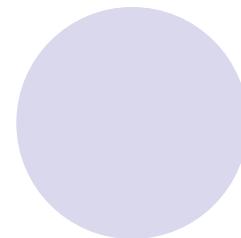
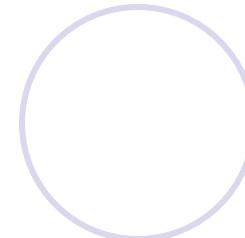
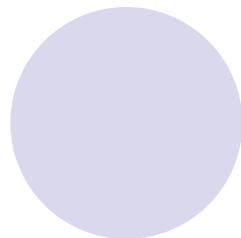
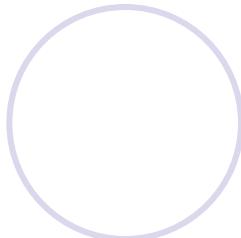
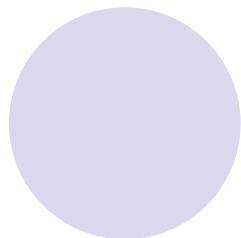


**I THANK THE ORGANIZERS TO GIVE ME THE OPPORTUNITY  
TO ATTEND THIS VERY INTERESTING SYMPOSIUM  
AND I APPRECIATE THEIR EFFORTS  
TO BRING TOGETHER SPECIALISTS IN THIS EXCITING FIELD!**



## **NOVEL BIPOLAR RESINS**

### **SYNTHESIS AND THEIR RETENTION PROPERTIES OF INORGANIC SALTS**

**VIOLETA NEACU, CORNELIA LUCA, SILVIA VASILIU**

"PETRU PONI" INSTITUTE OF MACROMOLECULAR CHEMISTRY, IASI  
ROMANIA



# CONTENT

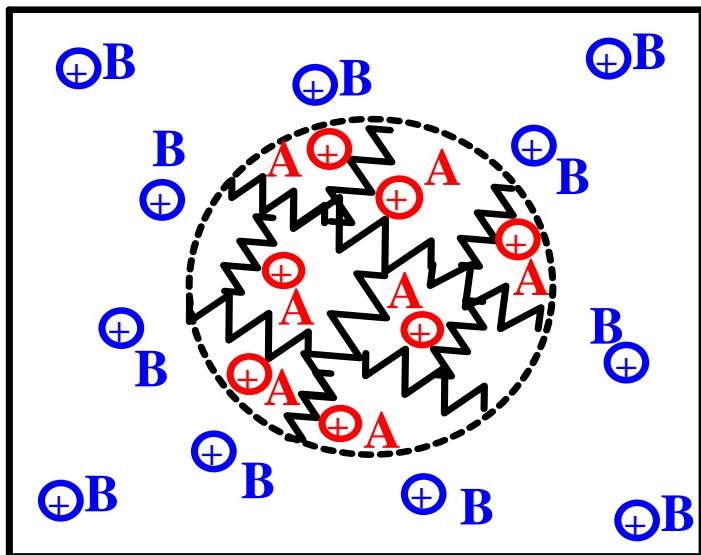


**I. SYNTHESIS OF THE BIPOLEAR ION EXCHANGERS BASED  
ON THE PYRIDINE CROSSLINKED COPOLYMER**

**II. RETENTION STUDY OF THE HEAVY METALS ON THE PYRIDINE  
BIPOLEAR RESINS**

## ION EXCHANGER

### *WHAT IS IT?*



**Ion exchangers are solid polyelectrolytes which can exchange their mobile ions for ions of the same charge from the surrounding medium.**

The ion exchangers are tools for the established procedures and technologies of the ion exchange.

## BENEFITS OF THE ION EXCHANGE PROCESS:

- ***highly efficient process, > 99.9% removal of desired ions***
- ***very high water recovery, > 97%***
- ***predictable performance***
- ***ability to remove selective impurities***
- ***re-use after regeneration up to several cycles***

## APPLICATIONS OF ION EXCHANGERS:

WATER TREATMENT

HYDROMETALLURGY

FOOD INDUSTRY

CHEMICAL PROCESS INDUSTRY

BIOCHEMISTRY AND BIOTECHNOLOGY, PHARMACEUTICALS

MEDICINE, POLLUTION CONTROL, ANALYTICAL CHEMISTRY.....

.....

## HOW DOES IT WORK?

ORGANIC

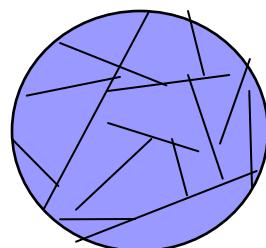
INORGANIC

NATURAL

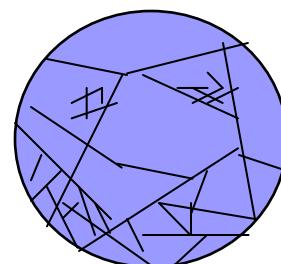
SYNTHETIC

Polymerization

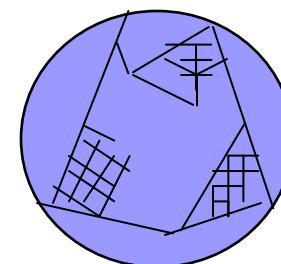
Polycondensation



GEL TYPE



ISOPOROUS TYPE



MACROPOROUS TYPE

## ION EXCHANGE MATERIALS

- Beads**
- Films**
- Fibers**
- Fabrics**
- Tubes**
- Foams**
- Plates**

### BEADS OR GRANULES

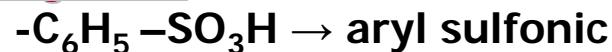
THERE ARE QUITE A NUMBER OF  
DIFFERENT TYPES OF ION EXCHANGERS BUT  
THOSE BASED ON BEADS OR GRANULES ORGANIC POLYMERS  
BECOME THE MOST IMPORTANT

## CATION EXCHANGER

- Weak Acid:

- COOH → carboxylic acid
- C<sub>6</sub>H<sub>5</sub>-OH → phenolic hydroxyl

- Strong Acid:



## ANION EXCHANGER:

- Weak Base:

- NH<sub>2</sub> → primary amine
- NHR → secondary amine
- NR<sub>2</sub> → tertiary amine

- Strong Base:

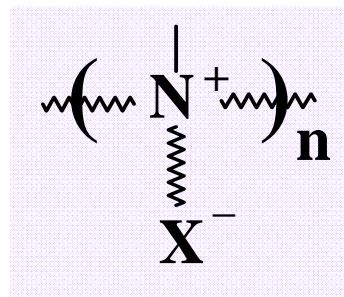
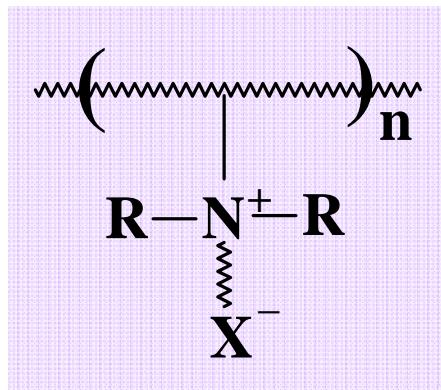
- >N<sup>+</sup>< → quaternary ammonium
- >P<sup>+</sup>< → phosphonium
- S<sup>+</sup>< → sulfonium

## BIPOLAR EXCHANGERS: mixture of acid and base groups

- Amphoteric

- Zwitterionic

## ZWITTERIONIC EXCHANGERS ION EXCHANGERS WITH BETAINE STRUCTURES



Where  $\text{X}^-$  = carboxylate

= sulfonate

= phosphate/  
phosphonate/  
phosphinate

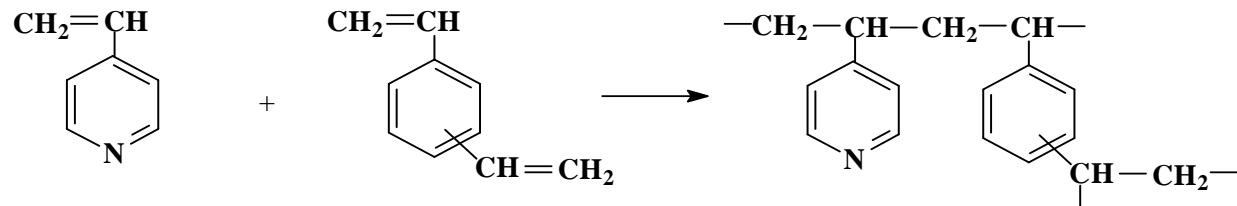
CROSSLINKED POLYCARBOXYBETAINES

CROSSLINKED POLYSULFOBETAINES

CROSSLINKED POLYPHOSPHOBETAINES

# SYNTHESIS OF CROSSLINKED POLYCARBOXYBETAINES

## 1. Synthesis of 4-vinylpyridine : divinylbenzene copolymers

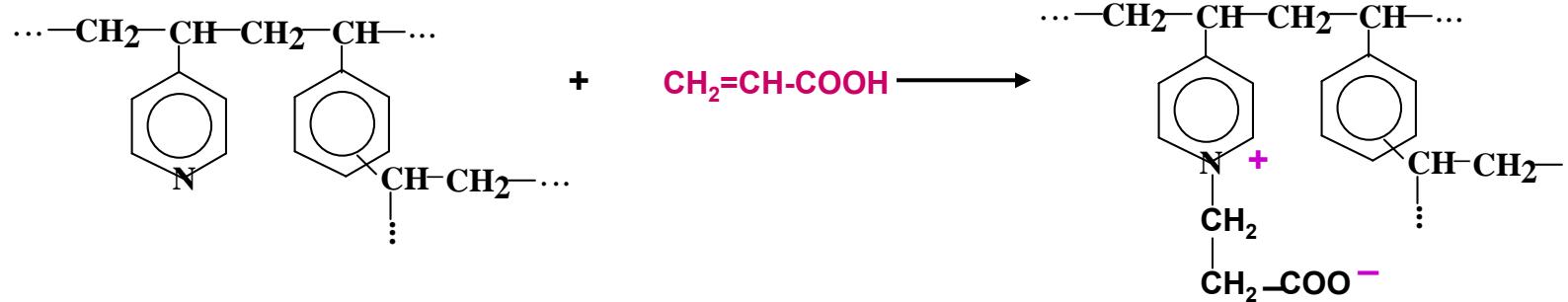


## 2. Synthesis of polycarboxybetaines

### Nucleophilic substitution



### Nucleophilic addition

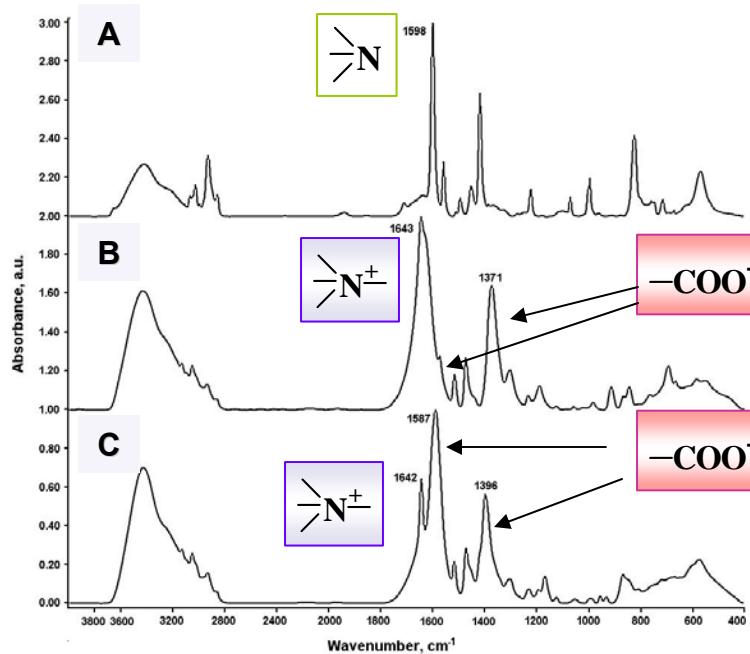


## FT-IR characterization of the bipolar pyridine resins

4-VP : DVB

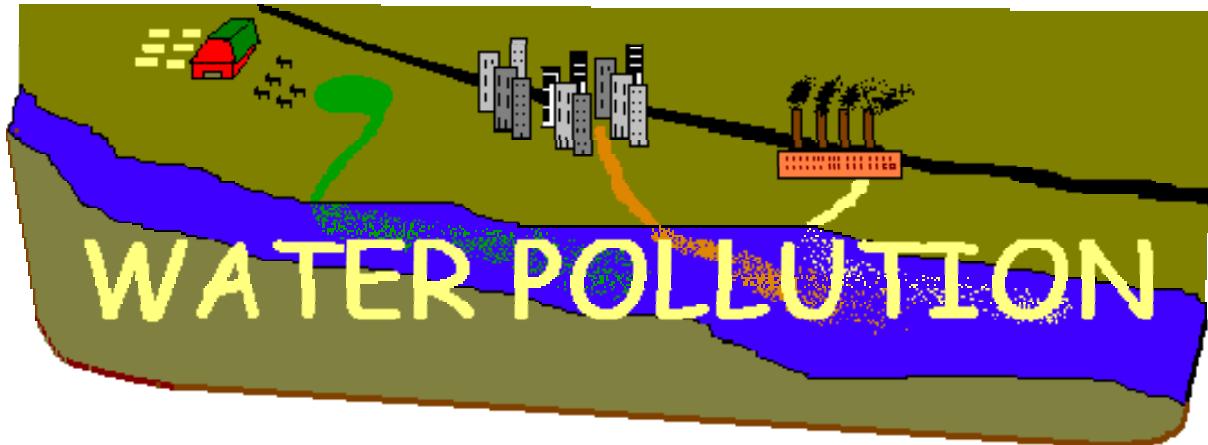
BPR1  
DB = 90%

BPR2  
DB = 94%



## Chemical stability of the bipolar pyridine resins

HCl → Na<sub>2</sub>CO<sub>3</sub>



The most polluting sources are the city sewage and industrial waste discharged into the rivers.

## TODAY

Roadways and automobiles are considered to be one of the largest sources of heavy metals

### COMMON METALS IN ROAD RUNOFF

Lead: leaded gasoline, tire wear, lubricating oil and grease, bearing wear

Zinc: tire wear, motor oil, grease, brake emissions, corrosion of galvanized parts

Iron: auto body rust, engine parts

Copper: bearing wear, engine parts, brake emissions

Cadmium: tire wear, fuel burning, batteries

Chromium: air conditioning coolants, engine parts, brake emissions

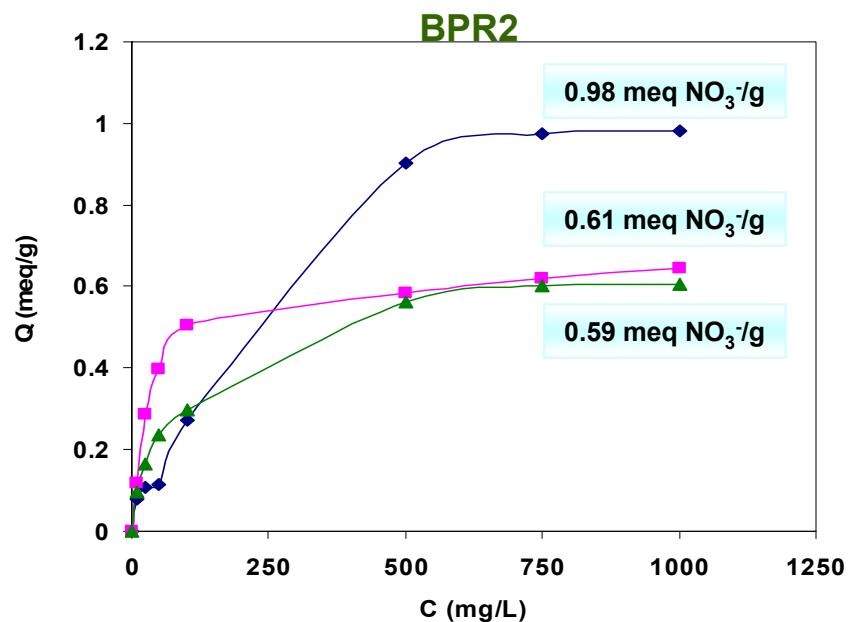
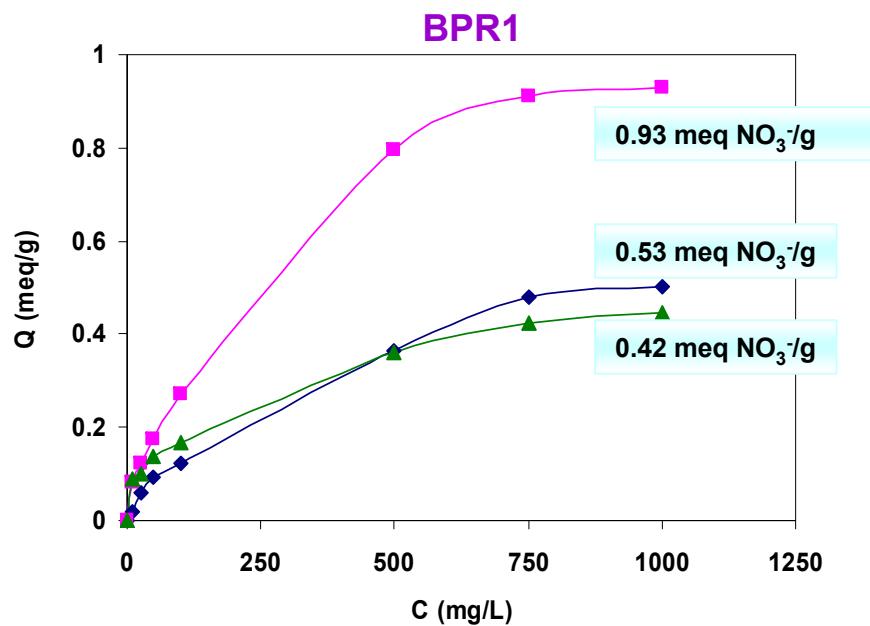
Nickel: diesel fuel and gasoline, lubricating oil, brake emissions

Aluminum: auto body corrosion

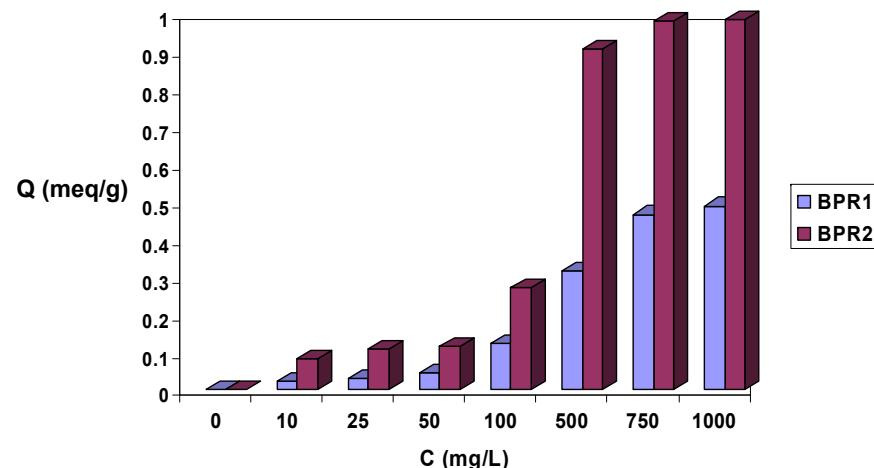
## METAL RETENTION STUDY ON THE CROSSLINKED POLYCARBOXYBETAINES

### 1. Thermodynamic study

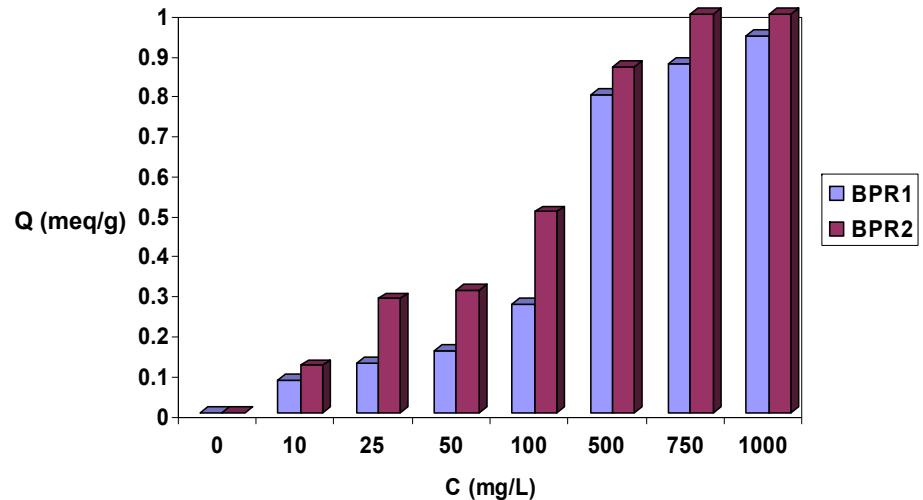
Cu      Cd      Co       $(\text{NO}_3^-)_2$



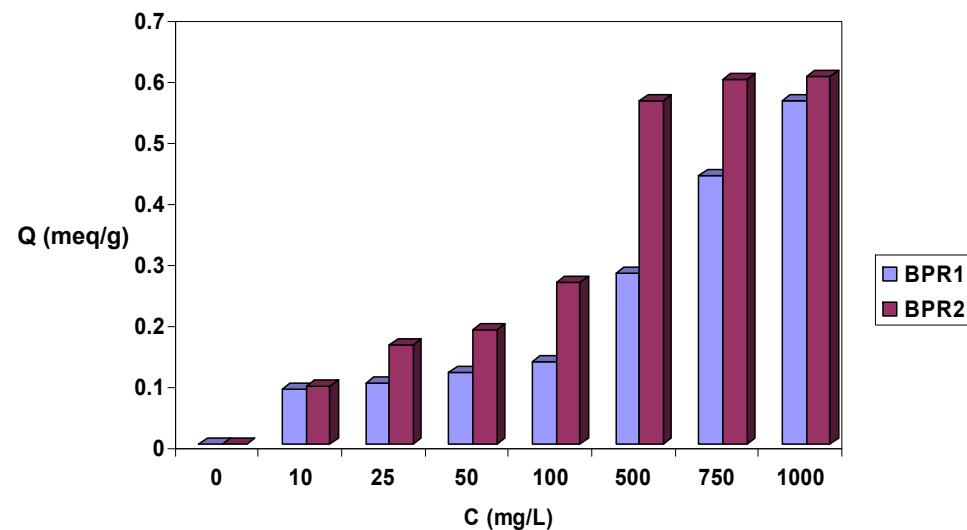
**Cd(II)**



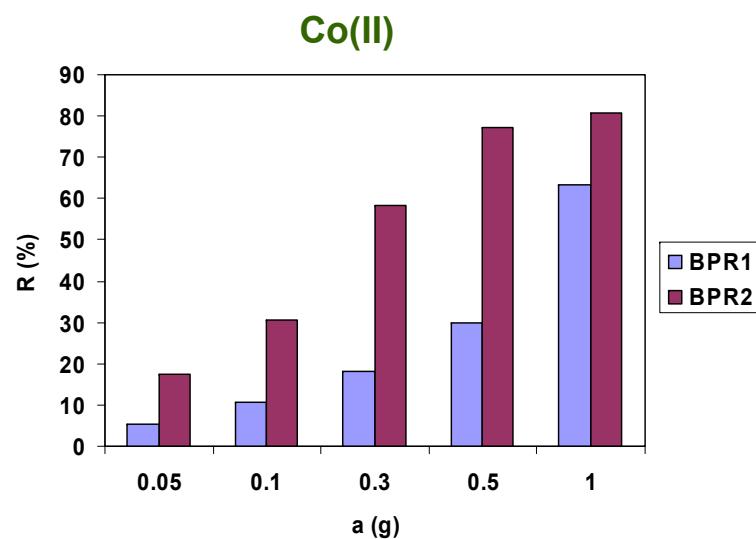
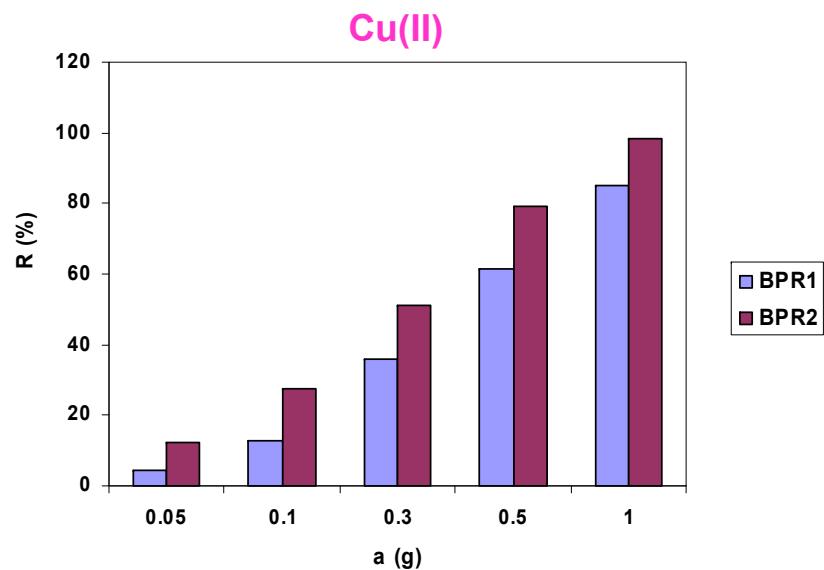
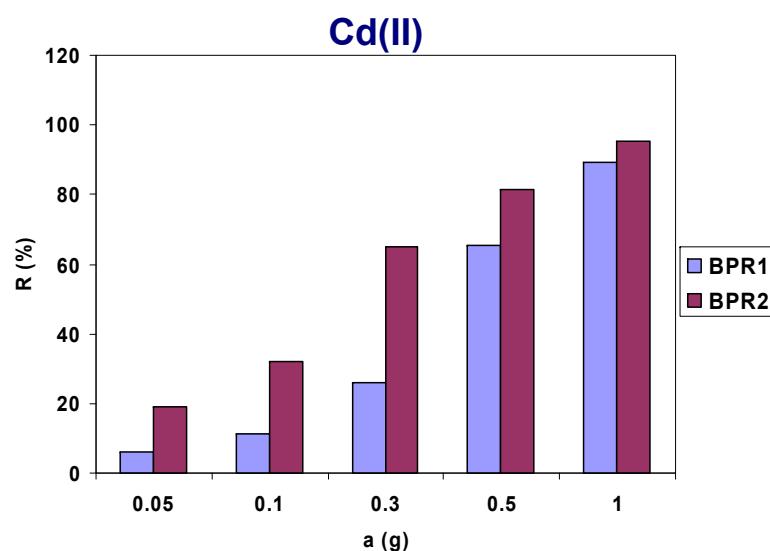
**Cu(II)**



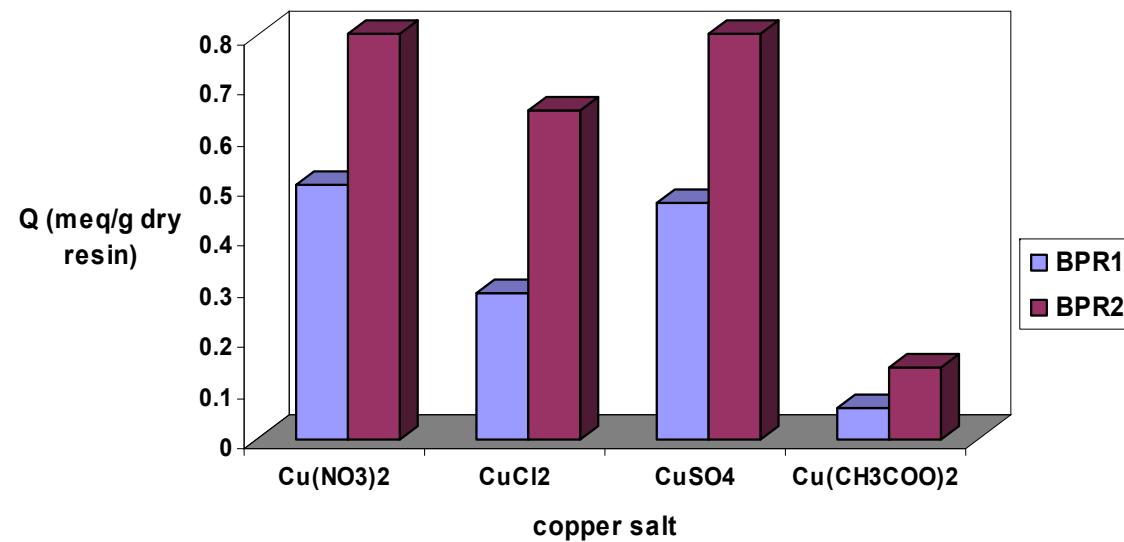
**Co(II)**



## Recovery factor of the studied heavy metals

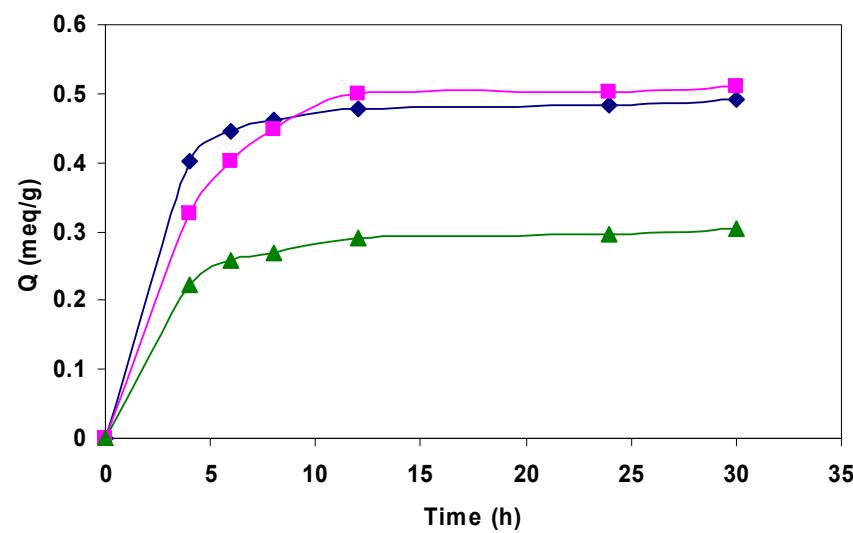


## Retention of Cu(II) from various salts

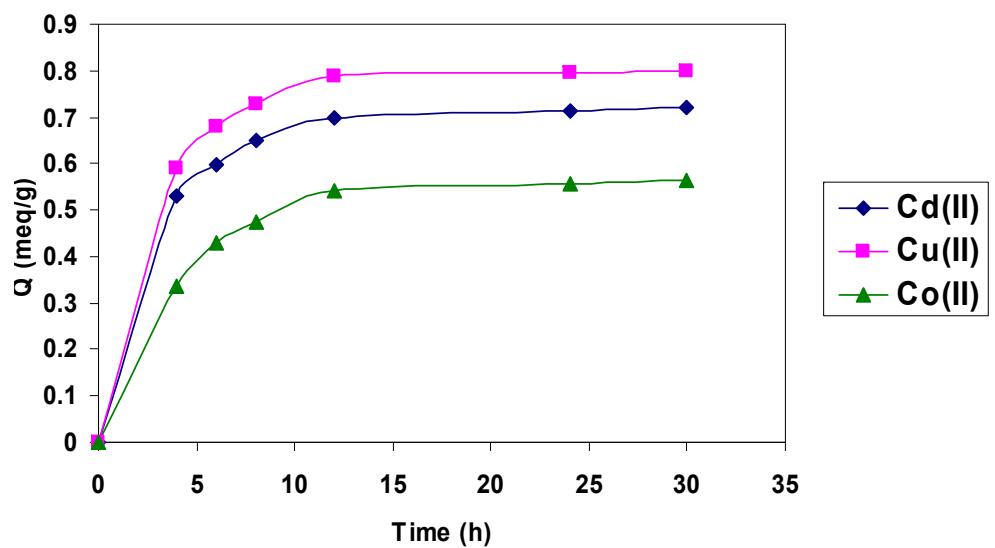


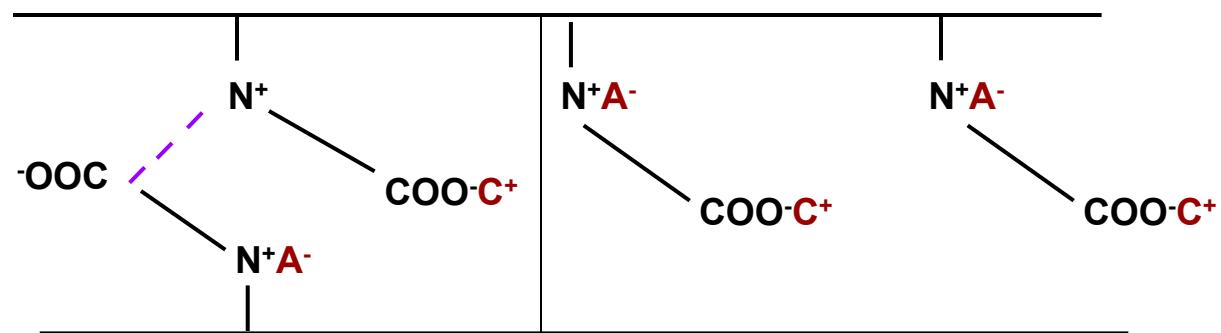
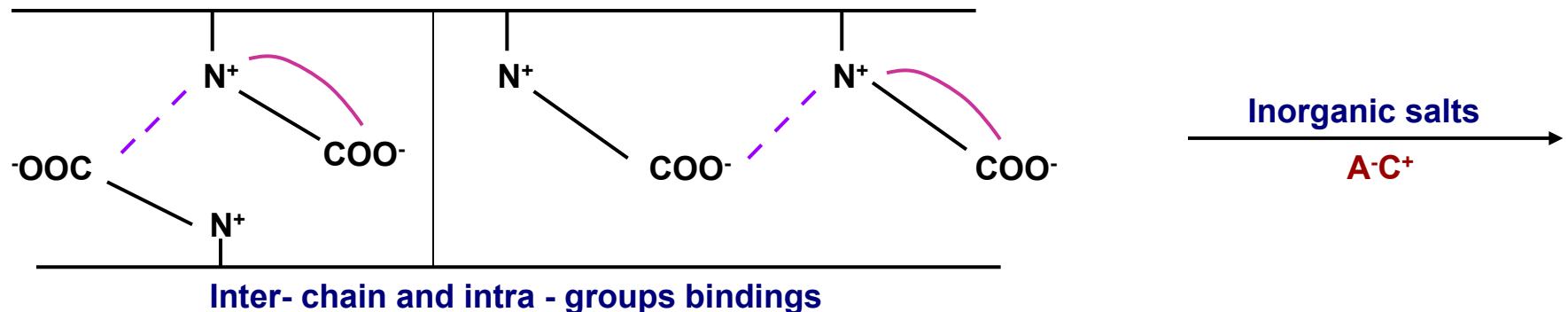
## 2. Kinetic study

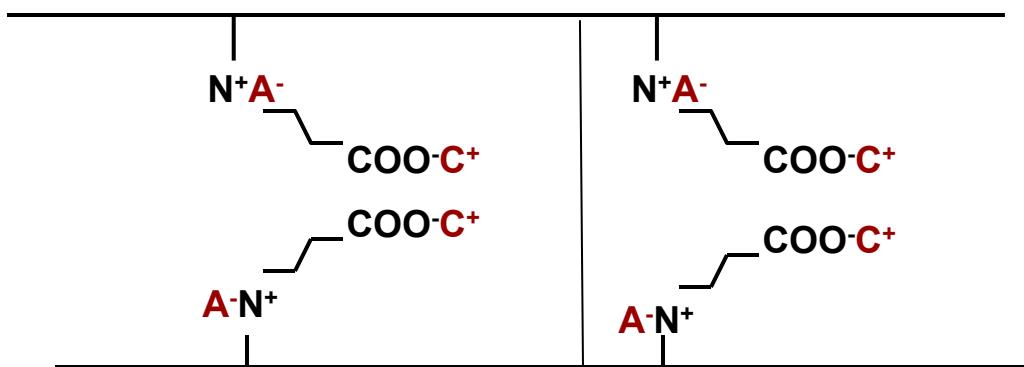
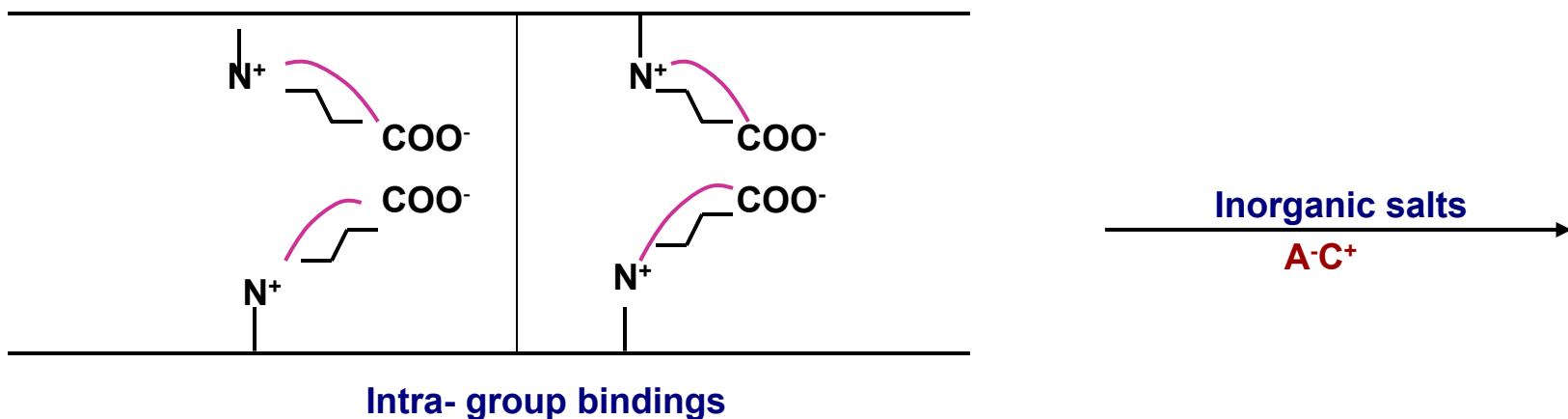
BPR1



BPR2

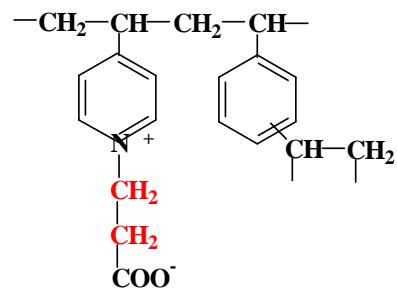
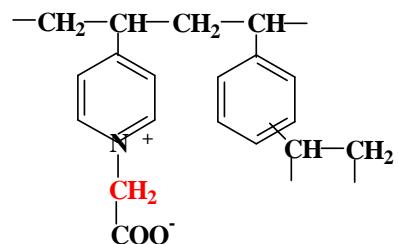


**BPR1**

**BPR2**

## CONCLUSIONS

### CROSSLINKED POLYCARBOXYBETAINES BASED ON 4-VINYLPYRIDINE : DIVINYLBENZENE



BIPOLAR ION EXCHANGERS CONCOMITENTLY BIND  
THE CATIONS AND ANIONS ( $\text{A}\cdot\text{C}^+$ ) FROM INORGANIC SALTS

# THANK YOU FOR YOUR ATTENTION!