



POLITECNICO DI MILANO

INNOVATIVE MATERIALS FOR HEAVY METALS REMOVAL FROM WATER

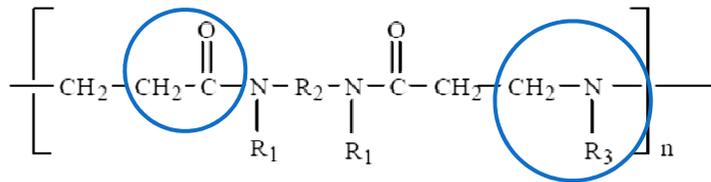
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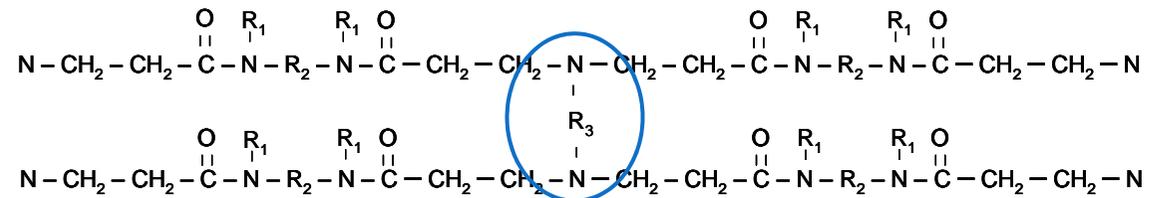


POLYAMIDOAMINE (PAA) HYDROGELS



LINEAR PAA

PAA HYDROGEL



“TARGET ORIENTED” MATERIALS

TO OVERCOME THE LIMITS OF THE EXISTENT TECHNOLOGIES
FOR HEAVY METALS REMOVAL FROM WATER

LOW SELECTIVITY

LOW REMOVAL CAPACITY

LONG EQUILIBRIUM TIMES

pH DEPENDANCE



AIM OF THE PROJECT

WATER/HYDROGEL INTERACTIONS

stability,
changes in chemical
composition of water.

IMPLEMENTATION IN WATER TREATMENT PLANTS

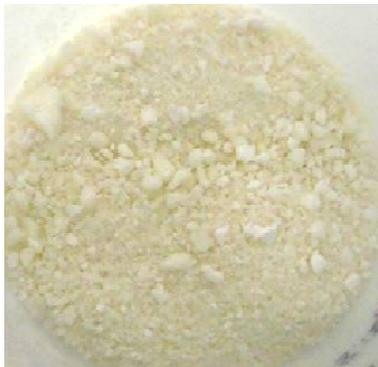
regeneration,
filterability,
breakthrough curves.

SUITABILITY FOR THE REMOVAL OF INORGANIC POLLUTANTS

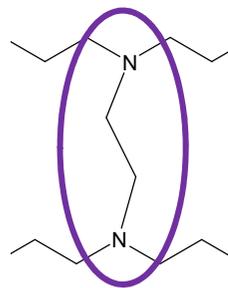
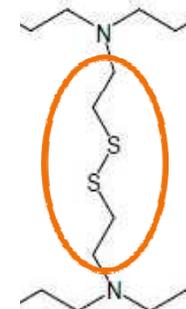
kinetics,
maximum complexing
capacity,
interferences.



PAA TESTED SAMPLES



MBA/CYS



MBA/EDA



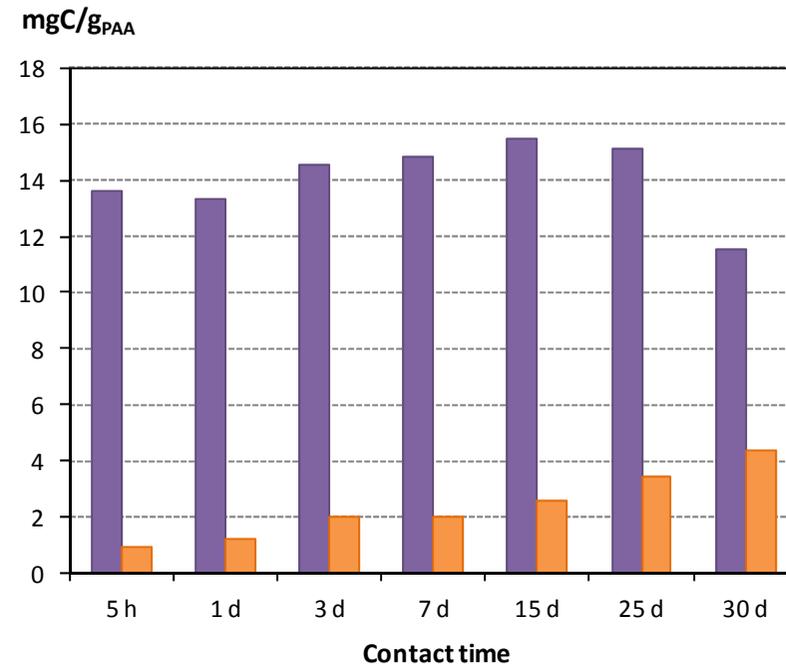


WATER/IDROGEL INTERACTIONS

- Absorption of large amount of water leading to a **VOLUMETRIC EXPANSION**

- **DEGRADATION** over time via hydrolysis

Release of Total Organic Carbon



- **ION EXCHANGE** of anions present in aqueous phase as WBA resin



REMOVAL OF Cu^{2+} : KINETIC TESTS

COMPLEXATION of HEAVY METALS IONS

due to tertiary aminic, carboxyl groups and disulphide groups

- Batch tests at different contact time
- Tap water with Cu(II) (2 mg/L)
- $T \sim 23/24^{\circ}\text{C}$
- Contact mode: mechanical mixing
- **S/L ratio = 1/150 – 1/300 – 1/600 g/mL**
- Analyses: pH, CES, C(Cu)

S/L [g/mL]	PARTICLE SIZE	EQUILIBRIUM CONDITIONS					
		MBA/EDA			MBA/CYS		
		Time [h]	Concentration [mgCu/L]	Complexing capacity [mgCu/g _{RESIN}]	Time [h]	Concentration [mgCu/L]	Complexing capacity [mgCu/g _{RESIN}]
1/150	1mm<d<2mm	16	0.22	0.27	6	0.26	0.26
	d<1mm	2	0.17	0.27	2	0.09	0.29
1/300	1mm<d<2mm	48	0.17	0.55	N.A.	N.A.	N.A.
	d<1mm	16	0.23	0.53	16	0.3	0.51
1/600	1mm<d<2mm	48	0.5	0.9	48	0.32	1.01
	d<1mm	24	0.28	1.03	N.A.	N.A.	N.A.



REMOVAL OF Cu^{2+} : KINETIC TESTS

**COMPLEXING CAPACITY
AT THE EQUILIBRIUM**



S/L RATIO

mass of copper provided
to the unit mass of
hydrogel

S/L [g/mL]	PARTICLE SIZE	EQUILIBRIUM CONDITIONS					
		MBA/EDA			MBA/CYS		
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REMOVAL OF Cu^{2+} : KINETIC TESTS

**RESIDUAL
CONCENTRATION
AT THE EQUILIBRIUM**

not influenced
by S/L ratio

different
from zero

DYNAMIC EQUILIBRIUM

established by

$$\Delta C = C_{\text{RESIN}} - C_{\text{WATER}}$$

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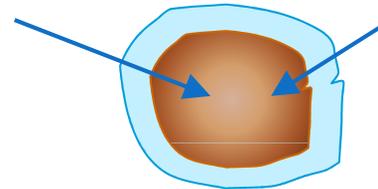


REMOVAL OF Cu^{2+} : KINETIC TESTS

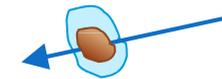
EQUILIBRIUM TIME



PARTICLE SIZE



$1 \text{ mm} < d < 2 \text{ mm}$



$d < 1 \text{ mm}$

S/L [g/mL]	PARTICLE SIZE	EQUILIBRIUM CONDITIONS					
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REMOVAL OF Cu^{2+} : KINETIC TESTS

DIFFUSION COEFFICIENTS

INTRAPARTICLE DIFFUSION

$$\frac{\partial q_m}{\partial t} = \left(\frac{D_s}{r^2} \right) \cdot \frac{\partial}{\partial r} \left(r^2 \frac{\partial q_m}{\partial r} \right)$$

D_s : effective surface diffusivity [cm^2/s]

FLUID - FILM DIFFUSION

$$\rho_s \left(\frac{\partial q_t}{\partial t} \right) = k_F \cdot a_p \cdot (c_t - c_s)$$

k_F : fluid film mass transfer coefficient [cm/s]

$$\frac{dC}{dt} = -K_L \cdot C^n - K_P \cdot C^m - \cancel{K_N \cdot C^p} - \cancel{K_{SS} \cdot C^q}$$

→ INTRAPARTICLE DIFFUSION

→ FILM DIFFUSION



REMOVAL OF Cu^{2+} : KINETIC TESTS

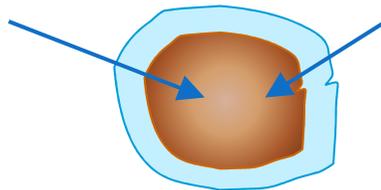
DIFFUSION COEFFICIENTS

$$\frac{dC}{dt} = -k_{MAX} \cdot \frac{C}{K_C + C}$$

$K_C = K_L + K_P$

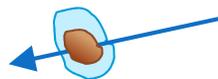
$1 \text{ mm} < d < 2 \text{ mm}$

- FILM DIFFUSION
- INTRAPARTICLE DIFFUSION

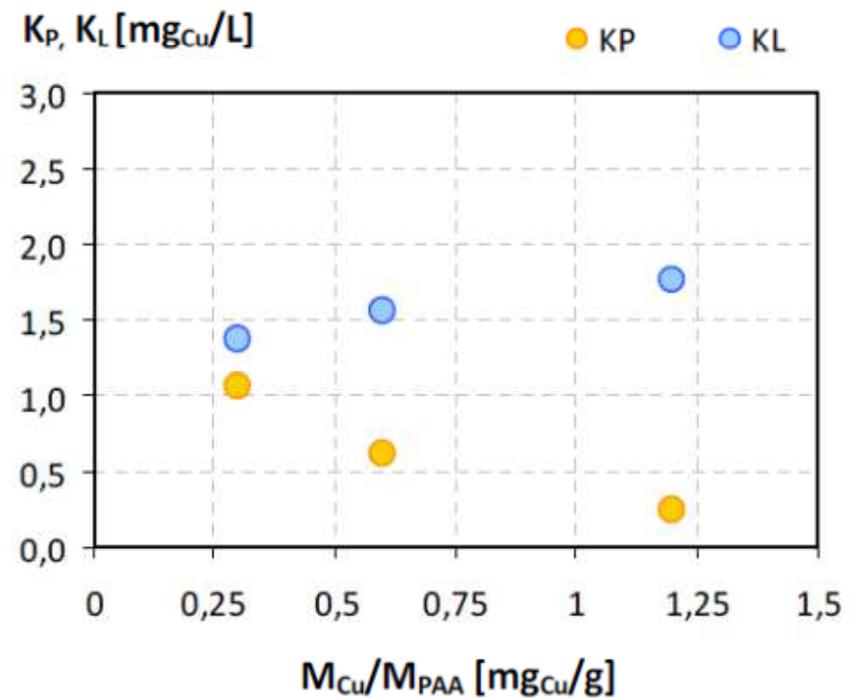


$d < 1 \text{ mm}$

- FILM DIFFUSION



MBA/CYS





CONCLUSIONS AND NEXT STEPS

- Influence of liquid-film on contaminant **DIFFUSION** into hydrogels
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-

- Batch isotherm tests to quantify **THE MAXIMUM COMPLEXING CAPACITY** of the hydrogels
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- Multistep batch tests compared to RSSCT to simulate **BREAKTHROUGH CURVES** and to obtain design data



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