2nd abundant natural polysaccharide next to cellulose)



Ref. (M. N. Ravi Kumar, 2000); (Kyzas & Bikiaris, 2015)

Features of chitosan

- Biocompatible
- Biodegradable
- Non-toxic
- Abundant and Low cost
- Renewable

Limitations

- Sensitive to pH and temperature
- Poor mechanical stability

Modifications

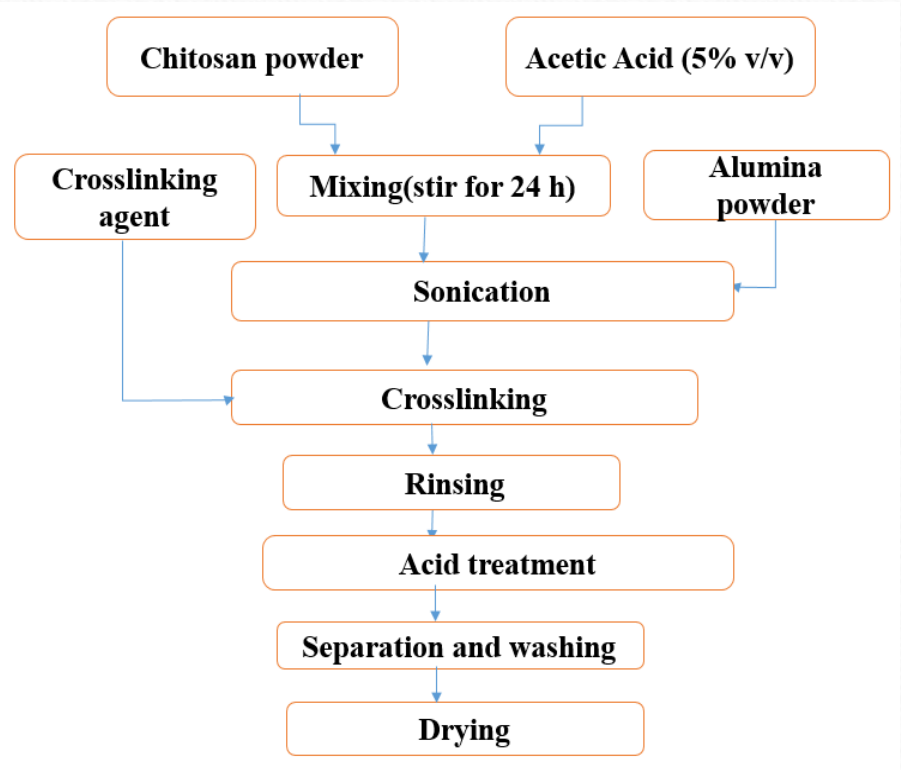
- Grafting, Crosslinking, Organic-inorganic hybrid composite formation

Experimental (Batch adsorption study)

- Approach
  - ✓ Adsorbent preparation and characterization
  - ✓ Adsorption (investigation of the effects of operating parameters)
  - ✓ Regeneration study
  - ✓ Adsorption equilibrium isotherm study
  - ✓ Kinetic study
  - ✓ Thermodynamic parameters

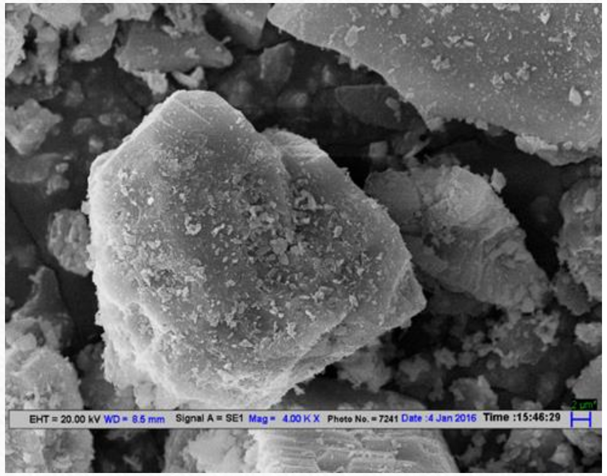
Preparation and Characterization

Preparation

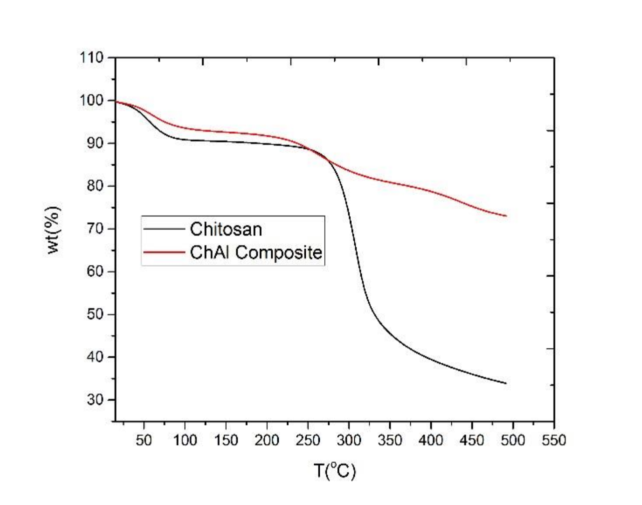


Characteristics of ChAl Composite

BET Surface area(m^2/g)	59.37
Pore Volume (m^3/g)	0.144
Pore Size(A)	97.23
Average Particle size(mm)	0.25
pH_{pzc}	7.6

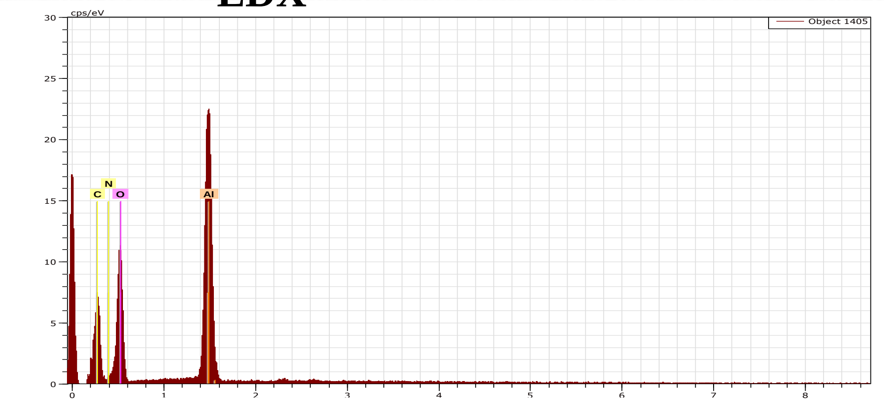


SEM image of ChAl composite



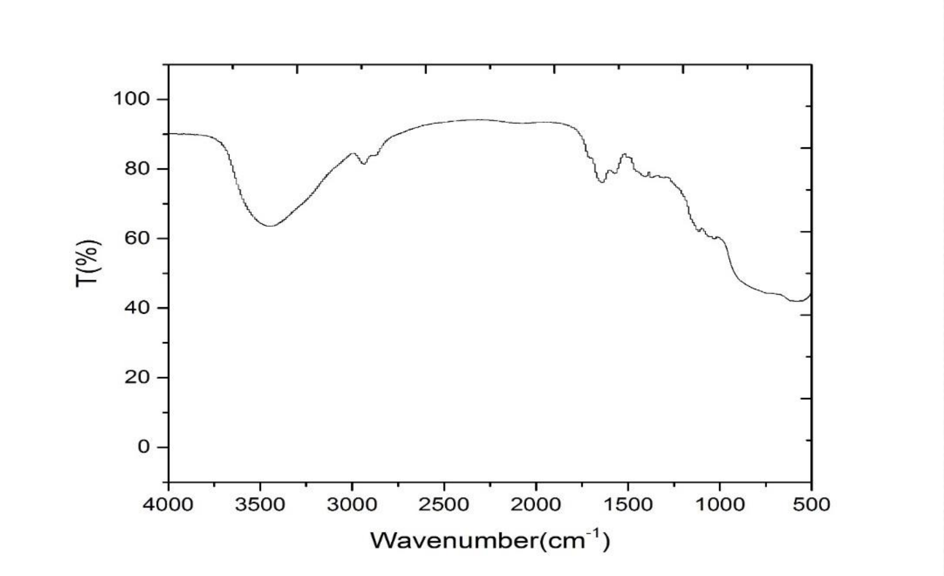
TGA curve of chitosan and ChAl composite

EDX



El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
O	8	K-series	49.08	49.08	49.12	16.9
C	6	K-series	20.46	20.46	27.27	7.7
Al	13	K-series	20.40	20.40	12.10	1.0
N	7	K-series	10.07	10.07	11.51	4.9
		Total:	100.00	100.00	100.00	

FT-IR spectra of ChAl composite



Wave No.(cm^{-1})	
3500	-OH and $-NH_2$
2900	Stretching of C-H in -CH and $-CH_2$.
1630	bending and vibration of -NH in $-NH_2$
1250	Stretching vibration of -CO in -COH
630	Al-O stretching

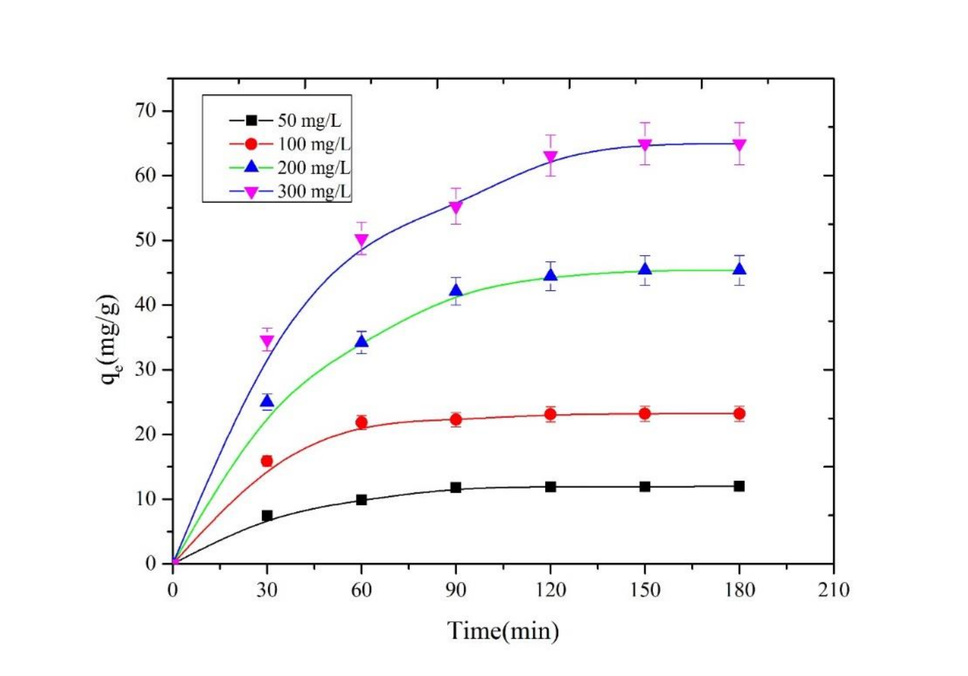
Adsorption study

- Batch adsorption was conducted in an orbital shaker
- Effects of significant parameters were investigated
- Exhausted adsorbent was regenerated

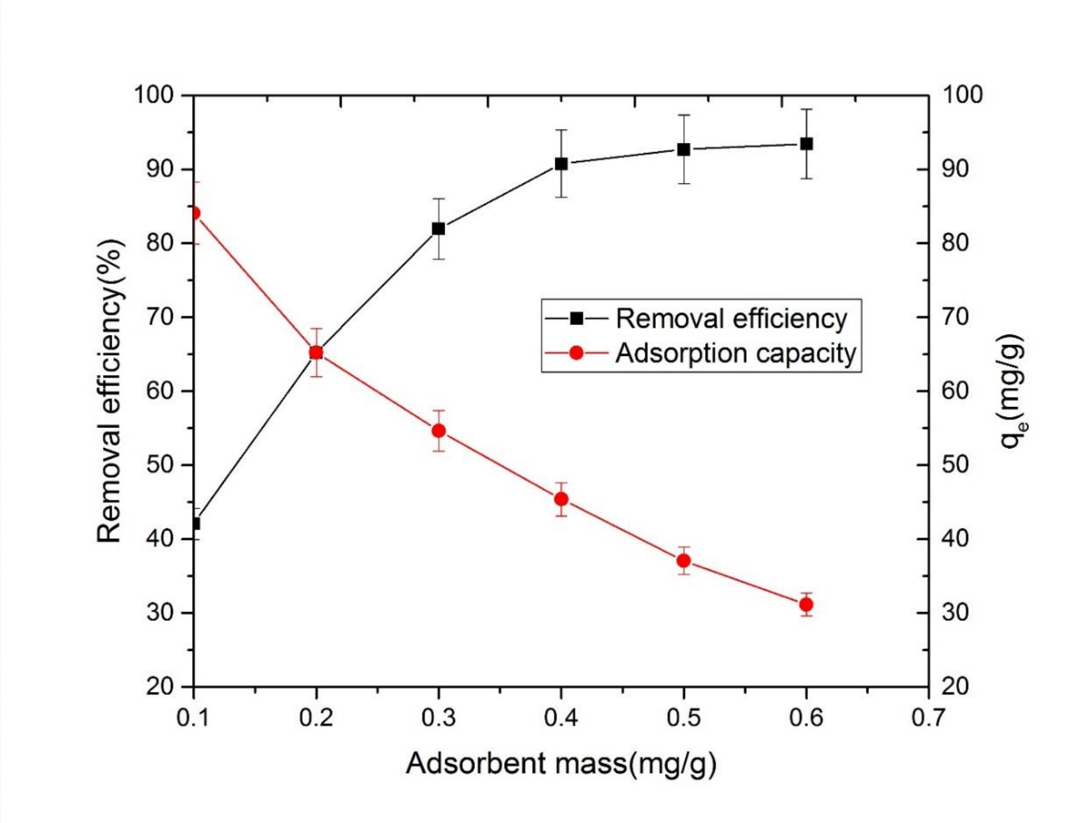
- $Removal\ efficiency\ (\%) = \frac{(C_0 - C_t)}{C_0}\ x\ 100$
- Adsorption capacity(mg/g): $q_t = \frac{(C_0 - C_t)V}{M}$

Results

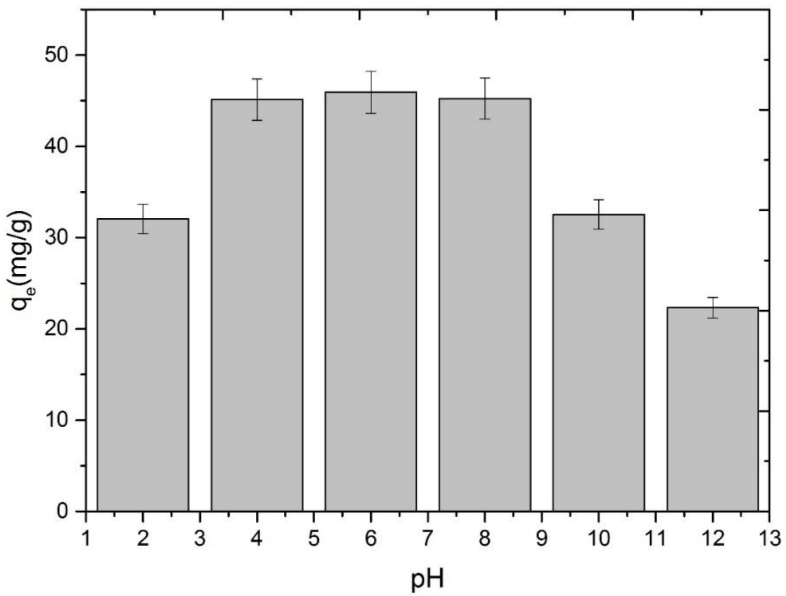
Effects of contact time and initial nitrate concentration



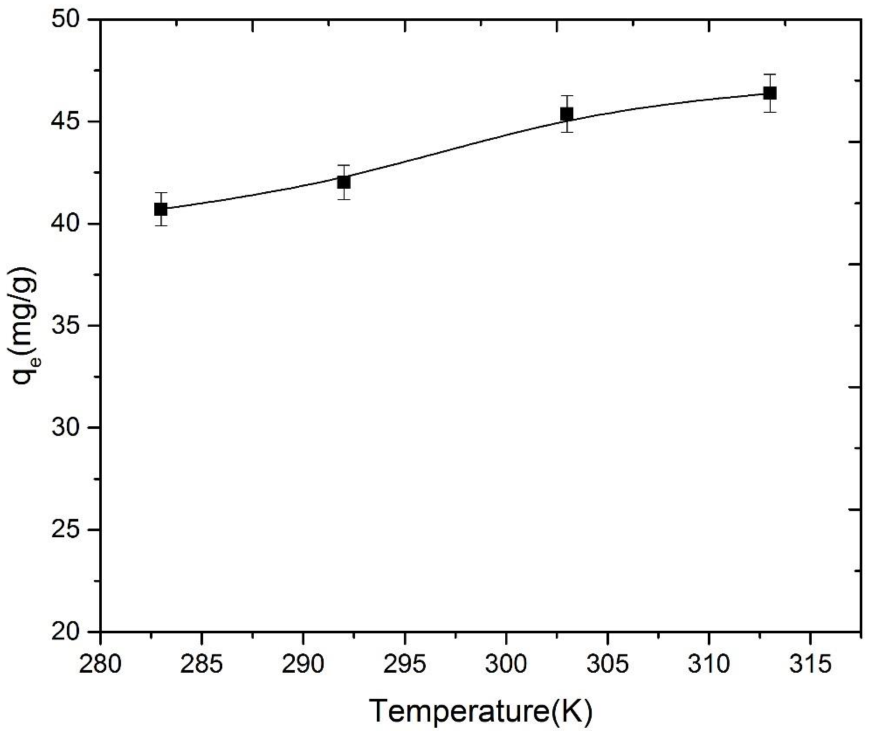
Effect of adsorbent dose



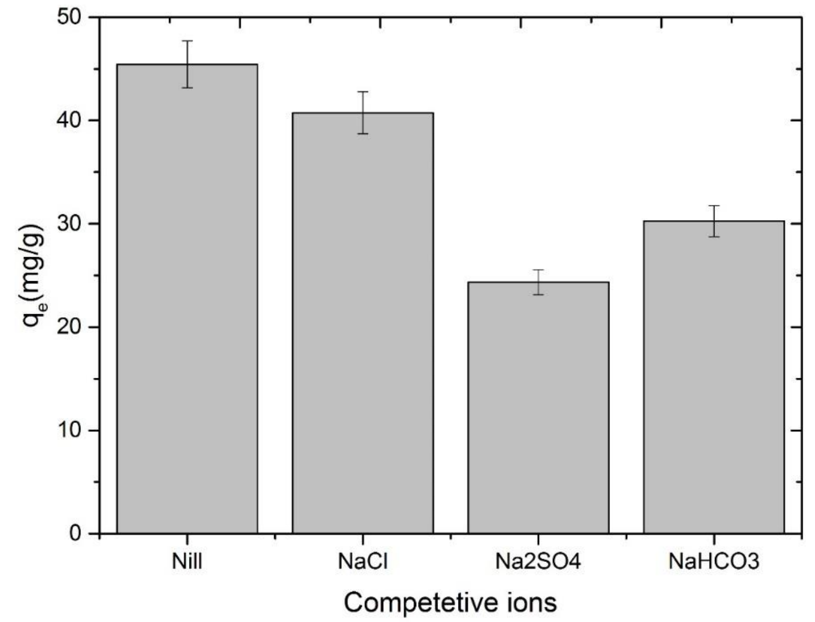
Effect of pH



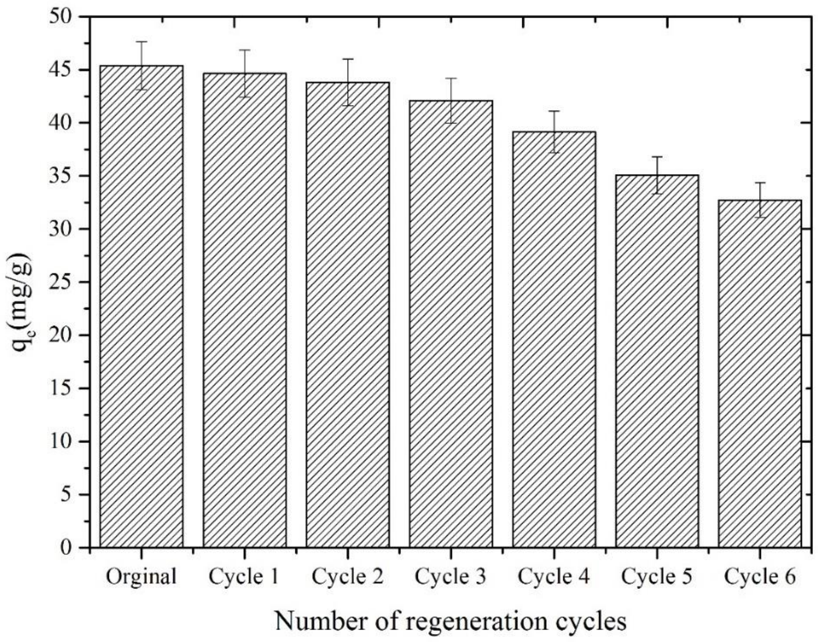
Effect of temperature on adsorption capacity



Effect of presence of other ions



Relationship between regeneration cycles and adsorption capacity



Adsorption Equilibrium Isotherms

Langmuir Isotherm

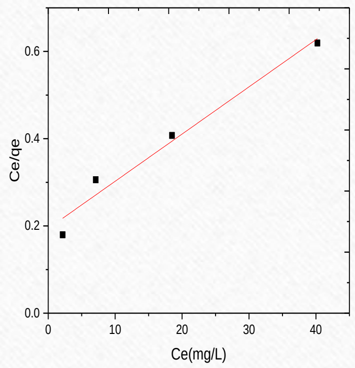
- The Langmuir adsorption model is given by

$$q_e = \frac{q_m b C_e}{1 + bC_e}$$

- The linearized form is, $\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$

- Dimensionless separation factor, $R_L = \frac{1}{1+bC_O}$

The value of R_L indicates the type of the isotherm to be either:
unfavorable ($R_L > 1$),
linear ($R_L = 1$),
favorable ($0 < R_L < 1$)
irreversible ($R_L = 0$).



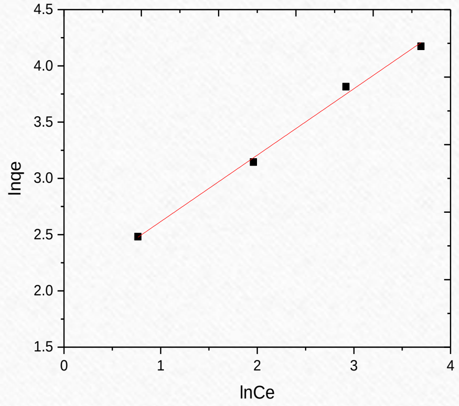
Freundlich Isotherm

The Freundlich equation is expressed as

$$q_e = K_f C_e^{1/n}$$

A linear form of this expression is

$$lnq_e = lnK_f + \frac{1}{n} lnC_e$$



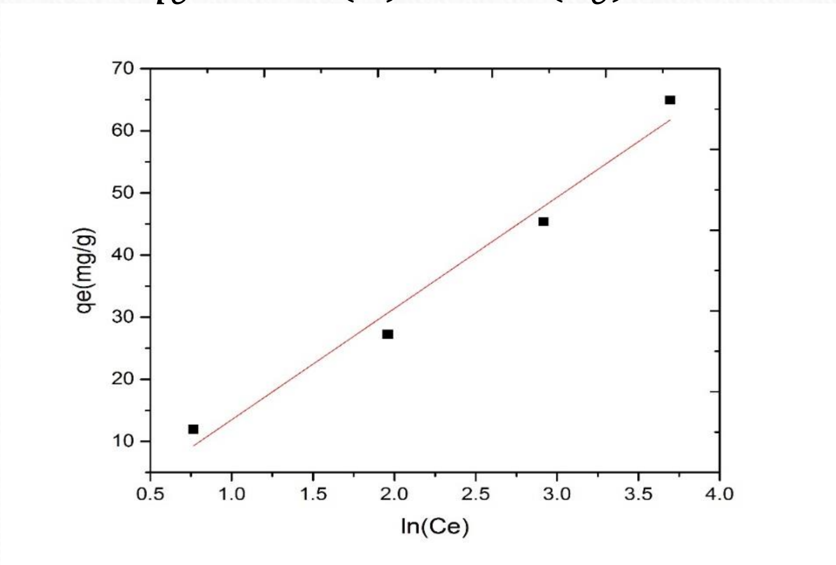
Temkin isotherm

$$q_e = \frac{RT}{b}\ln(AC_e)$$

$$q_e = \frac{RT}{b}\ln(A) + \frac{RT}{b}\ln(C_e)$$

$$\frac{RT}{B} = b$$

$$q_e = B\ln(A) + B\ln(C_e)$$



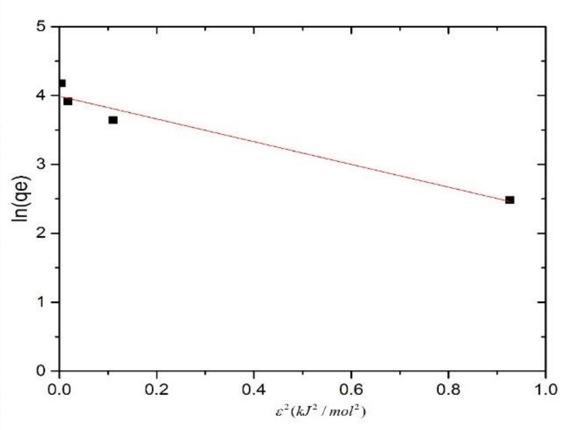
Dubinin–Radushkevich (D-R) Isotherm

$$\ln q_e = \ln q_o - \beta\,\varepsilon^2$$

$$\varepsilon = RT\ln\left(1 + \frac{1}{Ce}\right)$$

The mean adsorption energy (E)

$$E = \frac{1}{\sqrt{2\beta}}$$

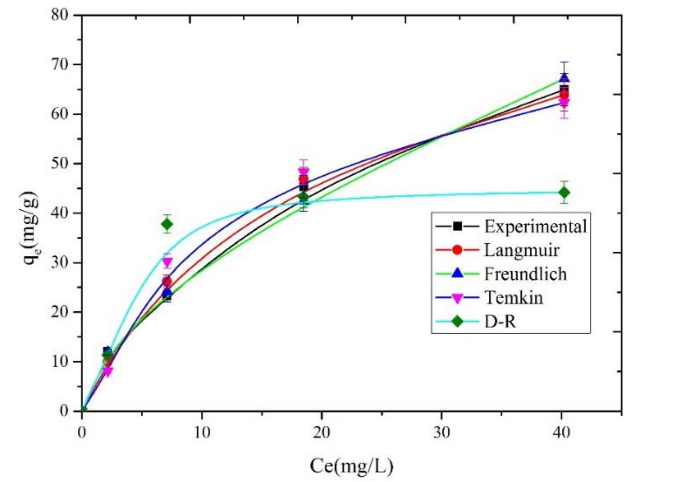


Adsorption isotherm parameters

Chi-square analysis (A. Sowmya & Meenakshi, 2013)

$$\chi 2 = \sum \frac{\left(q_e - q_{e,m}\right)^2}{q_{e,m}}$$

- Correlation coefficient (R^2) and chi-square ($\chi 2$) values are used to compare the applicability and suitability of isotherms



Isotherm	Parameters	
Langmuir	q_m(mg/g)	92.59
	b(L/g)	0.056
	R^2	0.97
	R_L	0.264
	$\chi 2$	0.84
Freundlich	1/n	0.59
	n	1.69
	K_f(mg/g)(L/mg)$^{1/n}$	7.58
	R^2	0.99
	$\chi 2$	0.31
D-R	β(mol^2/kJ^2)	1.48
	q_o(mg/g)	44.46
	E(kJ/mol)	0.58
	R^2	0.77
	$\chi 2$	1.47
Temkin	B(J/mol)	18.23
	R^2	0.96
	$\chi 2$	0.89

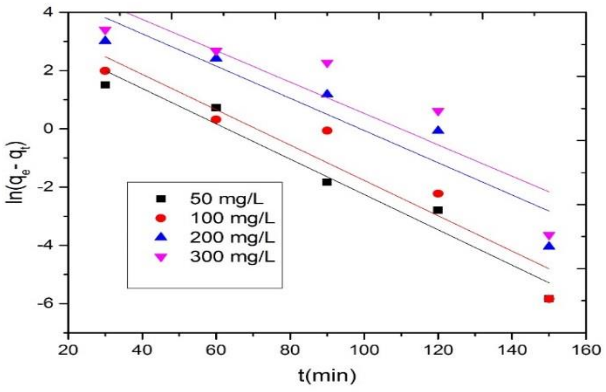
Adsorption Kinetics

Pseudo-first-order model

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

$$ln(q_e - q_t) = ln\, q_e - k_1 t$$

k_1 is rate constant of pseudo-first-order adsorption (1/min).



Pseudo-second-order model

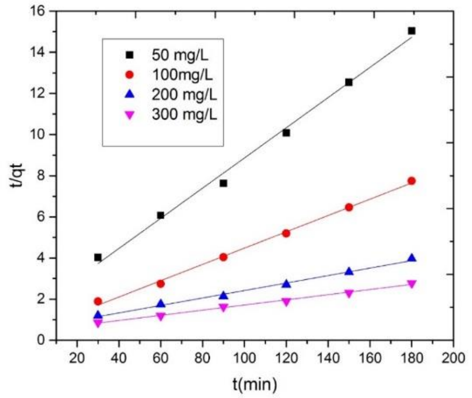
$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

$$h = k_2 q_e^2$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$$

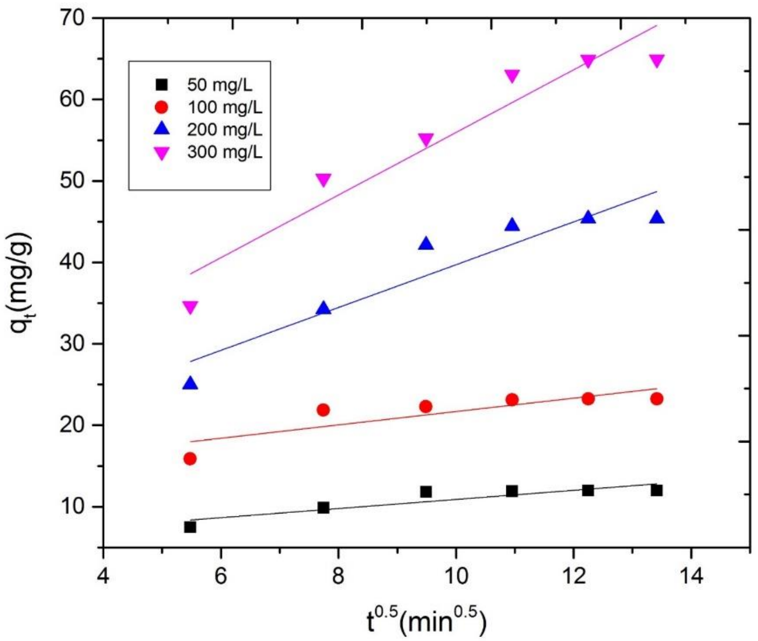
$$q_t = \frac{q_e^2\, k_2 t}{1 + q_e t}$$

k_2 is the pseudo-second-order rate constant (g/mg min)



Intraparticle diffusion model

$$q_t = k_i t^{0.5} + C$$



Kinetic parameters

Model	Parameter				
	Initial concentration(mg/g)	50	100	200	300
Pseudo-first-order	k_1(min^{-1})	0.06	0.061	0.06	0.05
	q_e(experimental)(mg/g)	11.96	23.22	45.38	64.94
	q_e(calculated)(mg/g)	45.41	73.65	239.31	371.44
	R^2	0.95	0.88	0.83	0.76
Pseudo-second-order	k_2(g/mg min)	0.004	0.003	0.001	0.001
	q_e(experimental)(mg/g)	11.96	23.22	45.38	64.94
	q_e(calculated)(mg/g)	13.64	25.25	54.95	80.00
	h	0.65	1.93	1.65	2.16
	R^2	0.99	0.99	0.97	0.97
Intraparticle diffusion	k_i(mg /g.$min^{0.5}$)	0.56	0.82	2.63	3.84
	R^2	0.76	0.64	0.86	0.91

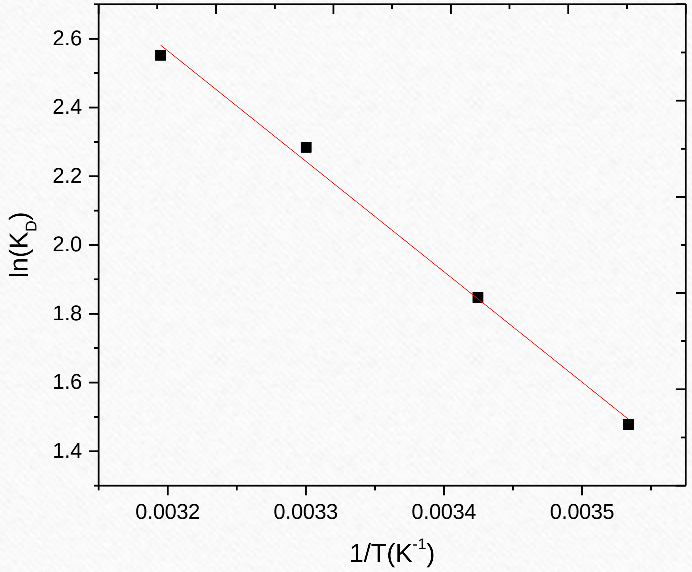
Thermodynamic parameters for the adsorption of nitrate on ChAl composite

$$\Delta G^o = -RT ln K_D$$ (P. S. and S. Chowdhury, 2003)

$$K_D = \frac{C_a}{C_e}$$

$$ln K_D = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$

Temperature(K)	Thermodynamic parameters		
	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (kJ/mol.K)
283	-3.48	26.92	0.11
293	-4.49		
303	-5.75		
313	-6.64		



Conclusions

- The adsorption data were well fitted with the Freundlich adsorption isotherm which indicates the heterogeneous nature of adsorption.
- The kinetic data indicates that the pseudo-second-order model better describes the adsorption process of nitrate onto the ChAl composite.
- Physical binding force involved in the adsorption of nitrate on ChAl composite was confirmed from E value calculated from the D-R isotherm.
- Thermodynamic parameters revealed that adsorption of nitrate was endothermic and spontaneous.
- Electrostatic interaction between the anion and the positive functional groups in the adsorbent was the main driving force for the adsorption of nitrate.
- Chitosan biopolymer can be used as an inexpensive, sustainable, reusable, and environment-friendly treatment option for nitrate contaminated drinking water..

Thank You