Removal of heavy metals from industrial waste on rice husk in an adsorbent reactor

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INTRODUCTION

- In recent years attention has been focused on the importance of preventing water pollution and numerous national and international laws regulate the use and impose standards and limits.

- Among the possible causes of water environment pollution, heavy metals are very dangerous, as they are not biodegradable, are persistent in nature, accumulate in tissues and in the food chain and they can be harmful even at low concentrations.

- Heavy metal contamination can be found in the aqueous waste of many industries (metal plating, mining operations, tanneries, chloralkali, radiator manufacturing, smelting, alloy industries and storage battery industries, etc).

- The effluents generated by these industries are therefore rich in heavy metals which should be treated before being discharged into common waste water.

→ **Cd^{2+} and Cr^{3+} contamination**

HEAVY METALS REMOVAL METHODS

• The conventional method for the removal of heavy metal from industrial wastewater generally involves a **chemical precipitation process.**

• Studies on the treatment of effluents containing heavy metals have shown that **adsorption** is a highly effective technique for the removal

→ **activated carbon**

• The need for safe and economical methods for the elimination of heavy metals from contaminated water has pushed research interest towards the production of **low cost alternatives** to commercially available activated carbon

→ **low cost agricultural waste by-products:** sugarcane bagasse, rice husk, sawdust, coconut husk, oil palm shells, etc.

➡ **Rice husk**

Available in large quantities as rice is one of the most popular food in the world.
It is removed during rice milling and it has a low nutritional value.

SOME INFOS ABOUT CHROMIUM AND CADMIUM

Chromium (III) is an essential element for human metabolism but in certain conditions can be oxidized to the hexavalent form, which is much more dangerous.

→ widely used in many industrial processes such as leather tanning, pigment and varnish production, wood preservation, paper and glass production and also in the chemical, textile, steel and galvanic industries;
→ it helps muscle development and plays an important role in reducing glucose and cholesterol levels in the blood;
→ it is necessary to limit its presence in the water as an overdose can lead to intoxication.

Cadmium is a non-essential and non-beneficial element to plants and animals and toxic for the human body:

→ widely used in electronic and chemical industry, in the production of pigments and coted surfaces;
→ it is released to the environment in wastewater by contamination from fertilizers and local air pollution;
→ contamination in drinking-water may also be caused by impurities in the pipes, solders and some metal fittings;
→ in the air is mainly the result of industrial activities as refining of non-ferrous metals, combustion of carbon and petroleum products, burning of household waste, metallurgy.

METAL LAW LIMITS

Chromium:

→ Italian national legislation (D. Lgs. 2006/152) limits total chromium less than 2 mg/L into surface waters and less than 4 mg/L in the sewage system;

→ in drinking water maximum total chromium limit is 0.05 mg/L (WHO 2011).

Cadmium:

→ Italian national legislation (D. Lgs. 2006/152) limits Cd^{2+} concentration less then 0.02 mg/L for superficial water and wastewater;

→ law limit for cadmium in domestic wastewater is 0.03 mg/l;

→ in drinking water limit is 0.003 mg/l (WHO 2011).

ADSORBENT

Rice husk from an italian local rice mill

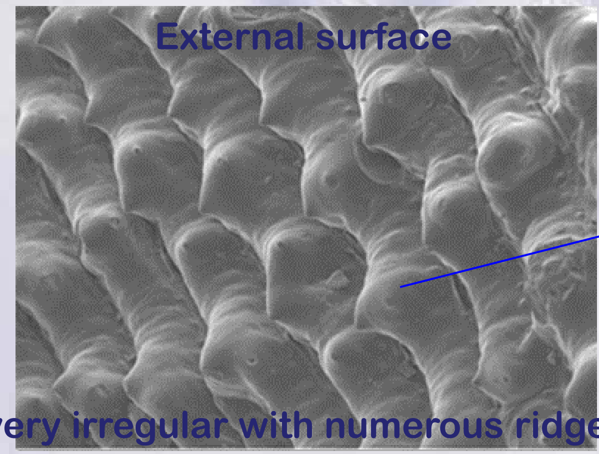
- boiled in distilled water 5 hours @ 120 °C,
- washed few times with distilled water in order to eliminate all superficial substances and turbidity,
- then placed in oven for 12 hours @ 150 °C for dried.

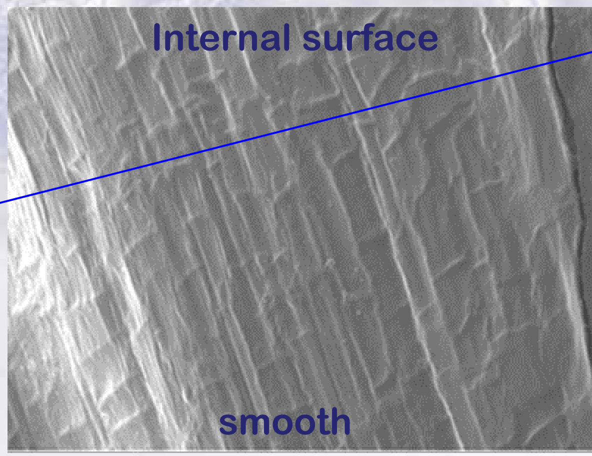
Elements	%wt (ext surf)	%wt (int surf)
C	22,29	46,51
O	56,90	51,24
Si	20,81	2,25
Total	100	100

EDX analisys

Carboxylic groups (-COOH)

Silanolic groups (-SiOH)

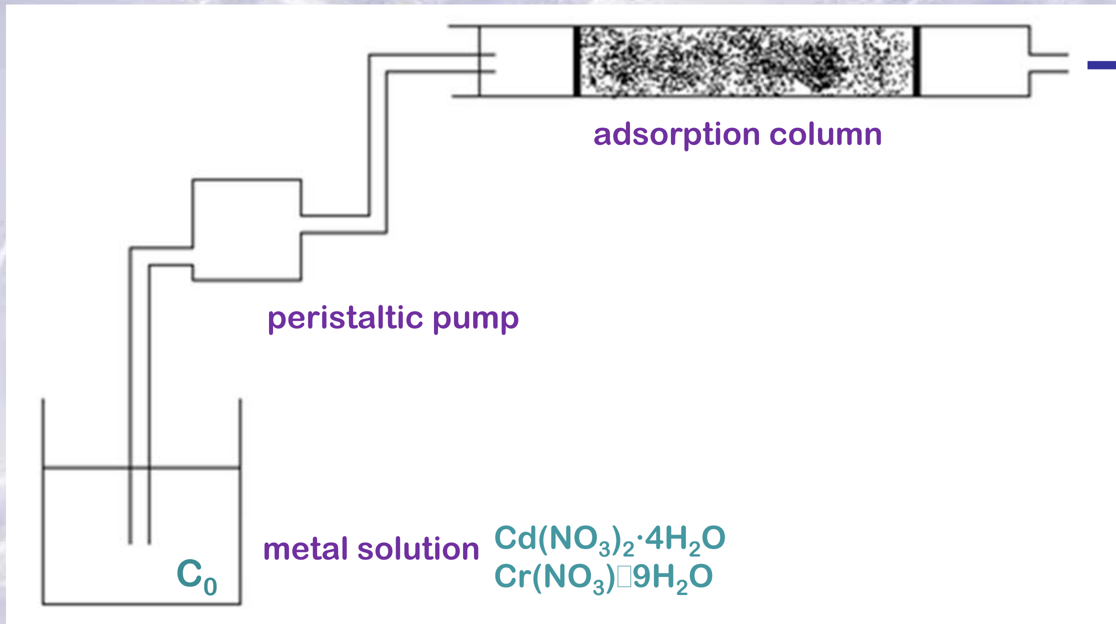




Irregular surface important for phycal adsorption

FESEM analisys

METHODOLOGY OF ADSORPTION TEST

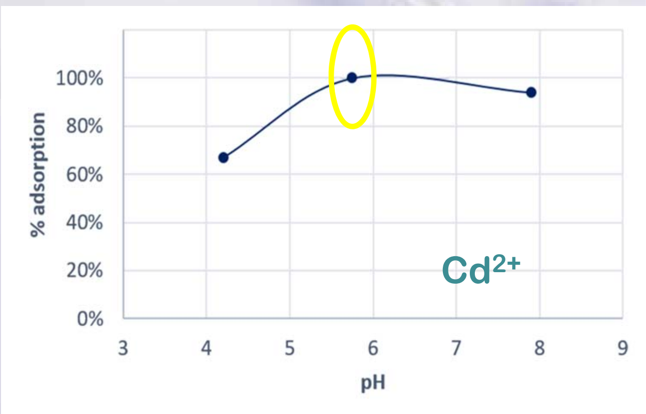


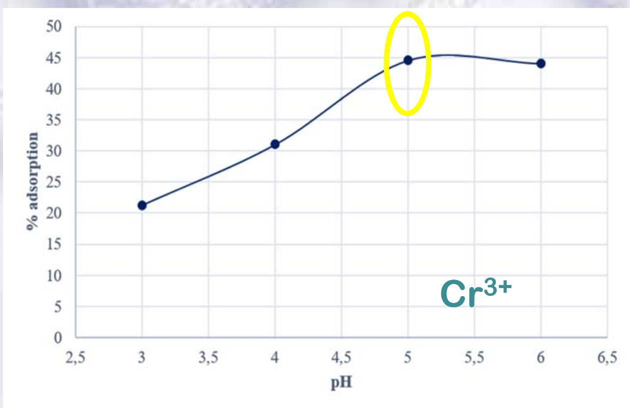
ICP-MS

Cd^{2+} and Cr^{3+} concentratrion at different time

$$\frac{C_0 - C}{C_0} \times 100$$

pH operationg conditions: ***5 - 5,8***



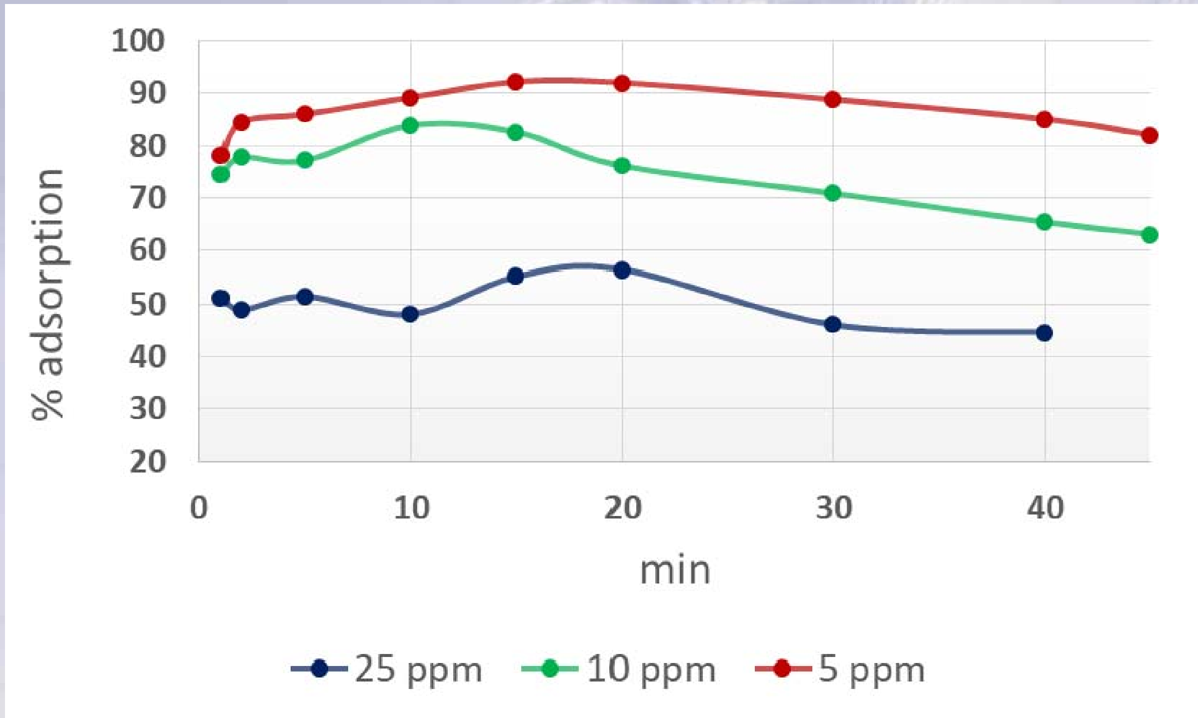


PRELIMINARY RELEASE TEST

Test in batch, with **10 g of rice husk** in distilled water for **180 minutes**
→ confirmation that the rice husk did not contain Cr and Cd
→ evaluation of which elements were released to the water

Time (min)	Na (ppb)	Si (ppb)	K (ppb)	Fe (ppb)	Cd (ppb)	Cr (ppb)
0	22,1116	3459,62	10,1513	0,541	0,00	0,00
2	22,9386	3812,63	439,311	0,7355	0,00	0,00
5	24,694	4014,38	720,235	0,7689	0,00	0,00
20	30,2633	4216,08	1259,24	1,3473	0,00	0,00
45	33,1851	8099,45	1625,55	1,8985	0,00	0,00
60	31,9119	9713,33	1739,93	2,5368	0,00	0,00
90	35,198	12638,5	1959,44	2,8662	0,00	0,00
120	34,9787	12991,5	1985,77	3,489	0,00	0,00
180	92,8437	17782,9	2273,83	2,9818	0,00	0,00

CADMIUM ADSORPTION TESTS

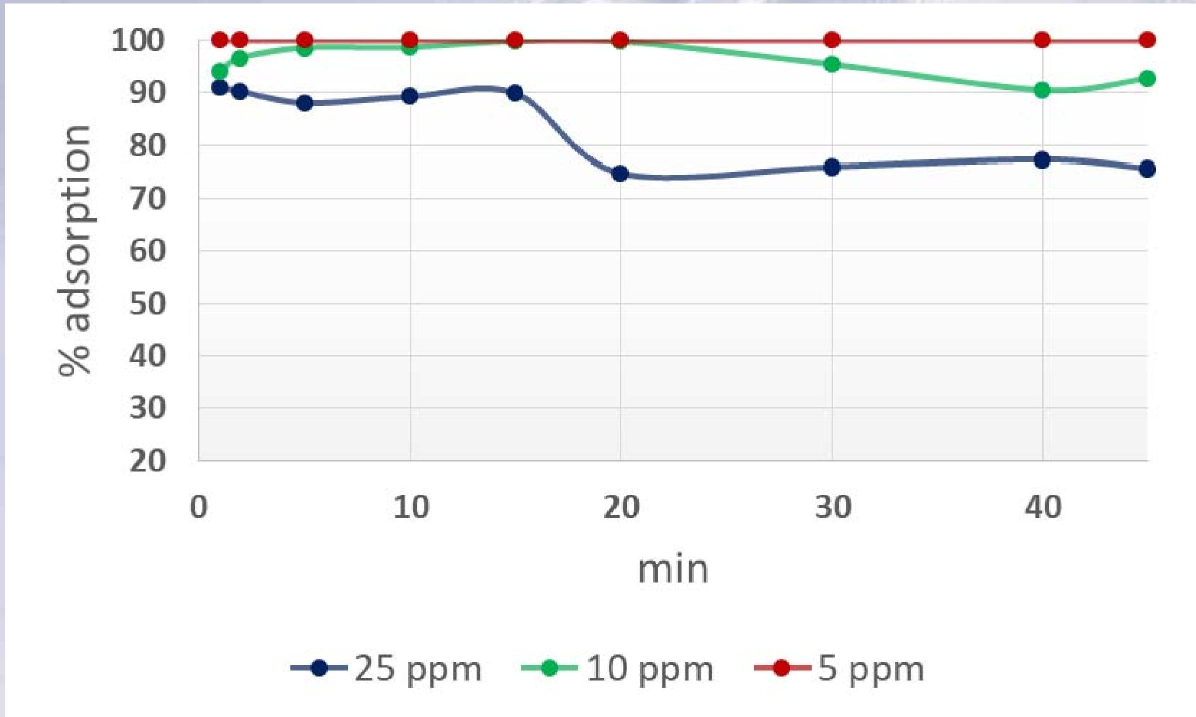


Operating conditions:

Cd^{2+} = 5 – 10 - 25 mg/L
Column diameter = 4 cm
Adsorbing bed lenght = 40 cm
Initial pH = 5.6±0.5

- **the percentage of adsorption increased as the concentration decreased;**
- **with 5 and 10 ppm of cadmium, the trend of the curves was slightly increasing up to 15-20 minutes, after which it decreased slowly;**
- **for the 25 ppm solution, Cd^{2+} was removed with a more constant pattern, till a maximum absorption concentration equal to about 50%;**

CADMIUM ADSORPTION TESTS



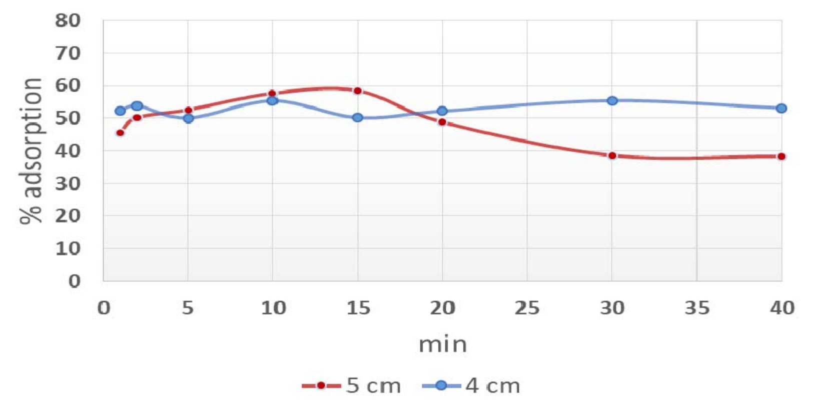
Operating conditions:

Cd^{2+} = 5 – 10 - 25 mg/L
Column diameter = 5 cm
Adsorbing bed lenght = 40 cm
Initial pH = 5.6±0.5

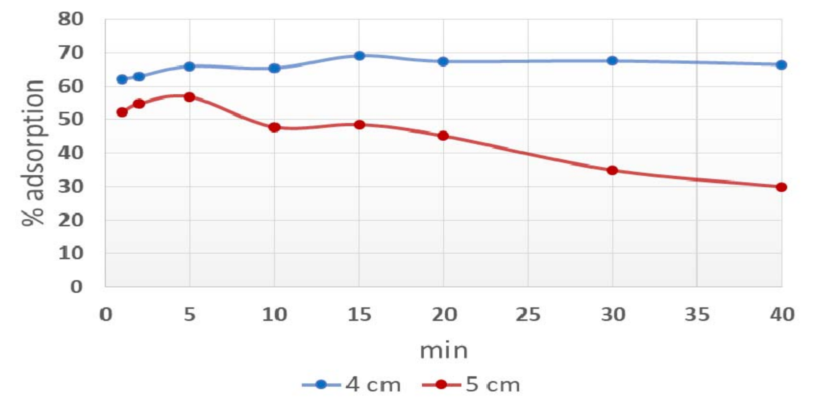
- increasing the diameter, and therefore the quantity of adsorbent material available, metal removal reached higher values;
- in the column with 5 cm diameter, Cd^{2+} with initial concentration equal to 5 ppm was completely removed, and abatement higher than 96% was obtained increasing concentration to 10 ppm;
- for 25 ppm concentration, increasing column diameter, Cd^{2+} removal reached about 90% in the first 15 min and then it was maintained around 75%.

CHROMIUM (III) ADSORPTION TESTS

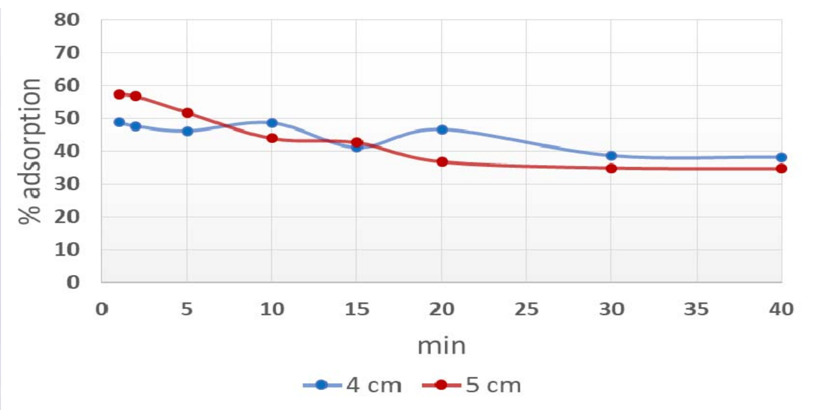
C_0 = 5 ppm



C_0 = 10 ppm



C_0 = 25 ppm



Operating conditions:

Cr^{3+} = 5 – 10 - 25 mg/L
Column diameter = 4 – 5 cm
Adsorbing bed lenght = 40 cm
Initial pH = 5±0.5

- with Cr_0^{3+} = 5 ppm, in the first minutes the trend of the concentration was approximately equal, then, after about 15 minutes the smaller adsorbing bed allowed higher adsorption ≈ 55%;
- by increasing chromium concentration to 10 ppm, the trend of the abatement curves appeared more regular and, again, the best performances were achieved with the smallest absorbent bed (≈ 50%);
- with the highest Cr(III) concentration results shown a oscillating trend in the first 15 minutes and subsequently a slightly better result for the 4 cm diameter column (≈ 45%);
- for all columns, there was no total exploitation of the bed but there were still wet areas.

CHARACTERIZATION AFTER ADSORPTION

XRF analysis

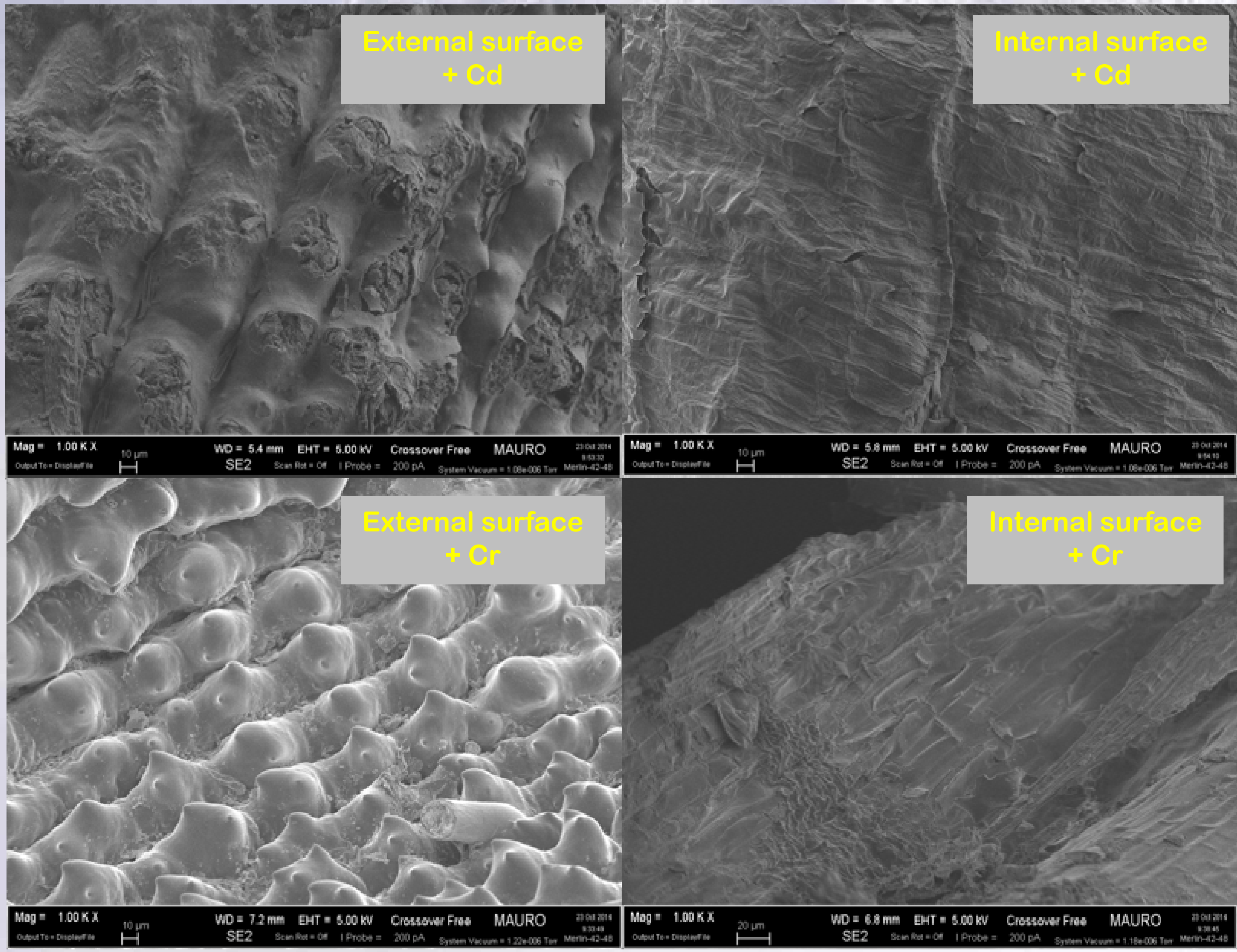
on rice husk ashes (5h @ 700 °C)

	Mg (%)	Si (%)	P (%)	S (%)	K (%)	Ca (%)	Mn (%)	Fe (%)	Cu (%)	Zn (%)	Cd (%)	Cr (%)
Fresh rice husk	1,20	87,70	3,36	0,22	3,75	2,59	0,82	0,24	0,08	0,07	-	-
Rice husk + Cd	0,39	95,70	0,16	0,16	0,59	2,00	0,49	0,28	-	-	0,25	-
Rice husk + Cr	0,48	92,10	0,43	0,14	0,56	2,16	0,21	0,27	-	0,06	-	0,18

- the main element of rice husk ash was silicon, other elements were present in minimum quantities;
- some species reduced concentration during adsorption as they were released in water;
- cadmium and chromium were not present in the fresh rice husk, but only after adsorption processes.

CHARACTERIZATION AFTER ADSORPTION

FESEM analysis



the morphology of the rice husk changed probably due to mechanical effects in the adsorption process

many fractures on surface

The metal adsorption would be governed by both physical and chemical factors.

Physical aspects:

- Morphology can facilitate metal adsorption, due to the irregular surface.
- Most of the absorption in the first minutes of contact between the solution and adsorbent was due to the initial large number of vacant surface sites available for adsorption and then partially saturated by metal ions

Chemical aspects:

• Silanolic groups (-SiOH) present on the surface of the rice husk imparted a considerable **metal cation exchange** capacity to the material: $Me^{n+} \leftrightarrow H^{+}$
→ higher exchange for Cd^{2+} that needs only $2H^{+}$

• Higher adsorption of Cd(II) than Cr(III) on rice husk could be attributed to **ionic radius**
→ Cr^{3+} offered a smaller ionic radius (0,52 Å) than Cd^{2+} (0,97 Å), then it embraced a smaller number of hydroxyls (-OH) and carboxyls (-COOH), present on the surface.

↓

Better adsorption for Cd^{2+}

CONCLUSIONS

- ✓ Overall, the rice husk showed a greater adsorbing capacity towards cadmium, even at high concentrations.
- ✓ In particular, using larger diameter column an almost total abatement was achieved.
- ✓ As expected, with the same size of the adsorbent bed, increasing the concentration of cadmium, the adsorbent capacity decreased.
- ✓ The adsorption of the chromium (III) into columns of the same dimensions reached just over 50%, showing a not total exploitation of the adsorbent bed, in addition to having an irregular trend over time.
- ✓ Lower number of proton to exchange with superficial H^+ and larger ionic radius favored Cd^{2+} adsorption on rice husk.

the rice husk showed a greater affinity with cadmium

THANK YOU FOR THE ATTENTION!