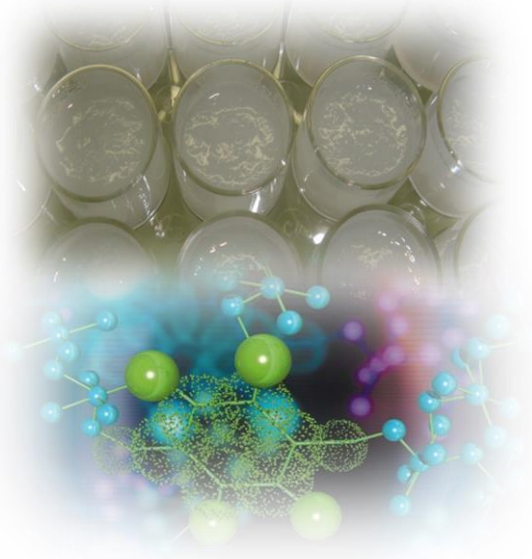
# Magnetic Chitosan/Polyvinyl Alcohol Nanocomposite Hydrogels: Synthesis, Characterization and Application in the Removal of Heavy Metals


Ahmed Abd El-Fattah, Ph.D

Department of Chemistry, College of Science, University of Bahrain, Kingdom of Bahrain

# Outline

- Introduction
- Scope of the work
- Experimental design
- Results & discussions
- Conclusions

# Introduction

# Heavy Metals: Hazardous Waste

- Most common heavy metals are lead (Pb), mercury (Hg), cadmium (Cd), cobalt (Co), nickel (Ni), and arsenic (As).
- High concentration of heavy metal are toxic to human health and aquatic life.
- They are mainly produced by ***industrial activities***, and deposit slowly in the surrounding water and soil.

# Heavy Metals: Hazardous Waste

- **Water pollution by heavy metals are dangerous due to their**

- **Bioaccumulation**

They are not broken down by bacteria and are effectively permanent

- **Toxic effect** kidney and liver problems and carcinogen

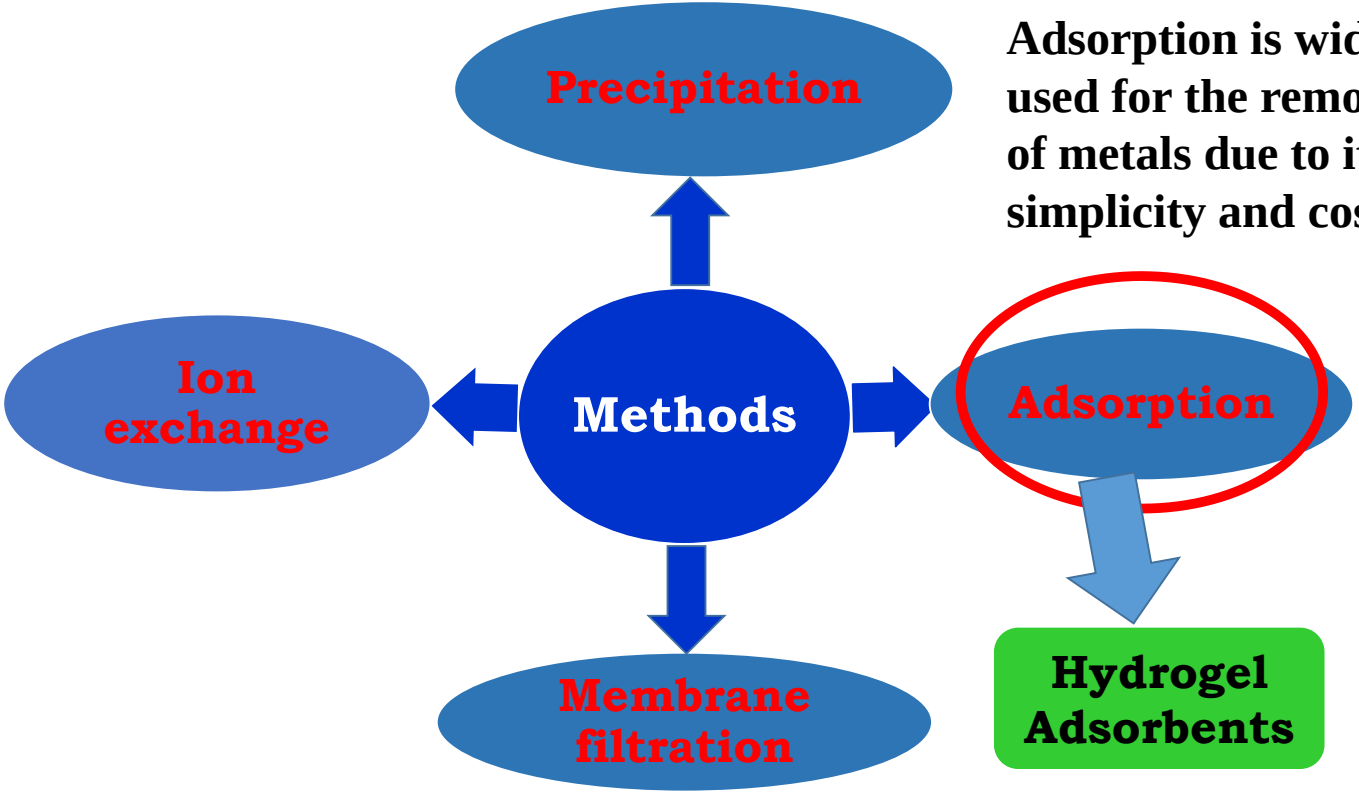
# Heavy Metals: Hazardous Waste

- Many researches have reported the serious pollution of ***groundwater*** and ***surface water*** caused by the heavy metals, which has led to the weakening of the quality of **drinking and irrigation water.**


**Water and Our Life**

# We need more of potable water

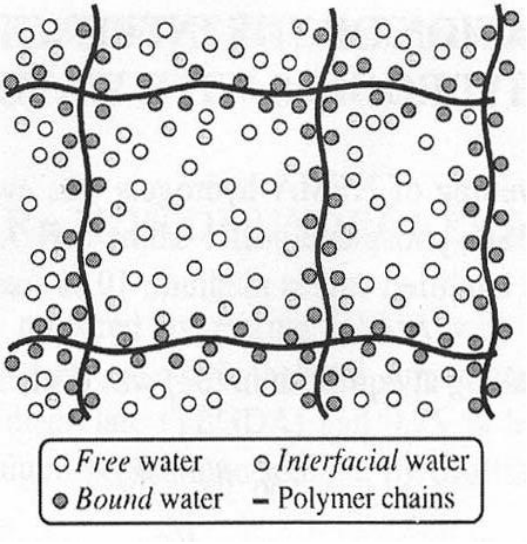
# Removal of Heavy Metals
# "Conventional Methods"




**Adsorption is widely used for the removal of metals due to its simplicity and cost**

# Polymeric Hydrogels

- 3D networks formed from hydrophilic polymers which are crosslinked to form insoluble polymer matrices.

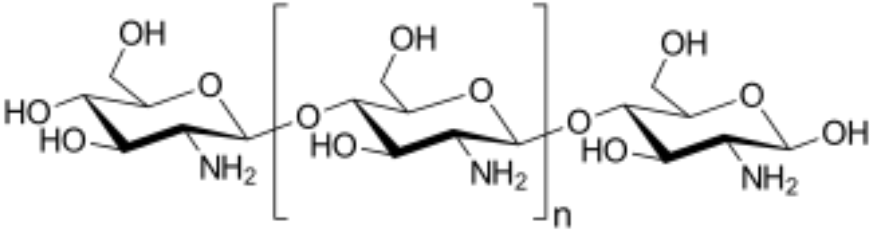



High degree of swelling in water

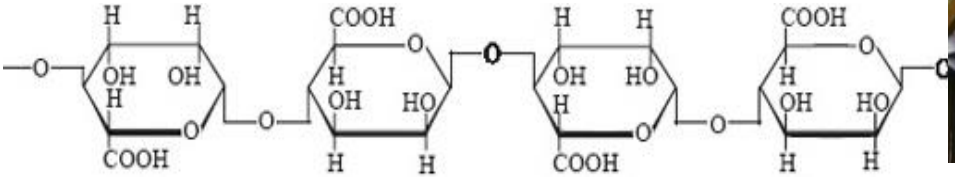
# Polymers for Hydrogel Preparation

- ***Natural polymers***
  - Anionic polymers: **alginate**, hyaluronic acid, pectin
  - Cationic polymers: **chitosan**, polylysine
  - Amphiphilc polymers: **collagen**, gelatin, fibrin
  - Neutral polymers: dextran, agarose

**Chitosan**



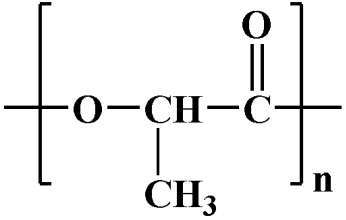

**Alginate**



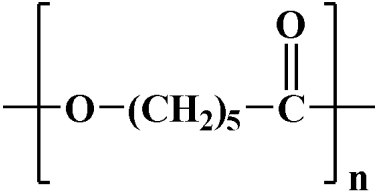

# Polymers for Hydrogel Preparation

- ***Synthetic polymers***

  - **Polyesters:** PLA, PCL,

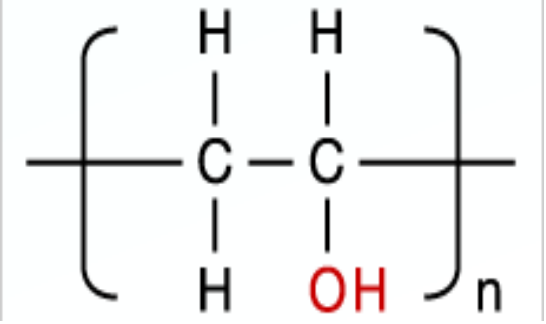



**PLA**




**PCL**

  - **Polyalcohol: PVA**




- ***Combinations of natural and synthetic polymers***

  Chitosan-co-PCL, alginate-g-PVA, alginate-co-acrylate

# Polymers for Hydrogel Preparation

## Advantages

- ❑Biocompatible
- ❑Biodegradable
- ❑Non-toxic
- ❑High adsorption capacity
- ❑Stability at different pHs

# Magnetic Adsorbent

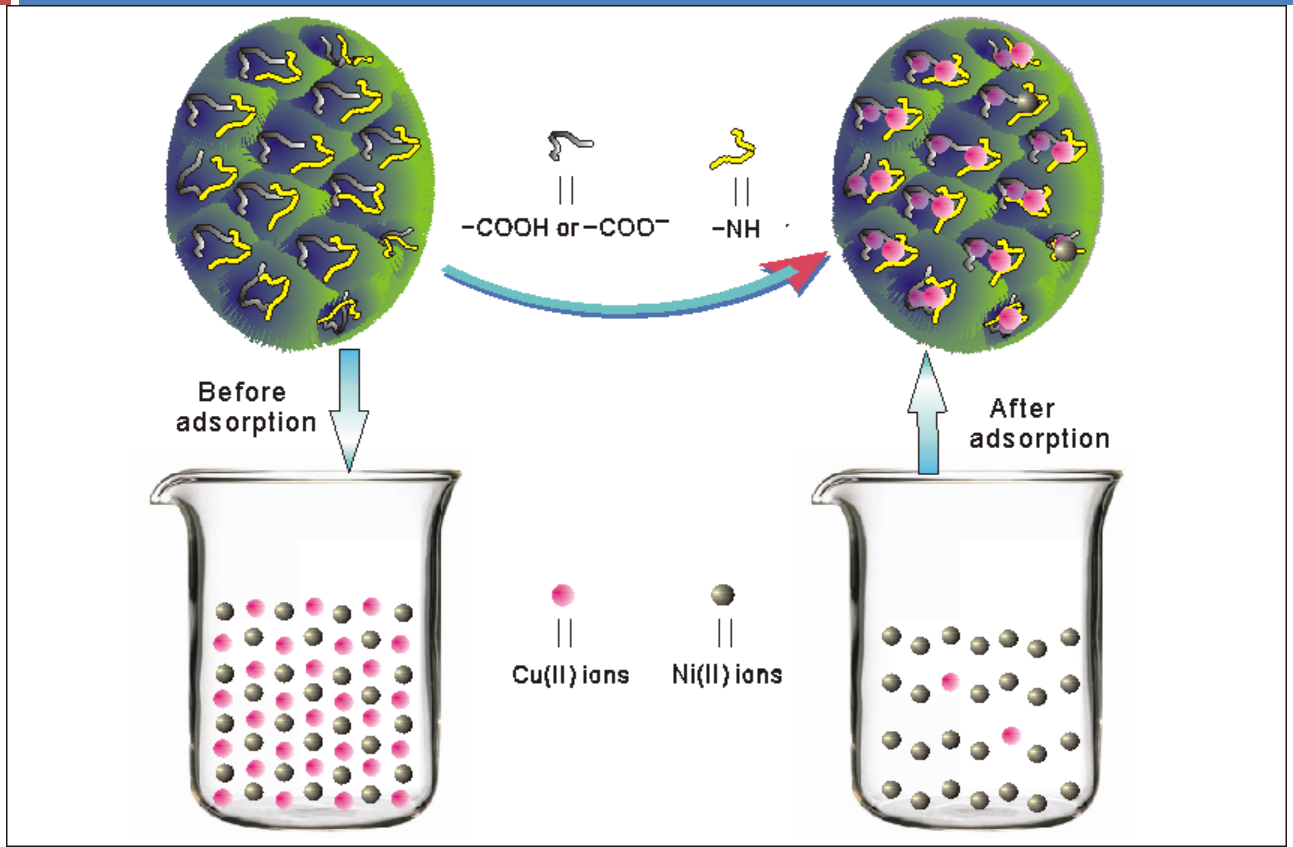
- In comparison with a traditional adsorbent, a magnetic adsorbent is considered to be an effective and rapid technique for separating heavy metals from aqueous solutions.
- Currently, iron oxide nanoparticles have been researched in the separation technologies field because of their cost-effective preparation.

# Nanocomposite Polymeric Hydrogel Adsorbents

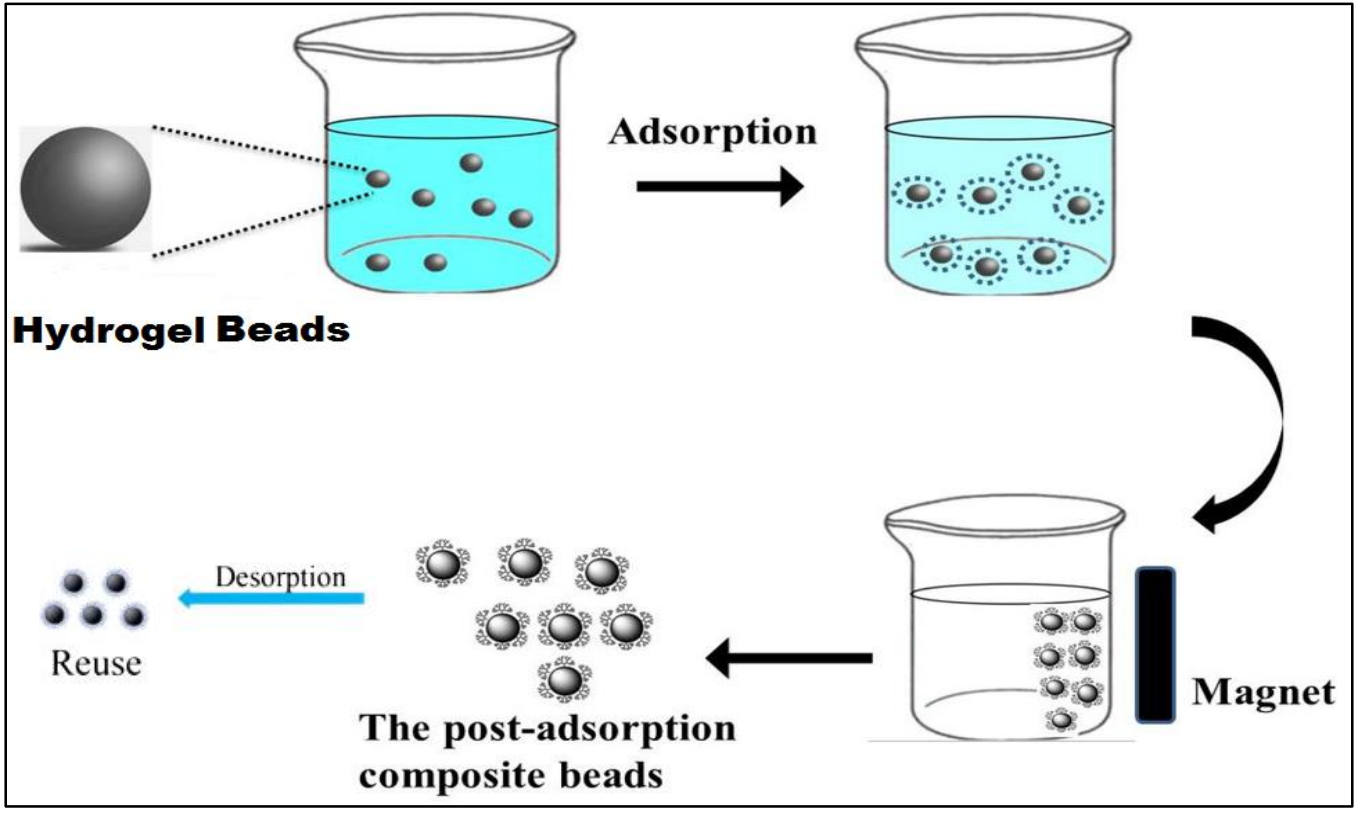
- The combination of biopolymer hydrogels and magnetic nanoparticles to form nanocomposite adsorbents leads to:

- **Improve the adsorption capacity**
- **Rapid the separation process**
- **Can be reuse**
- **Cost effective**

# Adsorption Mechanism



# Adsorption Mechanism



# AIM OF THE WORK

- Preparation and characterization of magnetic CS/PVA/$Fe_3O_4$ nanocomposite hydrogel beads for treatment of wastewater containing heavy metal such as: *$Co^{2+}$, $Ni^{2+}$ and, $Cd^{2+}$.*

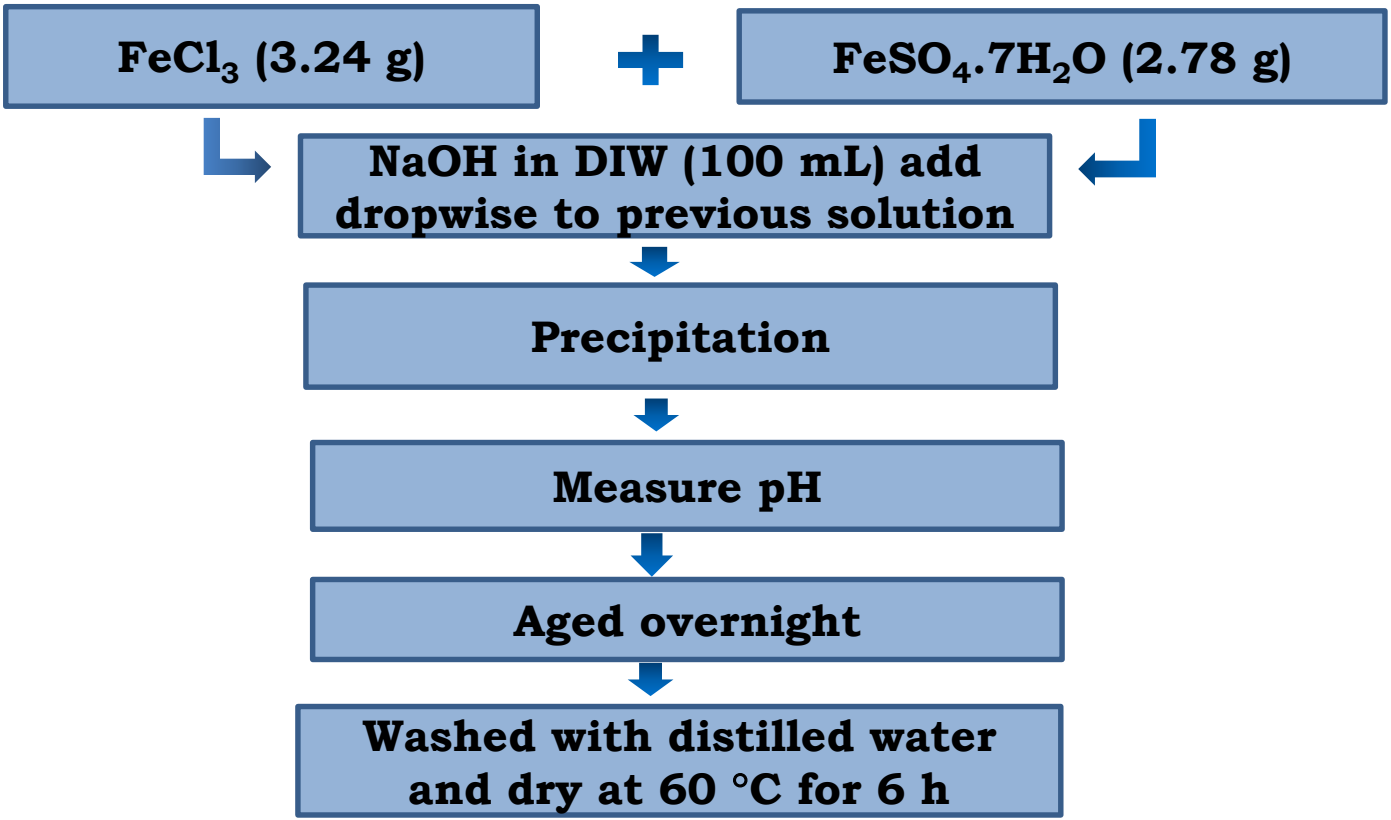
- Studying factors affecting the adsorption of heavy metal on the prepared hydrogel beads

# Materials and Methods

# Methods and Characterization

- $Fe_3O_4$ NPs
  - Coprecipitation
  - SEM
  - FT-IR
- Hydrogel beads
  - SEM
  - EDX
  - FT-IR
  - Atomic absorption spectroscopy
- Factors affect adsorption
  - pH
  - Weight of beads
  - Metal ion concentration
  - Contact time
- Adsorption isotherm
  - Langmiur
  - Freundlich
- Adsorption kinetics
  - Pseudo-first order
  - Pseudo-second order

# Magnetite Nanoparticles ($Fe_3O_4$ NPs)



# Preparation of Nanocomposite Hydrogel

CS (4 g) in acetic acid solution (100 mL, 3%)

PVA (4 g) in DIW (100 mL) Stirring overnight (70°C)

Mixing 30 min at 70°C

Adding $FeCl_3$+ $FeSO_4.7H_2O$ (0.02:0.01 mol) in DIW (25mL), stirring (30 min)

Dropwise to NaOH (300 mL, 10%), stirring 1 h

Washed by distilled water and preserved in NaOH

# Adsorption Parameters

| pH | Hydrogel beads weight | Metal ions concentration | Contact time |
|---|---|---|---|
| Range (1-8) | (2-10 g) | (50-250 mg/L) | 30 min until equilibrium |

The equilibrium adsorption capacity was calculated using equation:

$$q_e = \frac{(C_o - C_e)\,V}{W}$$

The metal removal percentage (R%) was calculated using Equation:

$$R\,(\%) = \frac{(C_o - C_e)\,.\,100}{C_o}$$

# Adsorption Isotherm

## Isotherm models

### Langmiur isotherm

$$C_e/q_e = C_e/q_m + 1/bq_m$$

$$R_L = 1 / (1+bC_o)$$

### Frenudlich isotherm

$$\ln q_e = \ln K_F + 1/n \ln C_e$$

# Adsorption Kinetics

**Kinetics models**

**Pseudo-first order**

$$\ln(q_e - q_t) = \ln q_e - K_1 t$$

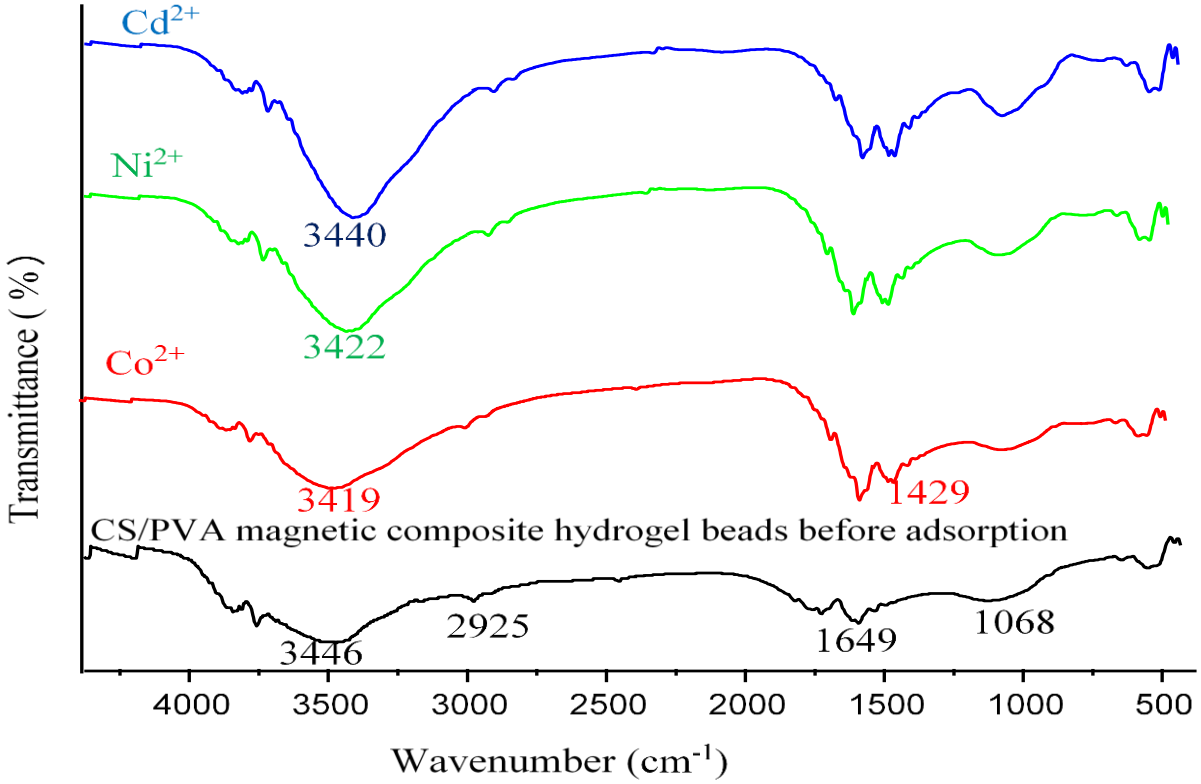
**Pseudo-second order**

$$t/q_t = 1/K_2 qe^2 + t/q_e$$

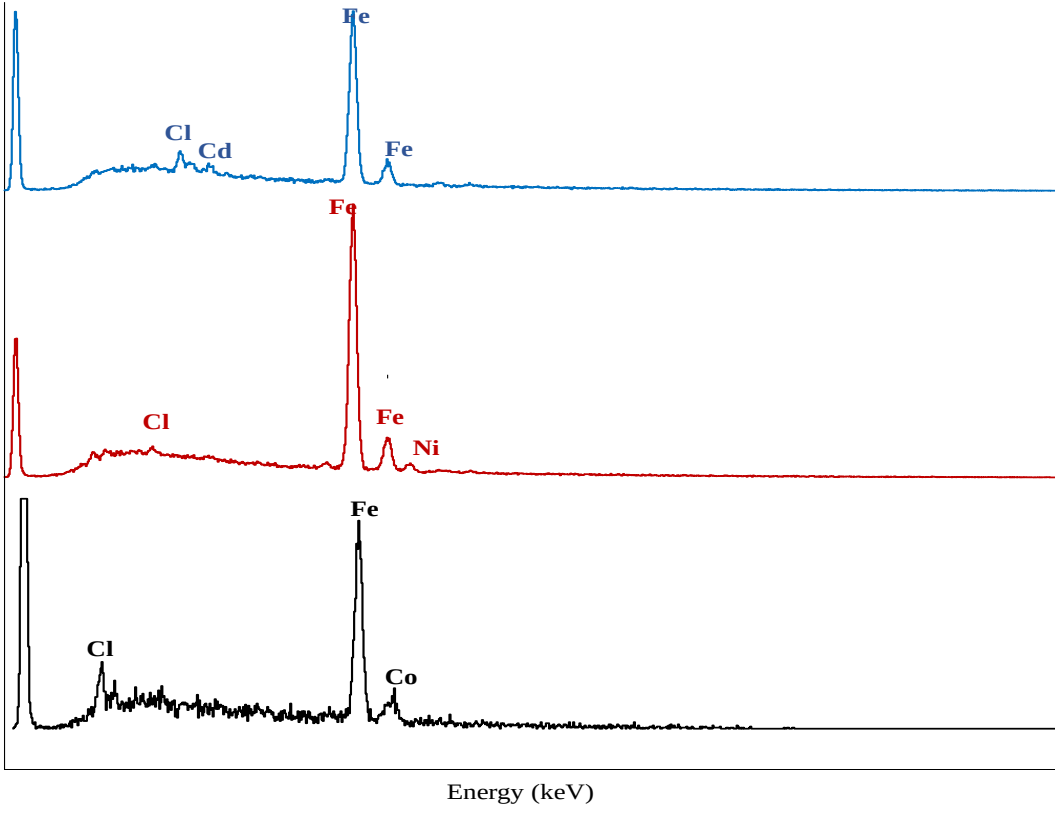
$$t/q_t = 1/h + (1/q_e)\, t$$

# Results and Discussion

# Characterization of CS/PVA/$Fe_3O_4$ hydrogel beads by FTIR

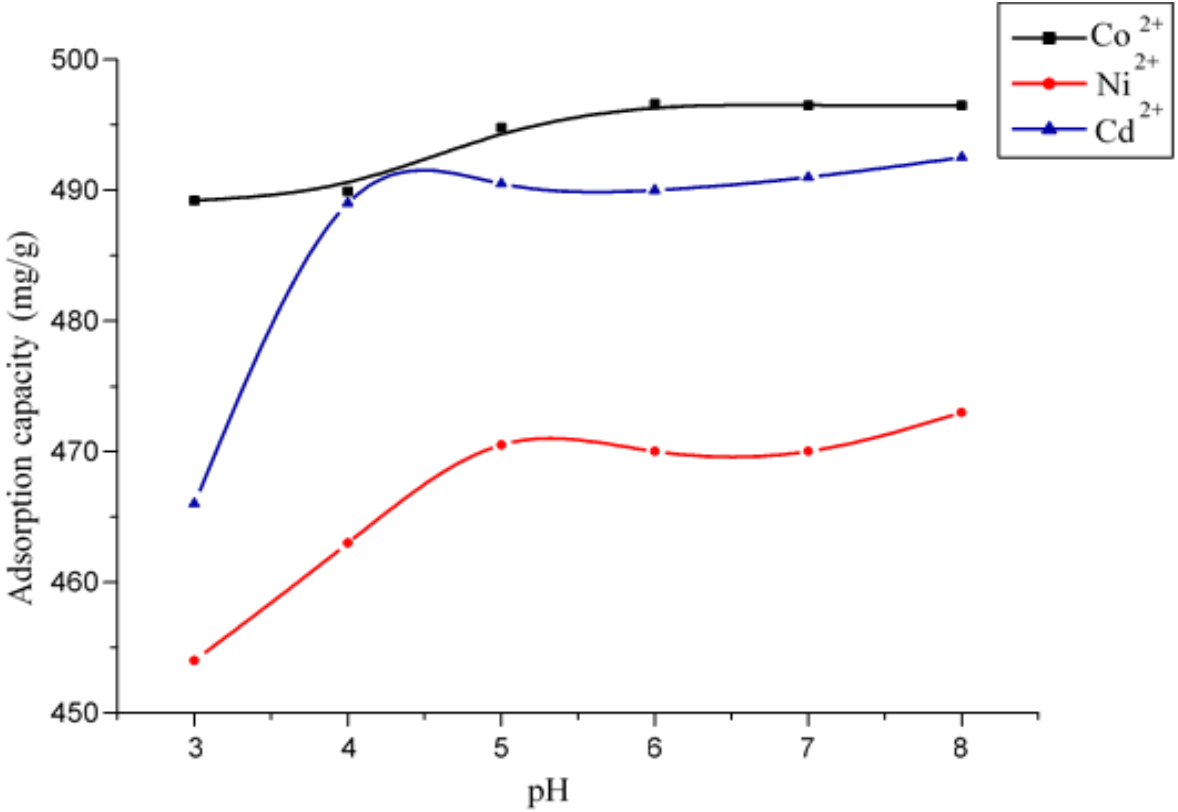


# Characterization of CS/PVA/$Fe_3O_4$ hydrogel beads by EDX

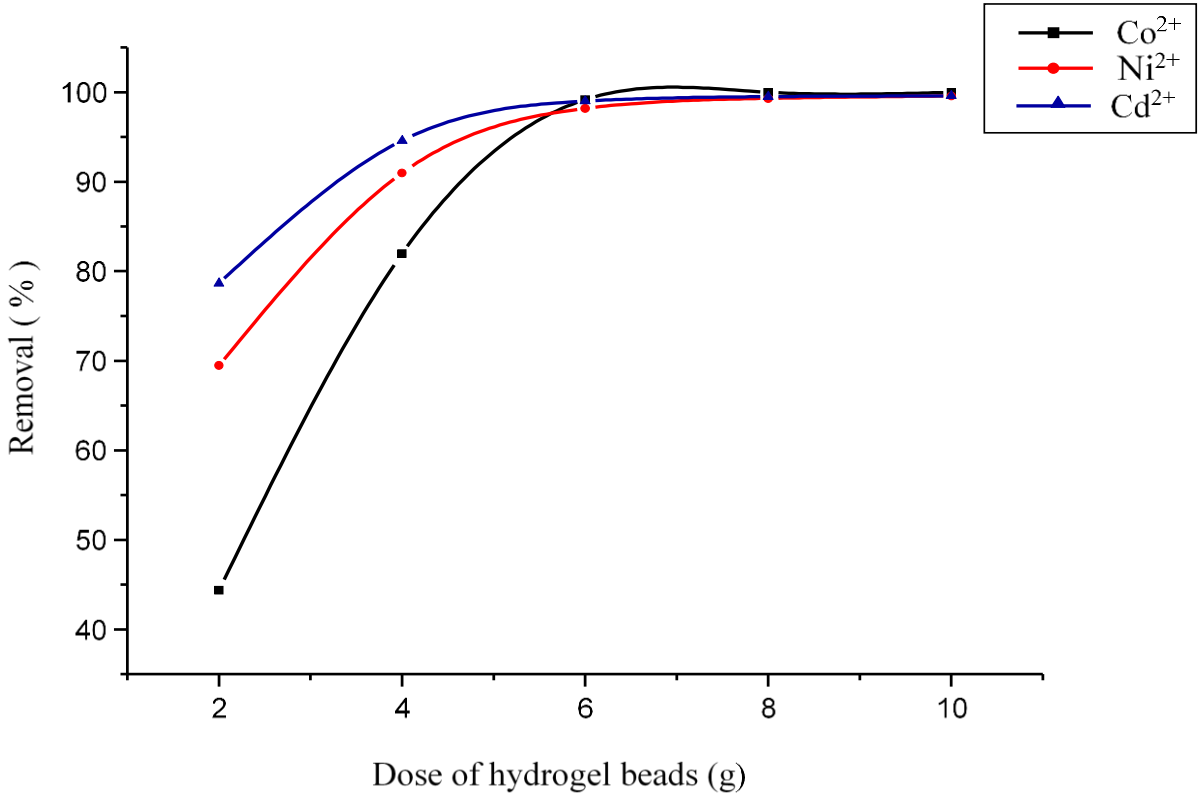


# *Characterization of CS/PVA/$Fe_3O_4$ hydrogel beads by SEM*

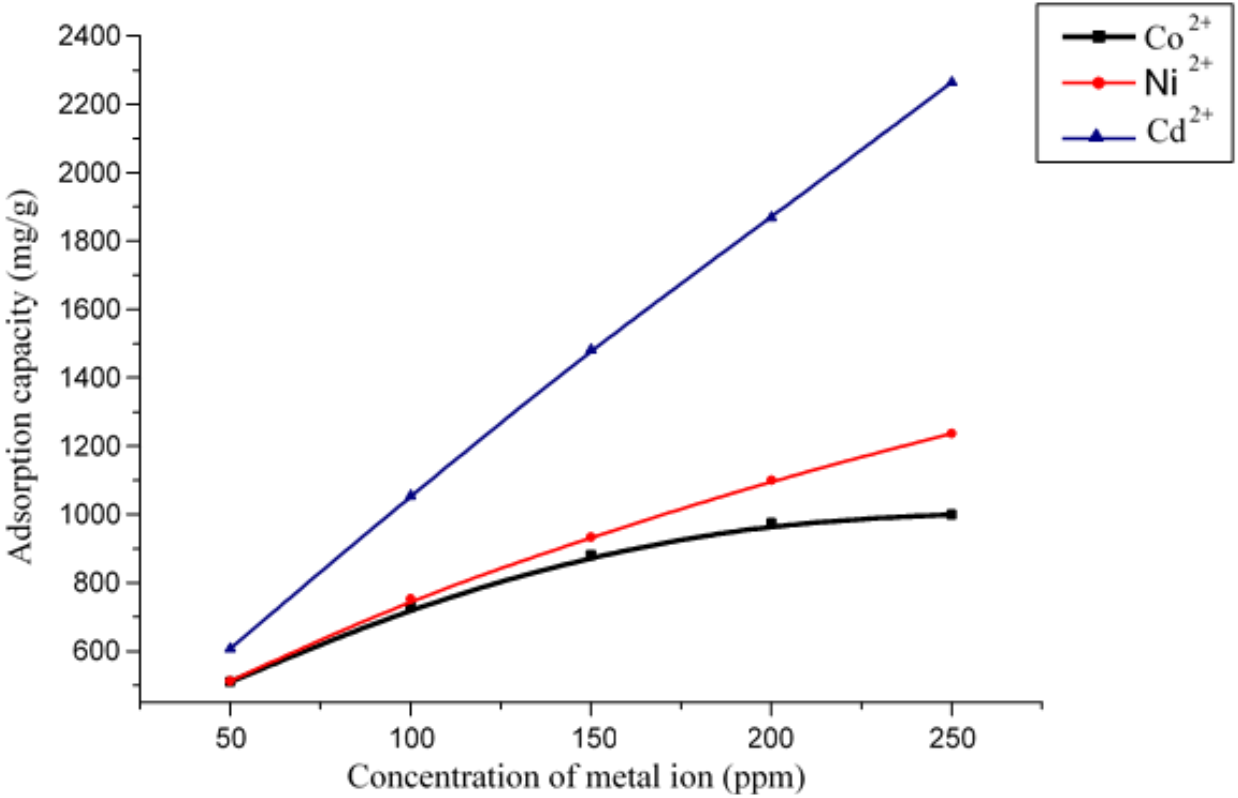
# *Effect of pH on the adsorption of $Co^{2+}$, $Ni^{2+}$ and $Cd^{2+}$ ions onto the hydrogel beads*



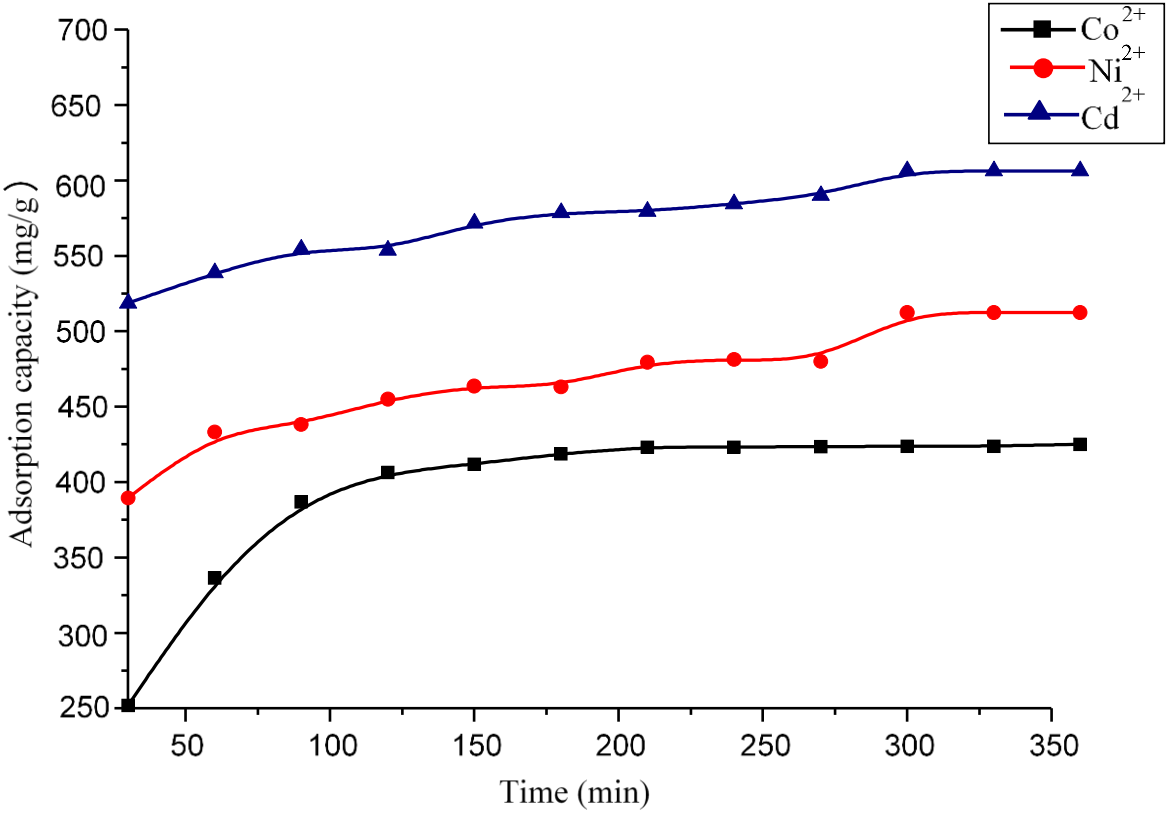
# *Effect of hydrogel beads dosage on the removal of $Co^{2+}$, $Ni^{2+}$ and $Cd^{2+}$ ions*



# *Effect of metal ion concentration on the adsorption of $Co^{2+}$, $Ni^{2+}$ and $Cd^{2+}$ ions*



# *Effect of contact time on the adsorption of $Co^{2+}$, $Ni^{2+}$ and $Cd^{2+}$ ions*



# Conclusion

- CS/PVA/$Fe_3O_4$ magnetic hydrogel beads were prepared, characterized and used as adsorbent for $Co^{2+}$, $Ni^{2+}$ and $Cd^{2+}$ ions from aqueous solution.
- Adsorption of $Co^{2+}$, $Ni^{2+}$ and $Cd^{2+}$ ions is due to attraction between the adsorbents surface and heavy metals.
- The optimum operating parameters for higher adsorption of Co (II), Ni (II), and Cd (II) ions onto the hydrogel beads were 0.38 g hydrogel beads, pH 6, 50 mg/L metal ion concentration, 6 h contact time and 300 rpm shaking speed.

# Conclusion

- A simple preparation procedure, cheap chitosan feedstock, great adsorption capacity, and good reusability make the beads an economically and environmentally friendly adsorbent for removal of the tested heavy metal ions from the aqueous environment.


Thank
you!