Petroleum and Chemical Engineering – Sultan Qaboos University

Biosorption of Petroleum Priority Pollutant on Immobilized and Free Algal

Presented by

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Layout

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- ✓ **Removal Techniques of Organic Materials**
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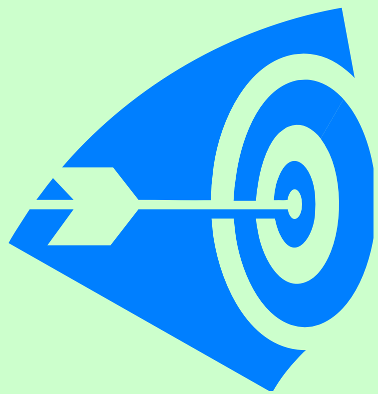
Main objective

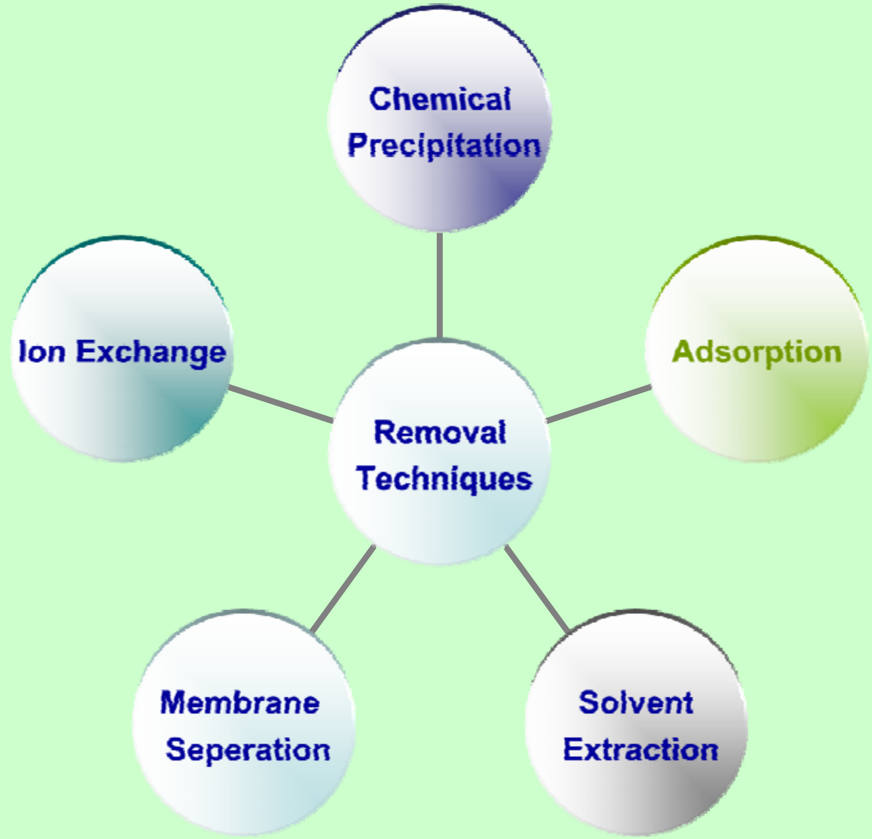
- The objective of this work is to investigate the technical feasibility of using immobilized algal biomass for the removal of **priority pollutants** from aqueous solutions.



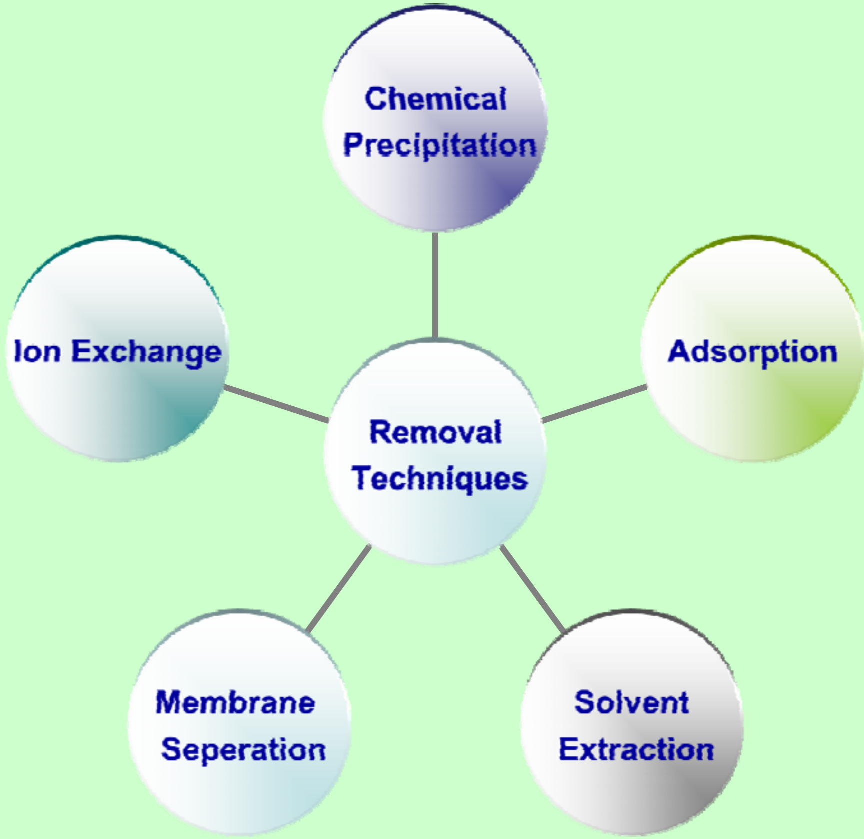
Selected Priority Pollutants

- Heavy metals
  - Zinc ions
- Organic
  - Naphthalene

Techniques for Removal of Heavy Metals



Techniques for Removal of Organics



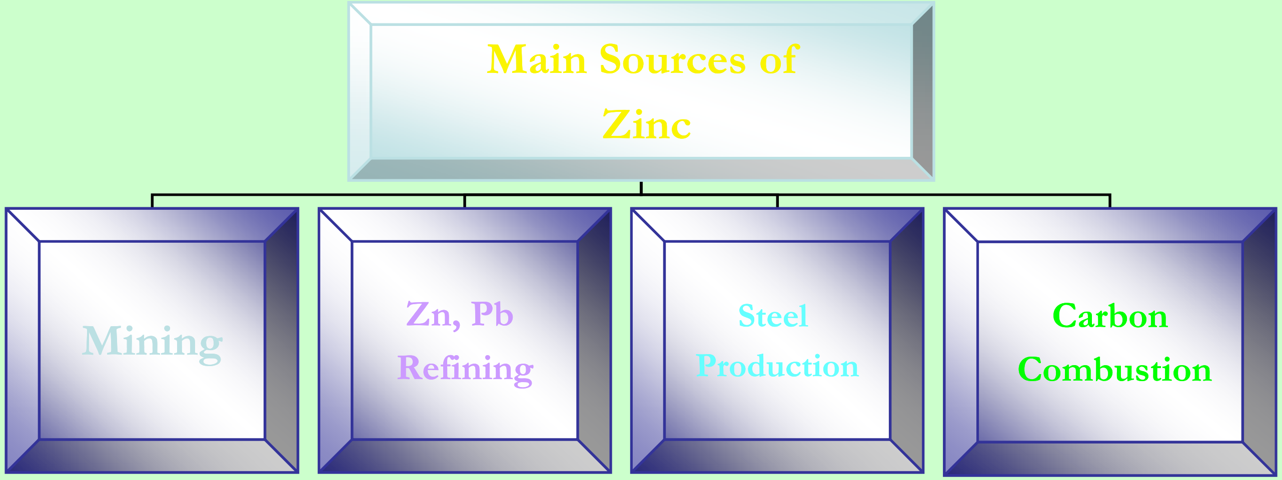
Zinc (Zn)

- Zinc is naturally released into the environment, although industrial activities are mostly responsible for zinc pollution.

- **Health Impact:**

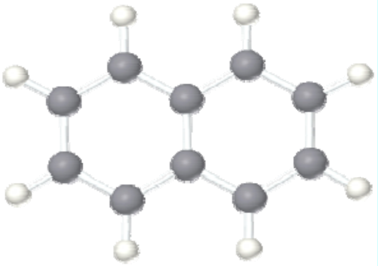
  Causes accumulative poisoning, cancer, brain damage, etc., when it is found above the tolerance levels.

Zinc (cont.)


Main Sources of Zinc
Mining
Zn, Pb Refining
Steel Production
Carbon Combustion

Naphthalene

- Naphthalene is a poly aromatic hydrocarbons (PAHs).
- Naphthalene was classified as a priority pollutant by the U.S. Environmental Protection Agency (1992).
- Health Impact:
  Naphthalene is moderately toxic and poisoning of naphthalene may occur by ingestion of large doses, inhalation, or skin absorption.



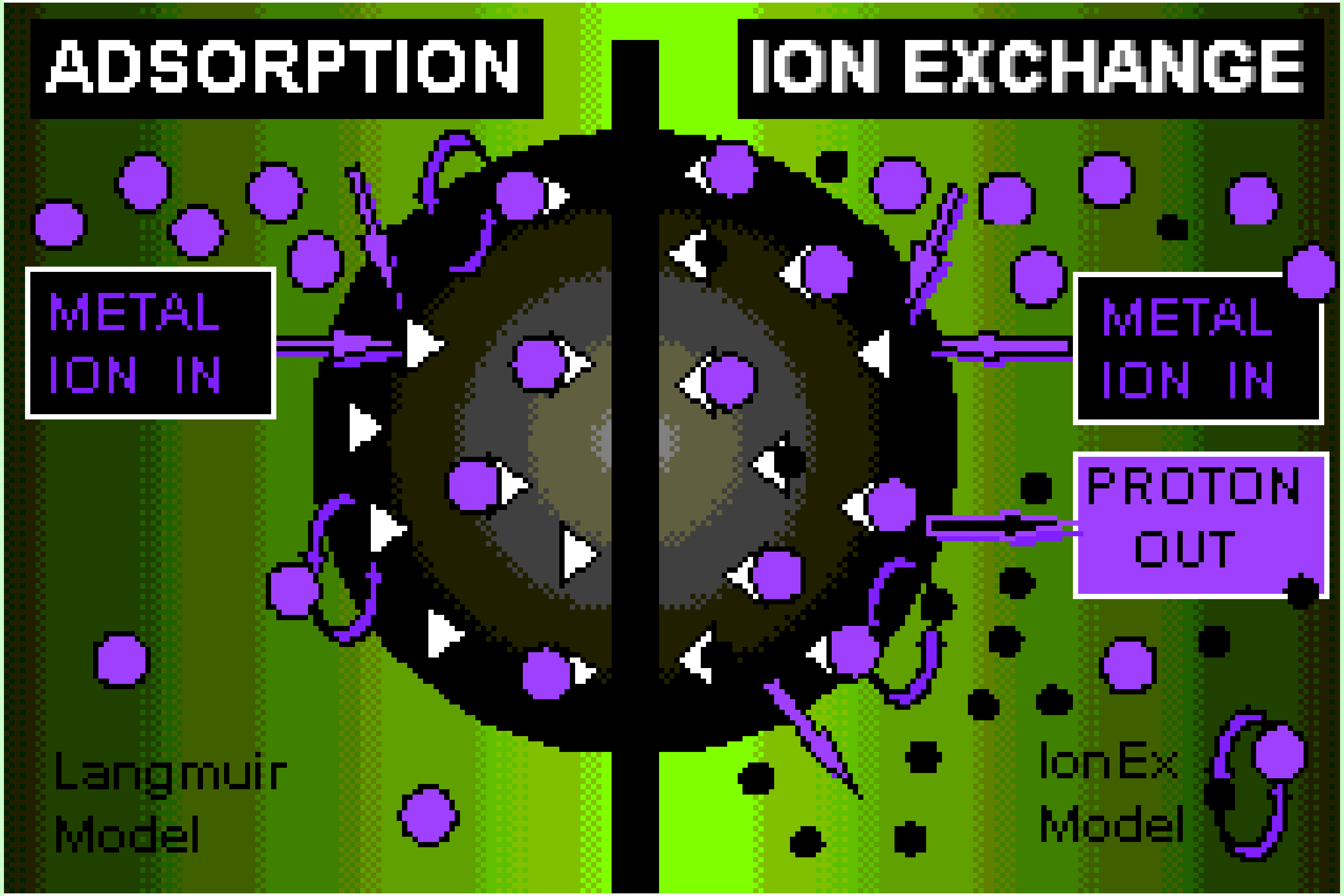
Naphthalene

Naphthalene

Main Sources of Naphthalene

- Coal
- Tar Based Industries

Adsorption and Biosorption



Adsorption

- The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another.

- The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate.

Biosorption

- **Biosorption is a property of certain types of sorbents of biological origin to bind and concentrate heavy metals from even very dilute aqueous solutions.**

- **Biosorption can be defined as the passive removal of metal ions by metabolically inactive biomass.**

Major sources of Biomass

- Waste biomass: from industrial large scale fermentations (e.g. from antibiotic enzyme, organic acid production processes, etc.
- Microorganisms: marine algae biomass (seaweeds) .
- Agricultural wastes: peat, cotton waste, rice husk, olive pomace.

Biosorption Mechanisms

- **Ion Exchange** Ion exchange is the interchange of ions which are formed by molecular or atomic species either losing or gaining electrons

$$2NaALG + Me^{+2} \leftrightarrow Me(ALG)_2 + 2\ Na$$

- **Sorption** The term adsorption implies a surface phenomenon, the actual sequestration may take place based on either physical phenomena (physical adsorption) or through a variety of chemical binding means (chemisorption).

- **Inorganic Microprecipitation**

Biosorption by Immobilized Cells

- Cell immobilization is an attractive technique to fix and retain biomass on suitable natural or synthetic materials support for a range of physical and biochemical unit operations.

- Immobilization may improve biosorption capacity.
- Facilitate separation of biomass from pollutant bearing solution.

Equilibrium Isotherm models

- **Langmuir Isotherm**

$$Q = \frac{Q_{\max} b C_e}{1 + b C_e}$$

Q_{max}: maximum surface coverage.

b : Coefficient related to the affinity between the sorbent and sorbate (l/mg).

- **Freundlich Isotherm**

$$Q_e = K C_e^{1/n}$$

K: adsorption capacity.

n: adsorption intensity

Equilibrium Isotherm models (Cont.)

- Dubinin-Radushkevich (D-R)

$$Q_e = Q_D e^{-B_D\left[RT\ln\left(1+\frac{1}{C_e}\right)\right]^2}$$

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

Q_D: Dubinin-Radushkevich isotherm constant, mmol/g.

B_D: Dubinin-Radushkevich isotherm constant, $l/J^2.mol^2$.

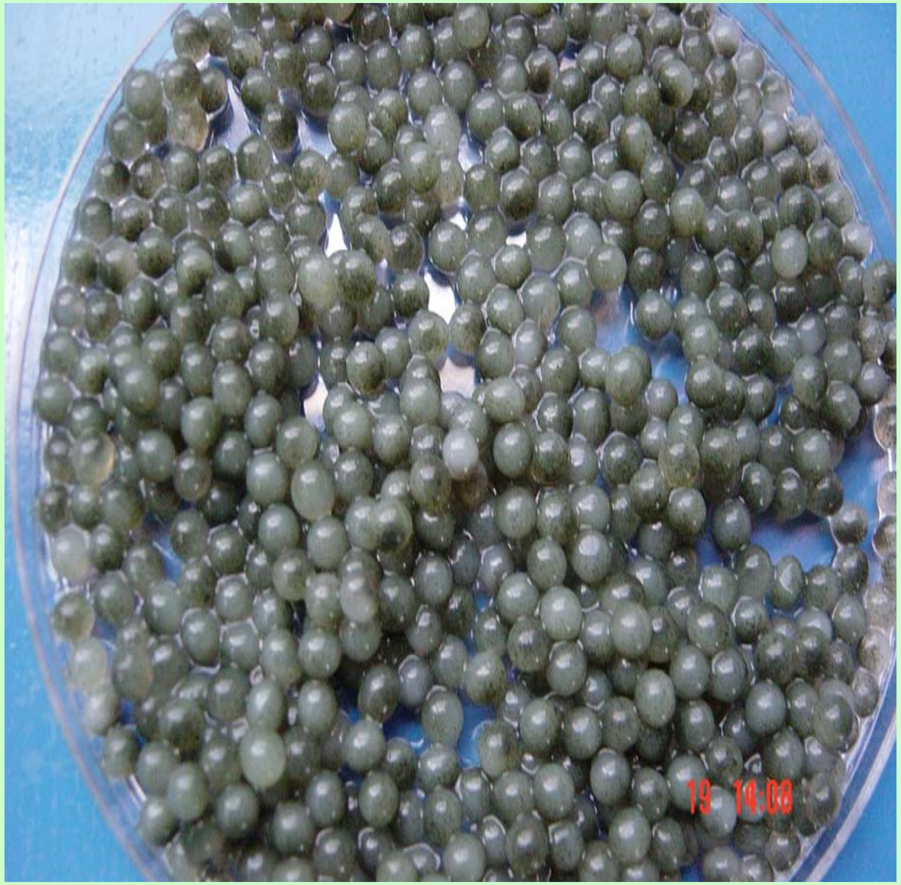
E: Mean free energy of sorption, kJ/mol.

Experimental Part

Materials

- **Adsorbate:**
  - ppm $ZnSO_4.7H_2O$
  - ppm Naphthalene

- **Adsorbent**
  - Green Algae (***Chlorella vulgaris***)



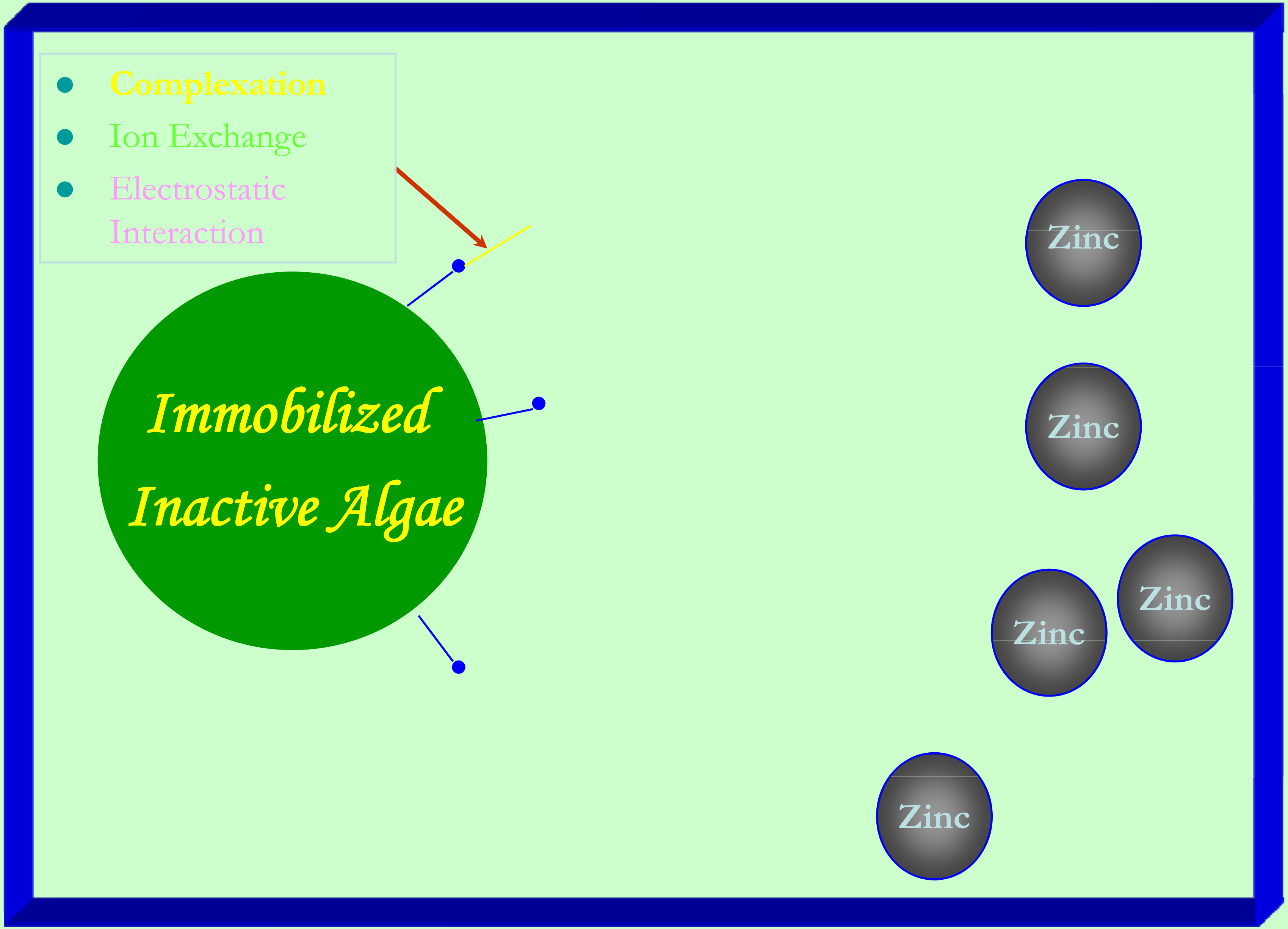
Immobilized Algal Beads prepared

Functional Groups on the Algal Cells

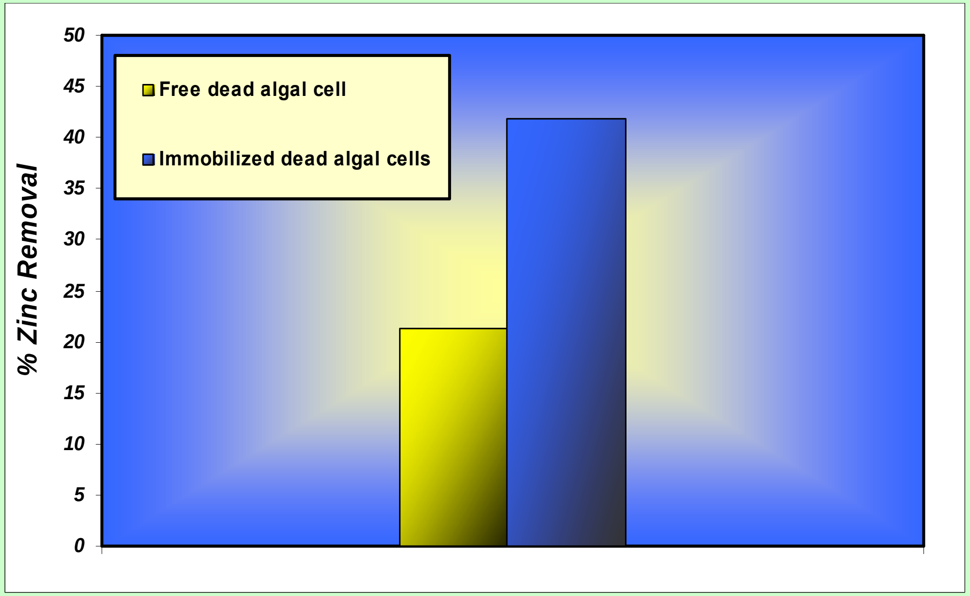
- The functional acidic groups on the prepared algal cells were determined using *Boehm's titration* method.

Functional Group	*Meq H/+g algae*
Carboxyl	**0.02**
Lactones and Lactols	**0.01**
Phenols	**0.035**

Experimental Results

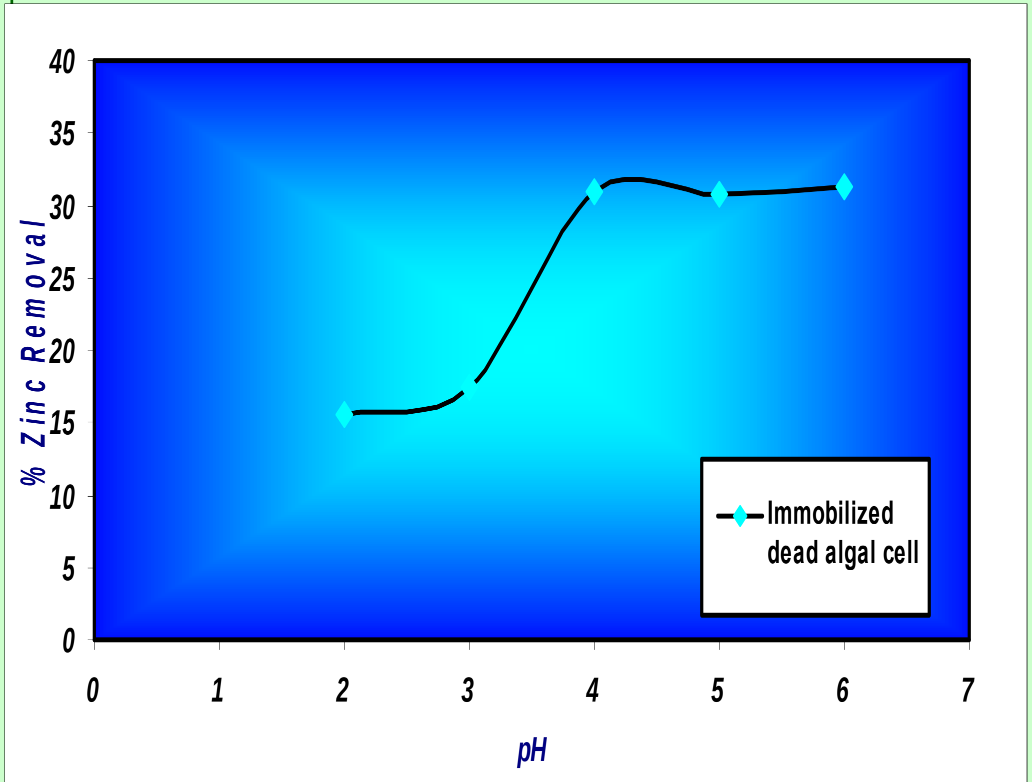

Complexation
Ion Exchange
Electrostatic Interaction
Immobilized Inactive Algae
Zinc
Zinc
Zinc
Zinc
Zinc

Comparison between Immobilized Inactive Algae and Suspension Algae



- **Immobilized algae gave around 45 % removal which is two times more than the percentage removal of suspension algae.**

Effect of pH

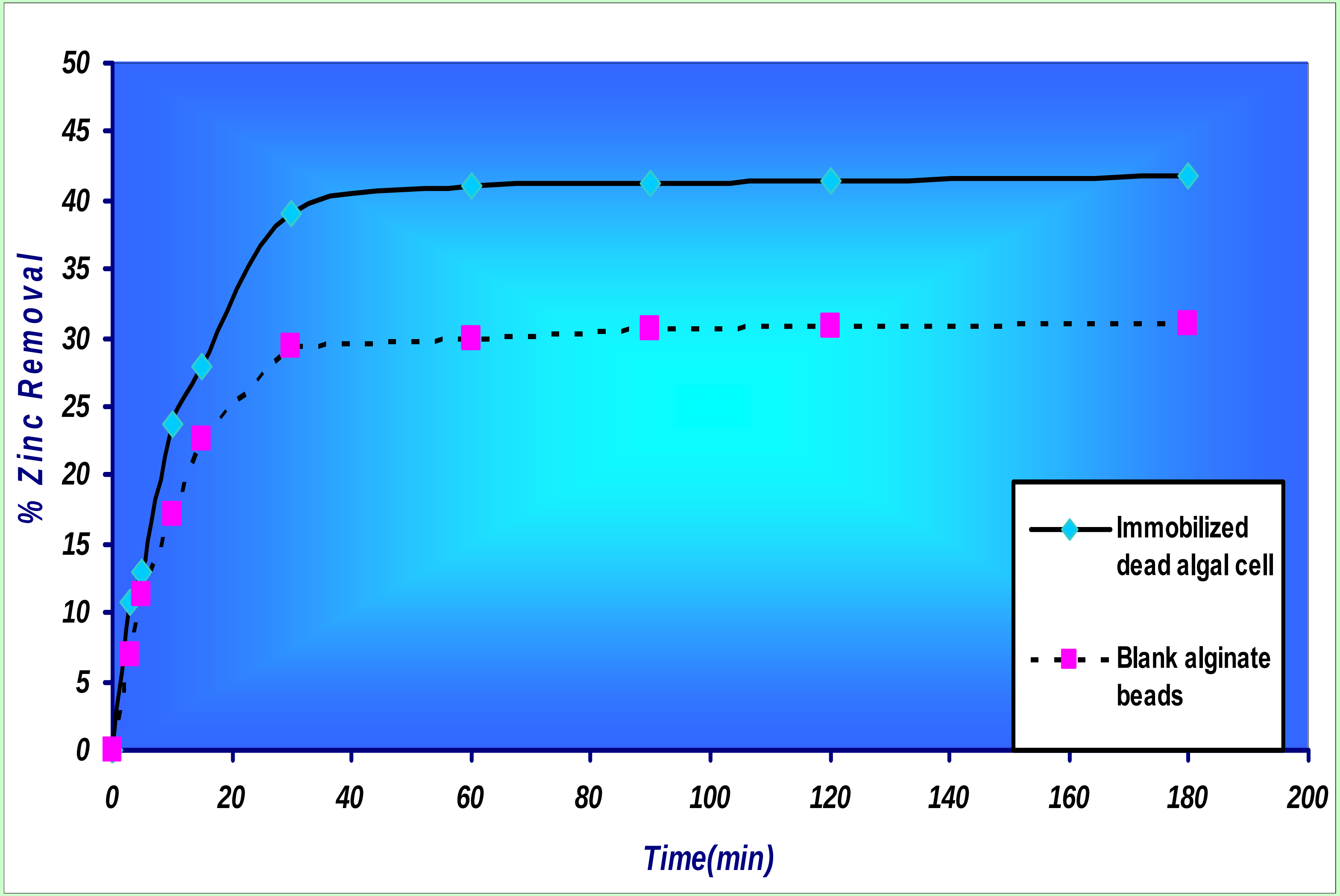


At low pH values ion exchange reaction involving metals are in competition with the high concentrations of H+ in the solution.

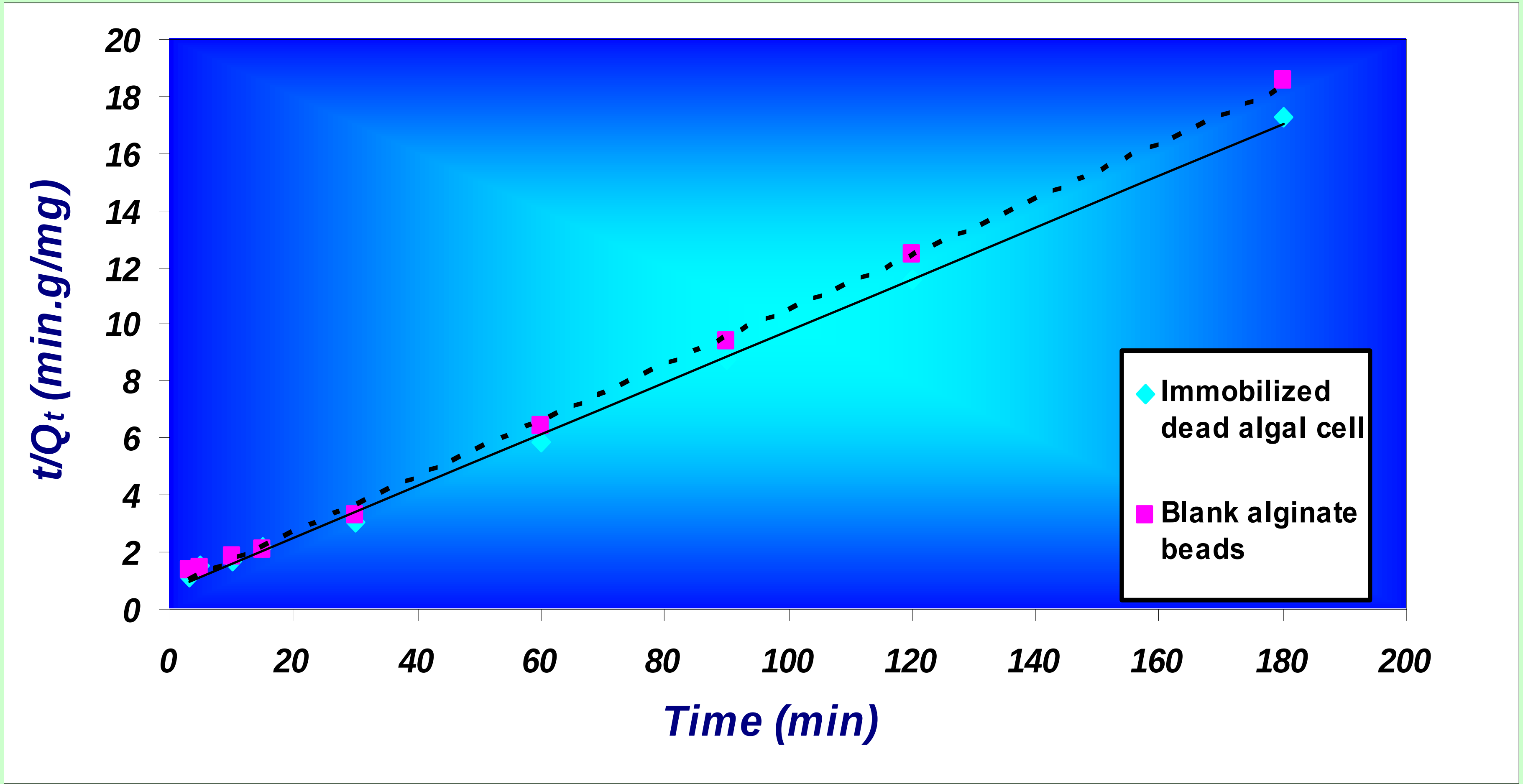
With increasing pH, more ligand, such as carboxyl groups, would be exposed and thus negative charges will result and attraction between these negative charges and the metals would increase the biosorption capacity on the cell surface.

No significant increase in zinc removal at pH values above 5.

Effect of Contact Time



Pseudo-Second Order Kinetics

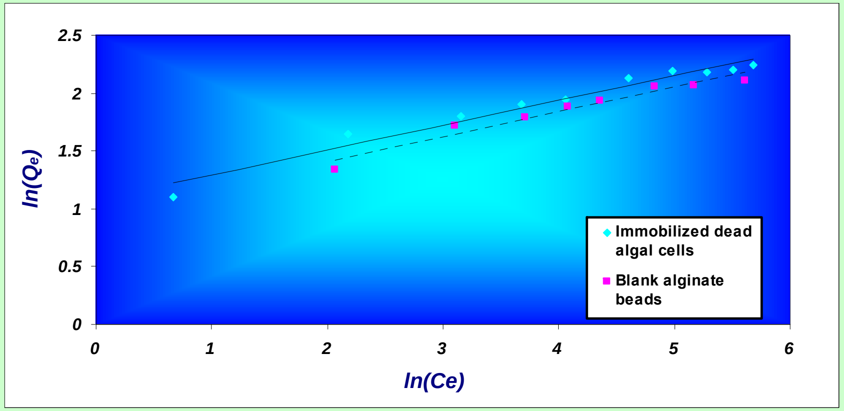


Pseudo-Second Order Kinetics (Cont.)

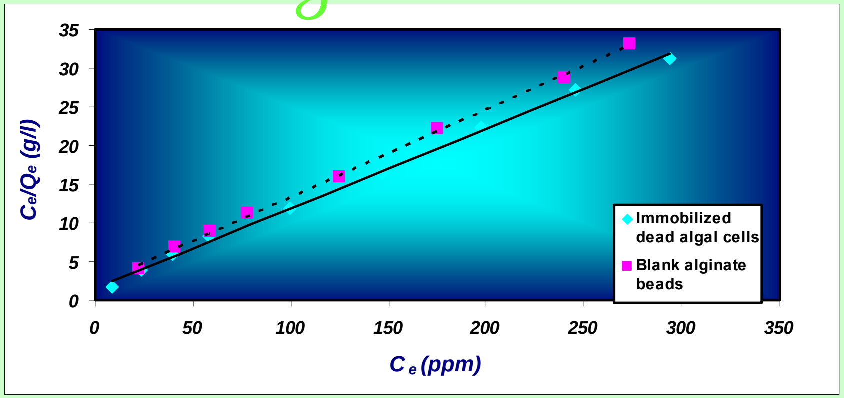
Biosorbents	*Pseudo-second order*		
	$k_{2,ads}$ (g/mg.min)	*Q_e (mg/g)*	*R^2*
Immobilized dead algal cells	*0.012*	*11.02*	*0.99*
Blank alginate beads	0.011	10.24	0.99

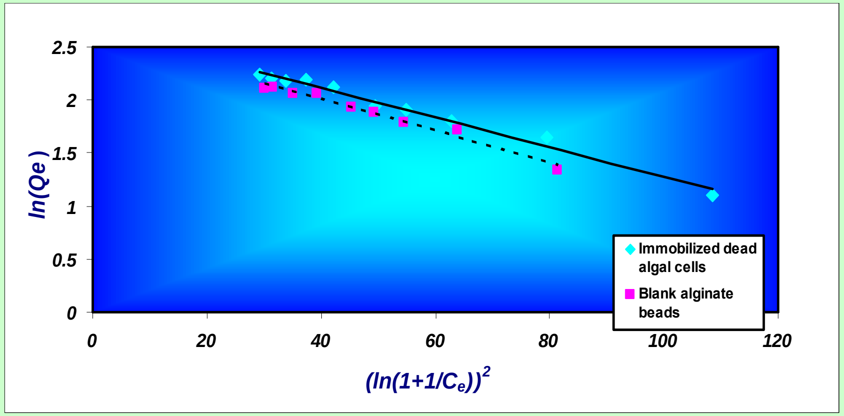
Biosorption Isotherms

Freundlich Isotherm

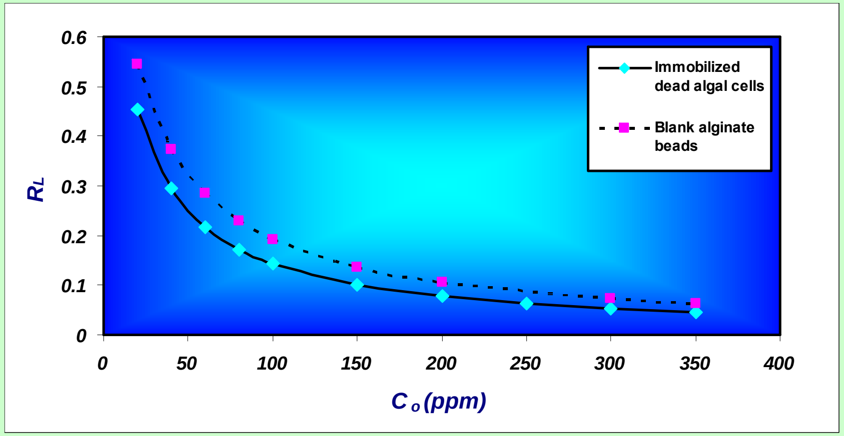


Langmuir Isotherm





Dubinin-Radushkevich

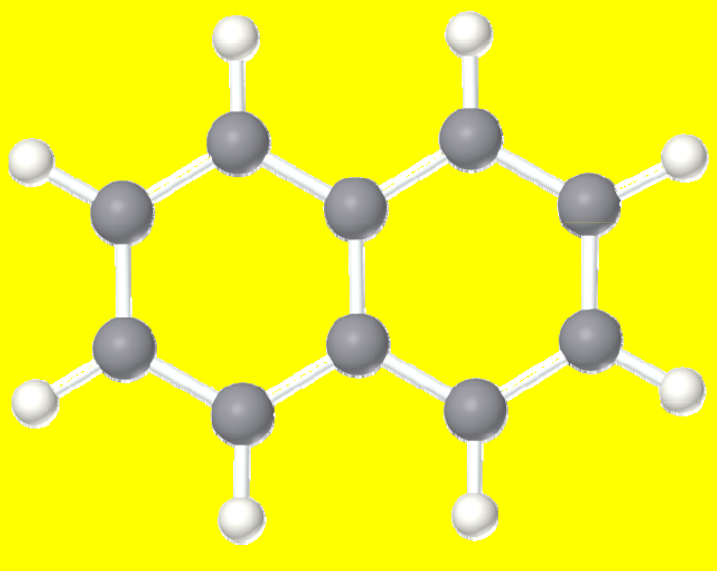


Seperation Factor

Model	Parameter	Blank alginate beads	Immobilized algal cells
Freundlich	K $(l/mg)^{1/n}$ (mg/g)	2.85	3.26
	n	5.01	5.15
	R^2	0.95	0.96
Langmuir	Q_m (mg/g)	9.25	9.67
	b (l/mg)	0.04	0.06
	R^2	0.99	0.99
D-R	Q_D(mmol/g)	8.83	9.44
	B_D $(l/J^2.mol^2)$	$2.01*10^{-9}$	$2*10^{-9}$
	E (kJ/mole)	14.35	14.85
	R^2	0.97	0.98

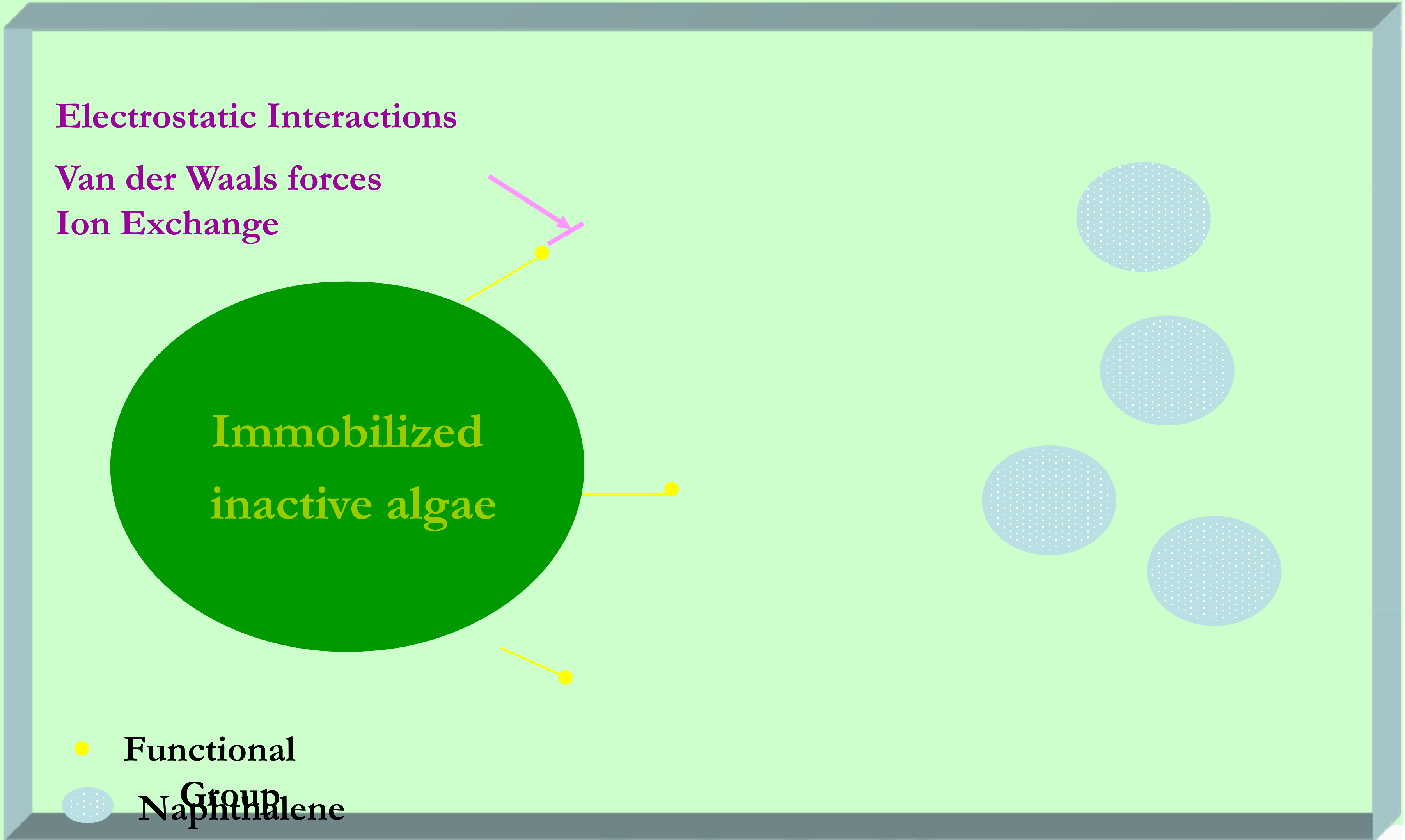
- Adsorption linear Isotherms parameters for the sorption of zinc ions by blank alginate beads and immobilized algal cells.

Naphthalene Biosorption

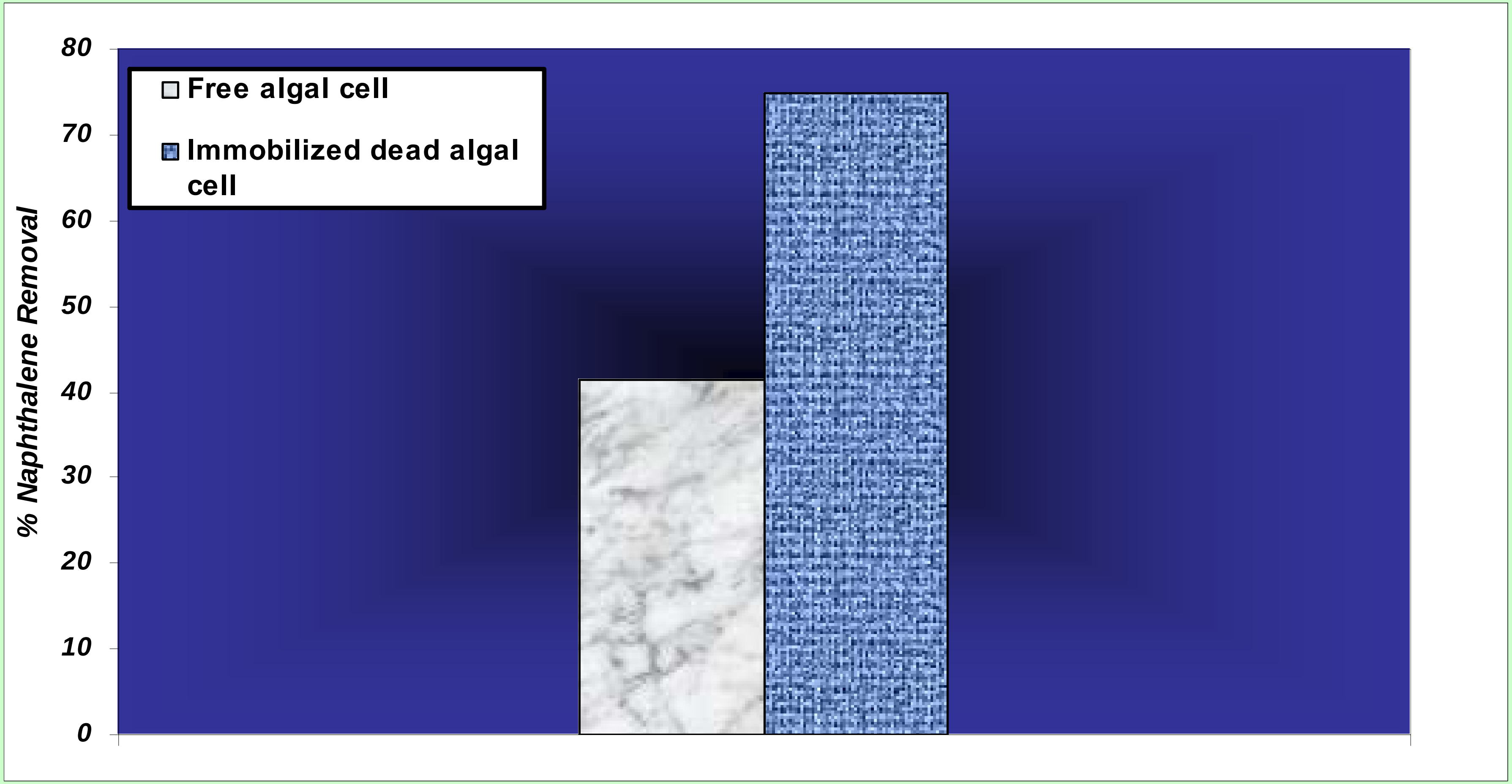


Naphthalene

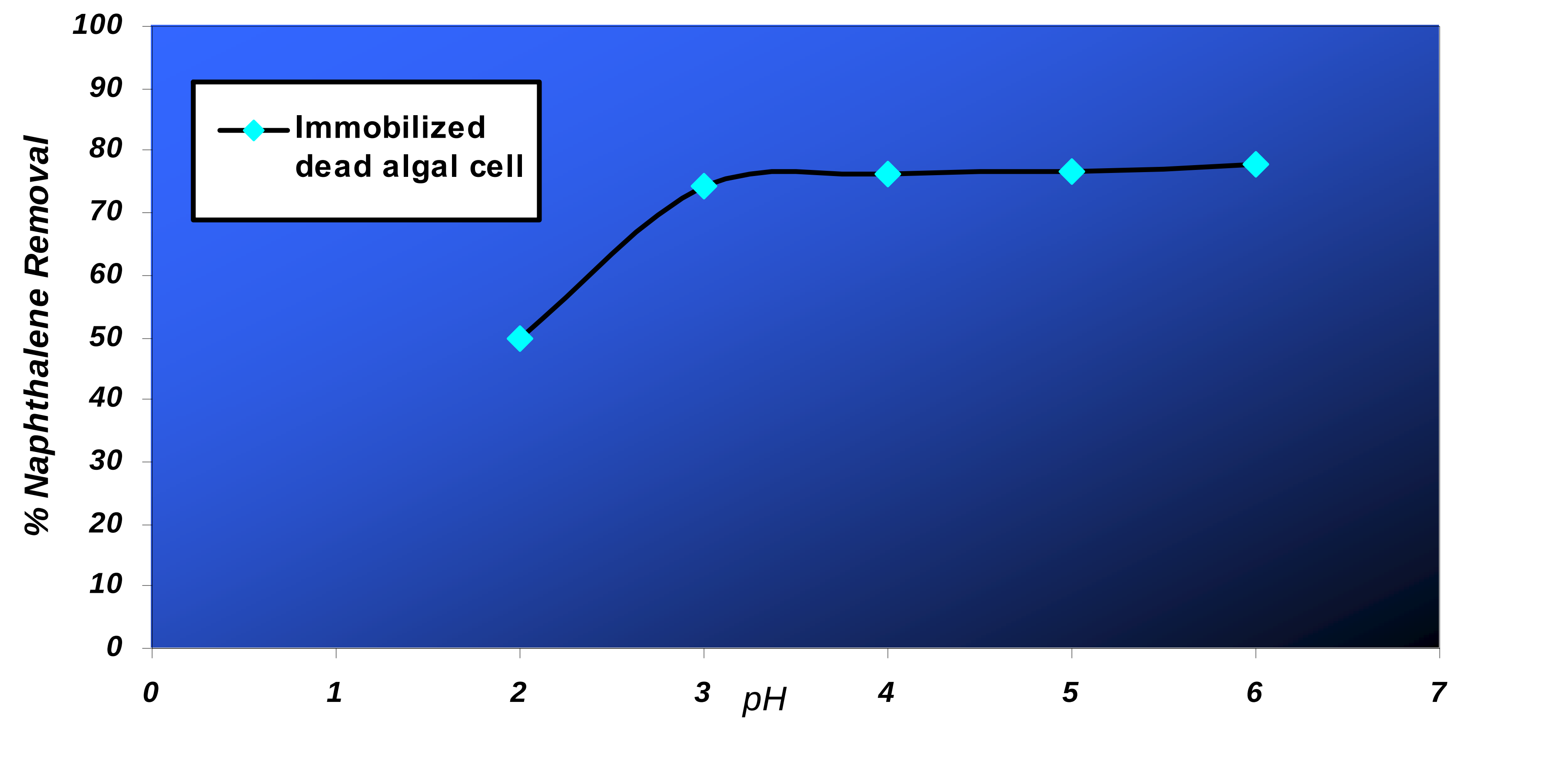
Mechanism of Naphthalene Biosorption



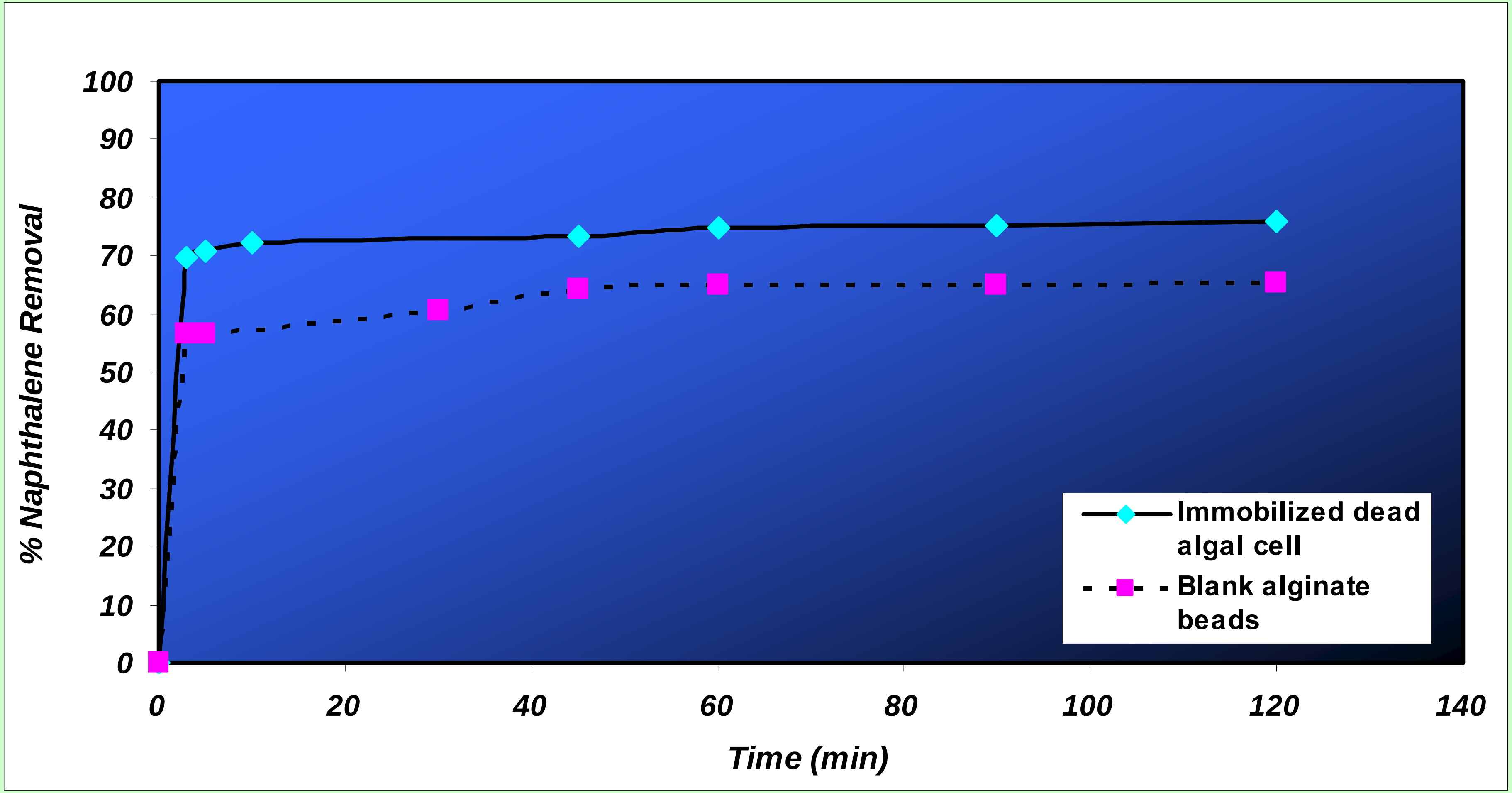
Comparison between Immobilized Inactive Algae and Suspension Algae



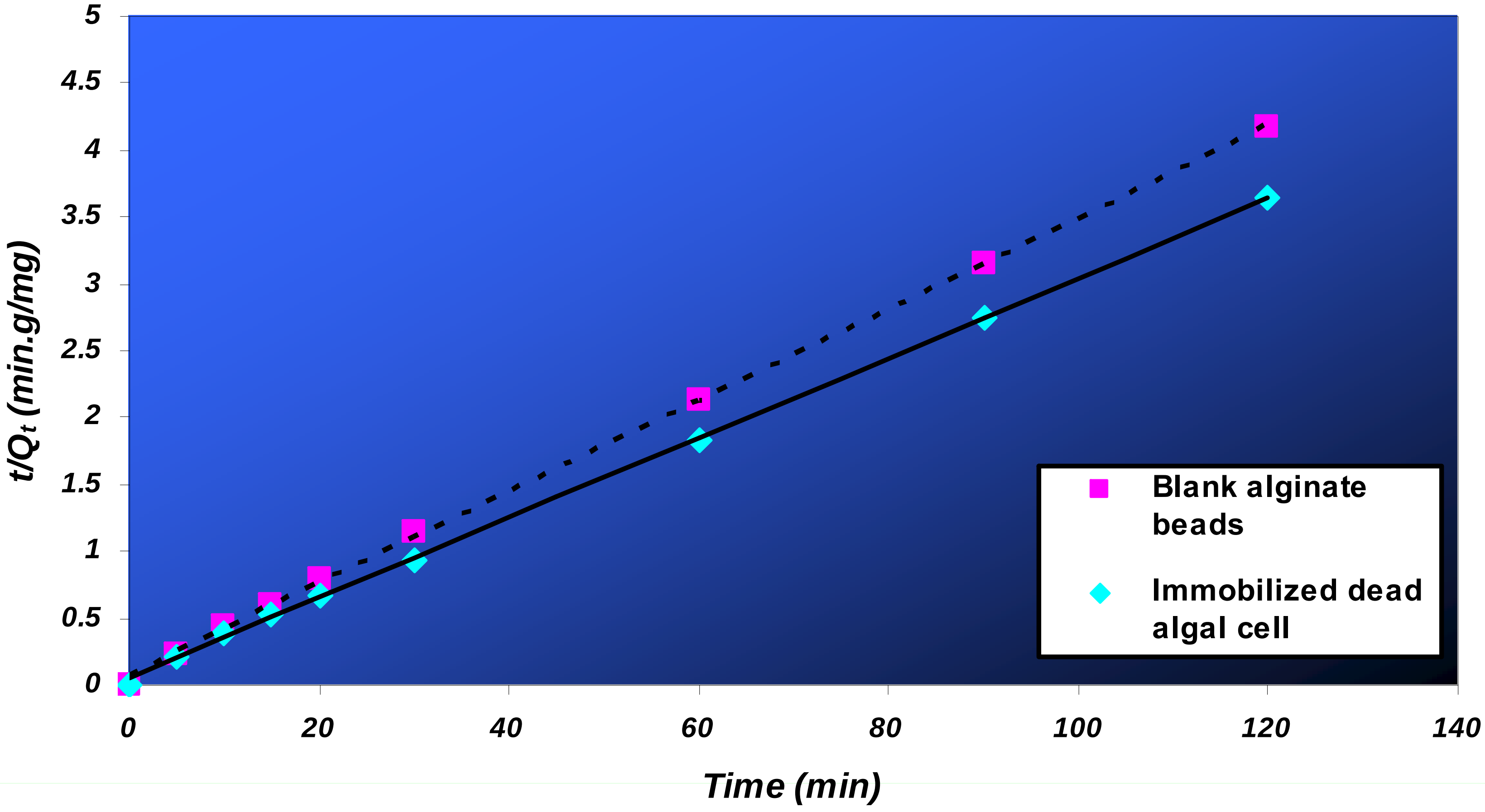
Effect of Initial pH on the Biosorption of Naphthalene



Kinetics of Naphthalene



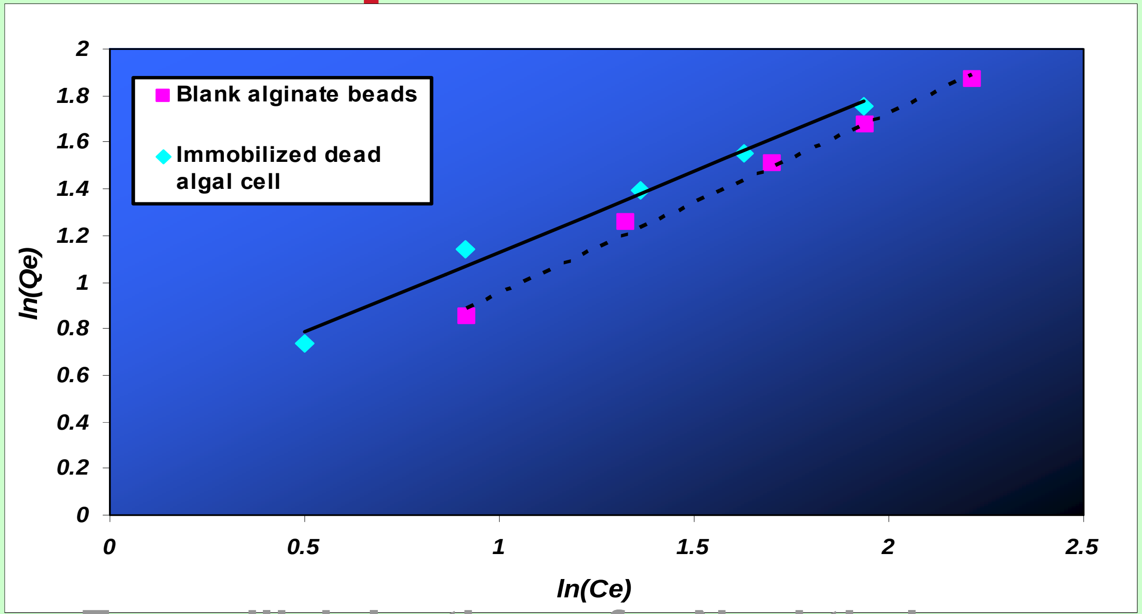
Pseudo Second Order Kinetics



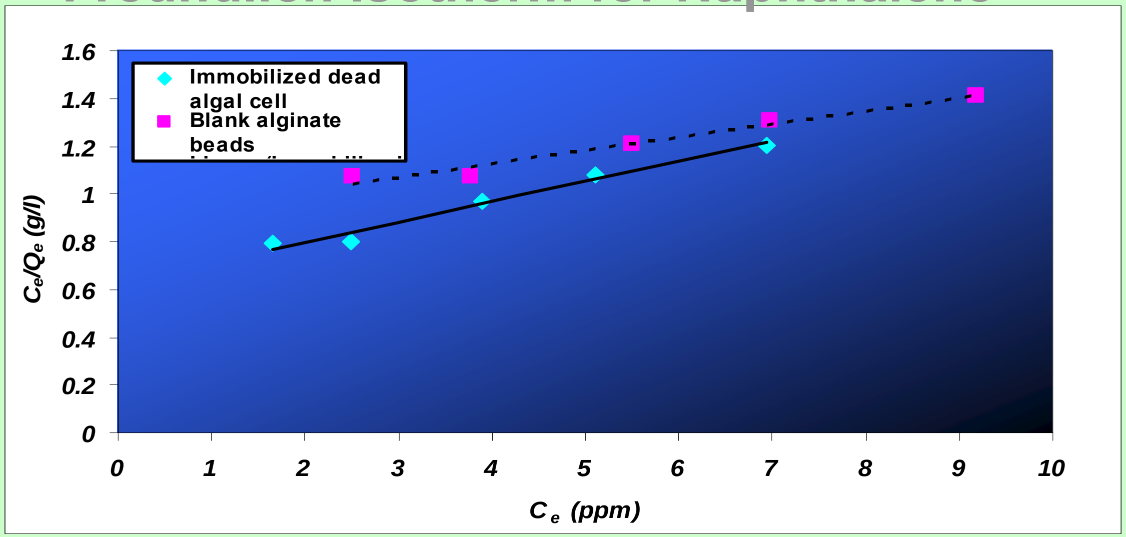
Pseudo Second Order Kinetics (Cont.)

Sorbents	Biosorbents	Pseudo-second order		
		$k_{2,ads}$ (g/mg.min)	Q_e (mg/g)	R^2
Naphthalene	Immobilized dead algal cells	0.46	4.54	0.99
	Blank alginate beads	0.23	4.92	0.99

Biosorption Isotherms

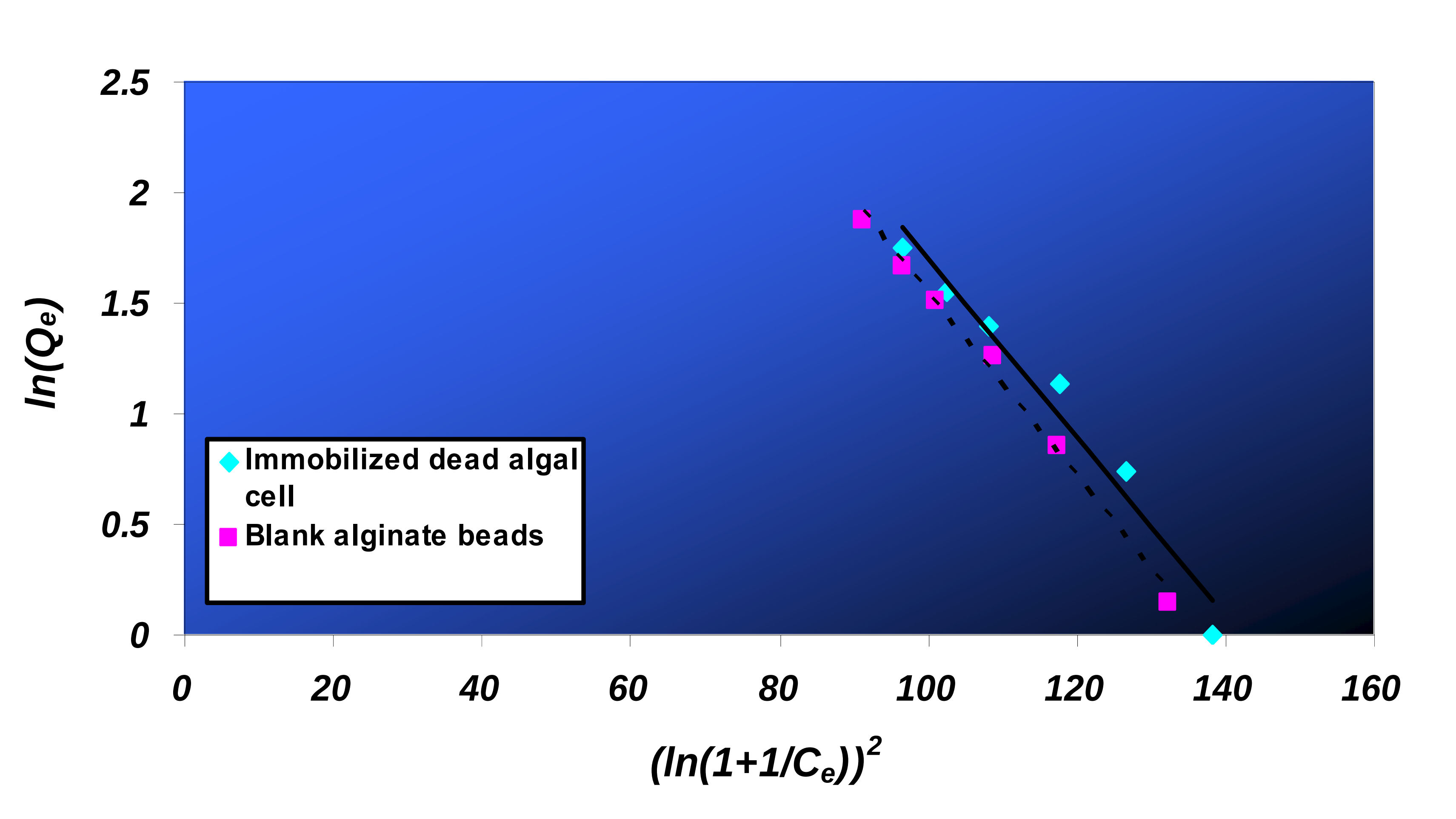


Freundlich Isotherm for Naphthalene



Langmuir Isotherm for Naphthalene

Biosorption Isotherms



D-R Isotherm for Naphthalene

Biosorption Isotherms (Cont.)

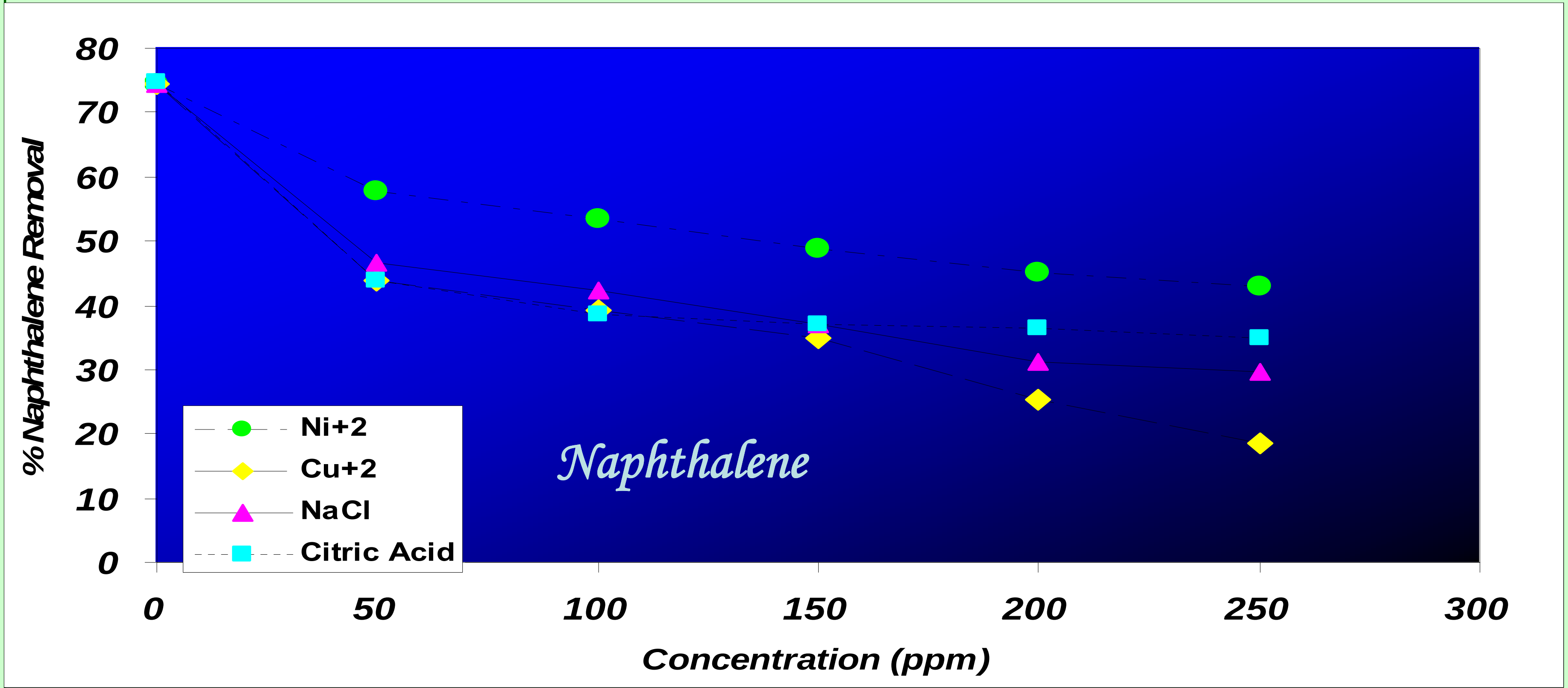
- Energy range of adsorption reactions, **8-16 kJ/mole** → ion-exchange mechanism.

- E for naphthalene was found to be **9.05** kJ/mole

Adsorption of Linear Isotherms Parameters

Sorbate	Model	Parameter	Blank alginate beads	Immobilized algal cells
Naphthalene	Freundlich	K(l/mg)1/n (mg/g)	1.19	2.2
		n	1.29	1.67
		R^2	0.99	0.98
	Langmuir	Q_m (mg/g)	17.98	11.87
		b (l/mg)	0.061	0.13
		R^2	0.97	0.96
	D-R	Q_D(mmol/g)	2.37	2.33
		B_D ($l/J^2.mol^2$)	$6.1*10^{-9}$	$6.0*10^{-9}$
		E (kJ/mole)	9.12	9.05
		R^2	0.99	0.96

Effect of Impurities on Biosorption of Phenol and Naphthalene



Conclusions

- This study proved the practical feasibility of using immobilized inactive algal cells for the removal of zinc, and naphthalene from refinery wastewaters.
- Sorption efficiency of immobilized biosorbents are greater than that of the suspension biosorbents.
- Optimum pH values were: 5.0 for zinc, and 4.0 for naphthalene.
- Biosorption kinetics was found to follow pseudo-second order kinetics.

Conclusions (Cont.)

- Langmuir, Freundlich, and D-R isotherm models have been found to describe the biosorption of zinc, and naphthalene on alginate beads and immobilized *Chlorella vulgaris*.

- The biosorption of the three pollutants on immobilized algal cells and blank alginate beads are expected to be a result of combination of:
  - Zinc: ion exchange, electrostatic interactions, and surface complexation mechanisms.
  - Naphthalene: ion exchange.

Main Recommendations

- Dynamic studies need to be conducted.
- The interference in a mixture of the three species is recommended.
- Experimental equilibrium isotherms for binary and ternary mixtures are recommended.
- Biosorption study on real refinery wastewater after primary treatment is recommended.