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

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Abstract

The demographic growth and rapid industrialization of the last decades have contributed to increasing the presence of heavy metals in wastewater. Among these we can mention cadmium and lead, which are industrially used and can pollute the waters. The techniques used for the removal of heavy metals from contaminated water include chemical precipitation, coagulation, solvent extraction, ion exchange, electrodialysis, electrochemical processes, photocatalytic degradation, reverse osmosis, membrane processes. However, many of these processes require a large amount of energy and reagents, while adsorption could be an alternative approach since it is economically feasible, effective and versatile. Activated carbon is commonly used as adsorbent, but in recent years research has focused on alternative adsorbents to further reduce costs, such as waste from industrial and agri-food activities.

In this paper, the adsorbent capacity of a by-product of the agrifood industry, the rice husk, was studied. The material was boiled and then characterized; the adsorption capacity of cadmium and trivalent chromium was evaluated in rice husk adsorbing columns, starting from solutions with different metals concentration (5, 10 and 25 ppm). Using columns of 4 and 5 cm in diameter, a higher reduction was achieved for cadmium compared to chromium in the same conditions, reaching in the largest column the almost complete abatement for the solutions at 10 and 5 ppm, and just over 20% of cadmium residue in the solution with an initial concentration of 25 ppm.

Keywords

heavy metals, adsorbent, rice husk, wastewater.

Introduction

In recent years attention has been focused on the importance of preventing water pollution. As it represents fundamental importance to human health, numerous national and international laws [1-3] regulate the use and impose standards and limits. Directive 2000/60/EC [1] of the European Parliament does not consider the water a commercial product, but a good to be protected and defended. Consequently, pollution should be eliminated by reducing the emissions of substances harmful to health or the environment. The EU water policy promote sustainable water development and progressive reduction of contaminants in wastewater that could pollute the environment [2]. In particular, the Directive 2006/11/EC [3] issued by the European Parliament aims to identify persistent, toxic and bio-accumulative substances.

According to this standard, the States must eliminate pollution by hazardous substances such as mercury and mercury compounds, cadmium and cadmium compounds. Moreover, pollution by hazardous substances, such as zinc, copper, nickel, chromium, lead, selenium, arsenic, antimony, molybdenum, titanium, tin, barium, beryllium, boron, uranium, vanadium, cobalt, thallium, tellurium, silver and their compounds, must also be reduced. [3]

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. In recent years, industrial activities and technological development cause the release of these elements in the environment.

The main risk for human health from heavy metals is due to exposure to lead, cadmium, chromium, mercury and arsenic. These metals and their effects on human health have been widely studied even by international organizations [4-6].

In this work, the attention has been focused on cadmium and trivalent chromium present as pollutants in wastewater.

Cadmium is a product of the refining of lead, zinc and copper metals; it is normally used in electronic and chemical industry, in the production of pigments and coted surfaces. Cadmium in the air is mainly the result of industrial activities (refining of non-ferrous metals, combustion of carbon and petroleum products, burning of household waste, metallurgy). The Cd presence in water is due to the soil erosion and human activities [6].

Basing on X Annex of Directive 2000/60/EC [1], cadmium and its compounds are considered very hazardous substances. According to the WHO Guidelines for Drinking Water Quality [5], guideline value in drinking water for cadmium is 0,003 mg/L. In Italy the maximum cadmium limit values for emissions into the surface water and the drain in sewage are 0.2 mg/L [1,6].

Chromium is a metal widely used in many industrial processes such as leather tanning, pigment and varnish production, wood preservation, paper and glass production. It is also widely used in the chemical, textile, steel and galvanic industries (metal alloys, chrome plating) [7]. Chromium (III) is an essential element for human metabolism: it helps muscle development and plays an important role in reducing glucose and cholesterol levels in the blood. Despite this, it is necessary to limit its presence in the water as an overdose can lead to intoxication. Furthermore, in certain conditions of temperature, humidity, pH and in the presence of other chemical species, chromium (III) can oxidize to the hexavalent form, which is much more dangerous.

In order to avoid exceeding the tolerable quantity of the organism, the WHO Guidelines for Drinking Water Quality [5] recommends a maximum total chromium content of 0.05 mg/L in the water. Italian national legislation [8] requires that discharges of industrial waste water into surface waters should have a hexavalent chromium concentration of less than 0.2 mg/L and total chromium less than 2 mg/L (4 mg/L in the sewage system).

The conventional method for the removal of heavy metal from industrial wastewater generally involves a chemical precipitation process [9-13]. Recently, studies on the treatment of effluents containing heavy metals have shown that adsorption is a highly effective technique for the removal of heavy metals from waste streams and activated carbon has been extensively used as adsorbent [14]. Despite its extensive use in the water and wastewater treatment industries, activated carbon remains an expensive material.

In these last years, the possibility to remove heavy metals by means of adsorption using different kind of adsorbents has been evaluated. In particular, attention has been focused on mineral, organic or biological materials and industrial by-products or agricultural waste, as an alternative to activated carbon [15,16].

Rice husk is the outer cover of paddy and accounts for 20–25% of its weight. It is removed during rice milling and its low nutritional value does not make it particularly suitable as a food for livestock. It is instead an excellent insulator, and it is used for example in the landfill pavement. It can also be used to produce energy through combustion even if, being mainly made of carbon and silica, once burned it produces large quantities of ash [17].

Rice husk is available in large quantities, as rice is one of the most popular food in the world. The annual world rice production is approximately 500 million metric tons, of which 10 – 20% is rice husk [18]. This high availability makes this material, composed of about 30% of cellulose, 20% lignin, 20% hemicellulose, potentially suitable for adsorption of heavy metals [17].

During the years, attention was focused on the utilization of unmodified or modified rice husk as an adsorbent for the removal of pollutants [19-21] and adsorption tests were carried out on batch systems. The adsorbing ability on the rice husk of different elements was tested by Krishnani et al. [22]. With batch and continuous tests they verified that it can be a valid alternative to activated carbon for nickel, zinc, cadmium, manganese, cobalt, copper, mercury and lead. Recently, as the results obtained in the batch studies may not be directly applied for industrial wastewater, columns studies have been performed to assess the required contact time between metal ions and adsorbent to better represent real conditions [19,23,24].

This study aims to evaluate the adsorption capacity of rice husk in a fixed-bed column, in order to reduce cadmium and trivalent chromium concentrations in industrial wastewater.

Materials and methods

The rice husk was provided from a local rice mill. Considering the results obtained in our previous work [25], it was chosen the simplest pretreatment to improve the adsorption capacity. The rice husk was boiled in distilled water at about 150 °C for 5 hours and subsequently it was washed few times with distilled water in order to eliminate all superficial substances and turbidity. The rice husk was then placed in oven for 12 hours at 150 °C, so as to dry it before the adsorption tests.

The adsorbent was characterized by means of Field Emission Scanning Electron Microscopy (FESEM) to evaluate morphology of fresh and used material, then X-Ray Fluorescence (XRF) analysis was carried out to determine elemental composition of rice husk ashes.

Synthetic wastewater solutions were prepared by dissolving analytical grade $Cd(NO_3)_2{\cdot}4H_2O$ and $Cr(NO_3){\cdot}9H_2O$ in distilled water to obtain 5, 10 and 25 mg of metal/L solutions, for both the metals. The initial pH of the solutions was measured and observed as 5.5±0.5 for both. During tests, in order to evaluate its influence on adsorption capacity, pH value was varied adjusting with 0.5 M, HCl and NaOH solutions.

Fixed bed column studies were conducted using columns of 4 and 5 cm diameter and 50 cm length. The column was packed with boiled rice husk between two supporting layers of glass wool. The bed depths were taken as 40 cm. The column was charged with Cd(II) and Cr(III) wastewater solutions with a volumetric flow rate of 100 mL/min. The samples were collected at certain time intervals and were analyzed for Cd^{2+} and Cr^{3+} ions using an Inductively Coupled

Plasma Mass Spectrometer (iCAP Q ICP-MS). Removal of the two metals was studied separately. Adsorption capacity was reported in percentage, calculated as:

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

where:

C_0 = metal initial concentration in the solution

C = metal concentration for each collection at different time

Experimental

In order to study the morphology of the rice husk, Field Emission Scanning Electron Microscopy (FESEM) was used. The internal and external surfaces were observed for the boiled husk (Fig. 1) and the husk after the adsorption of cadmium and chromium (Fig. 2). Furthermore, these samples were submitted to EDX analysis to understand if there is a different composition between the internal and external surfaces.

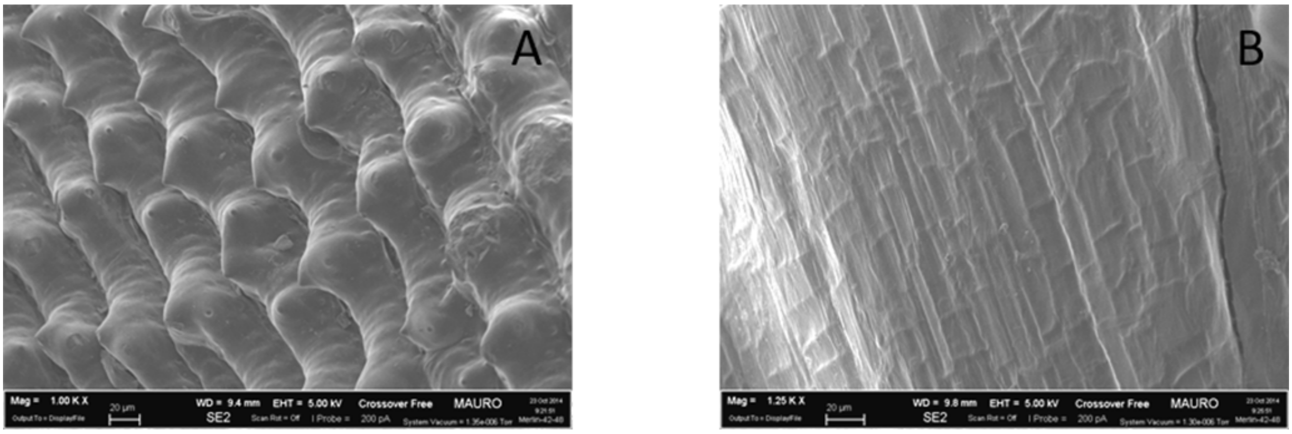

Fig. 1 FESEM images of boiled rice husk, external (A) and internal surface (B)

As visible, for boiled rice husk, the external surface (Fig. 1A) and the internal surface (Fig. 1B) are very different: externally surface appeared very irregular with numerous ridges, while the inner surface was smoother. By means of EDX analysis the different composition of the two surfaces was evaluated and results are reported in Table 1.

Table 1 EDX analysis on external and internal surface of rice husk

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

The elements mainly present in the rice husk were carbon, oxygen and silicon. The amount of oxygen is approximately equal in the inner and outer surfaces. Silicon was more abundant on the external surface (about 20%) then in the internal one (about 2%), the opposite was observed for carbon, which balanced the amount of silicon.

After adsorption process with the two metals, in both cases the morphology of the rice husk changed considerably, as shown in Figure 2, probably due to mechanical effects in the boiling phase and in the adsorption process, in fact many fractures on surface were pointed out.

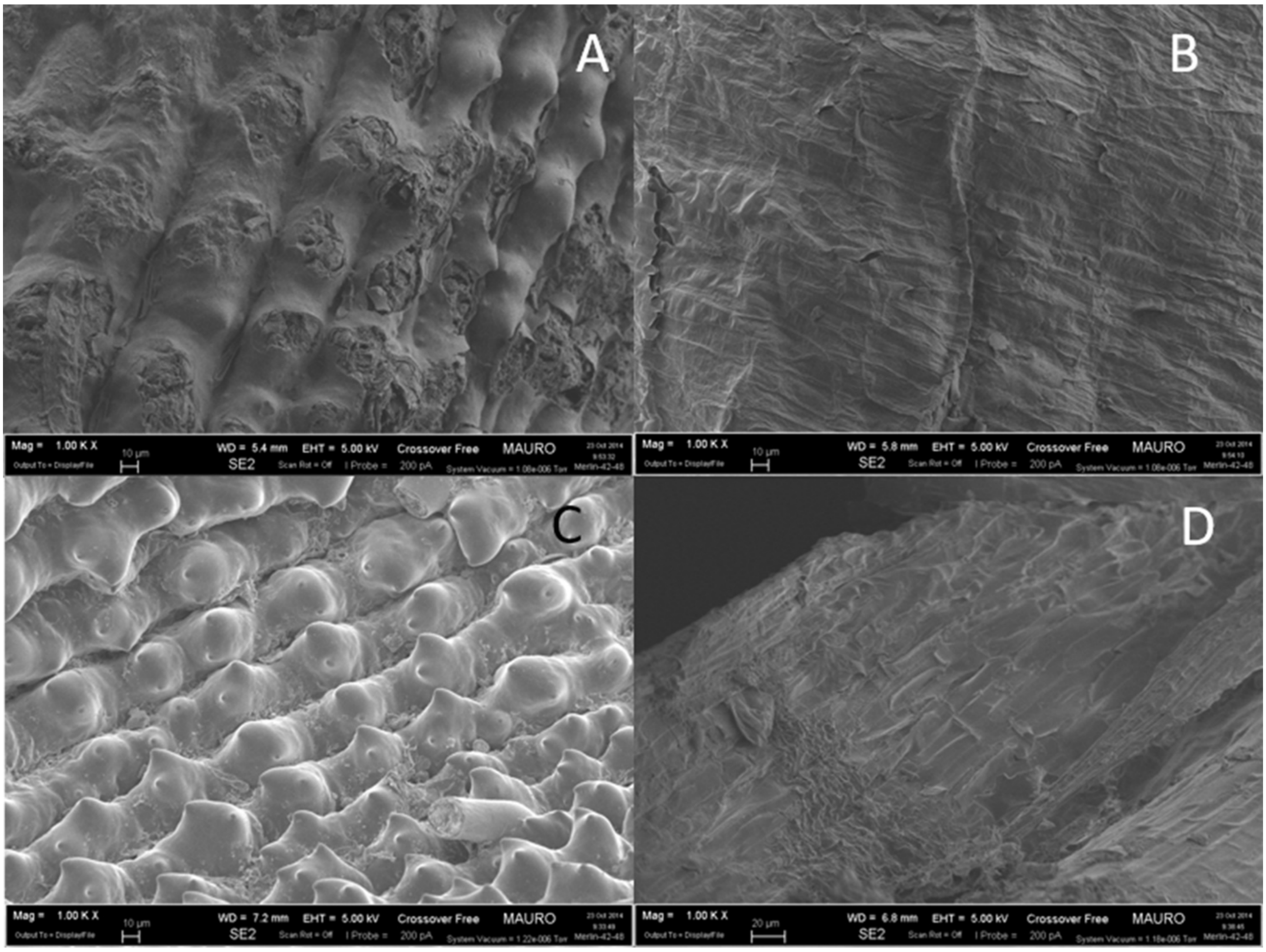

Fig 2 FESEM images of rice husk after adsorption process with cadmium (A,B) and chromium (C,D), external (A,C) and internal surface (B,D)

Subsequently, in order to evaluate the elemental composition of the rice husk, XRF spectrophotometry was used. Fresh and used samples were placed in the oven at 700 ° C for 5 hours, so as to obtain rice husk ashes that were pulverized with a mortar and pelletized for the analysis. The results are presented in Table 2.

Table 2 XRF analyses on rice husk ashes

	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	-	0,20

As expected, the main element of rice husk ash was silicon, other elements were present in minimum quantities: magnesium, phosphorus, sulphur, potassium, calcium, manganese, iron, copper and zinc. Cadmium and chromium, however, were not present in the fresh rice husk, but only after adsorption processes.

Moreover, for further confirmation that the rice husk did not contain Cr and Cd and to assess which elements were released to the water, a release test was carried out in distilled water. Test was carried out in batch, placing 10 g of rice husk in distilled water in a stirred vessel for 180 minutes. The solution was analysed at different time intervals to evaluate the composition and the results are shown in Table 3.

Table 3 Released elements in distilled water by rice husk

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

The elements released in distilled water by the rice husk were silicon, potassium, sodium and iron, whereas chromium and cadmium were not revealed, consequently the amount of these last present in the solution exiting from the adsorbing column represented only the percentage not adsorbed from initial solution.

Firstly, cadmium adsorption on rice husk was evaluated.

Since in the literature pH was considered a very influencing parameter on adsorbing capacity, first tests were carried out by varying initial pH of Cd^{2+} solution: values were adjusted to 4.2, 5.75 and 7.9, and results are shown in Fig. 3. In the first minutes the amount of adsorbed cadmium was similar for the three pH values, but after few minutes, for the solution at lower pH, adsorbed Cd^{2+} percentage decreased progressively.

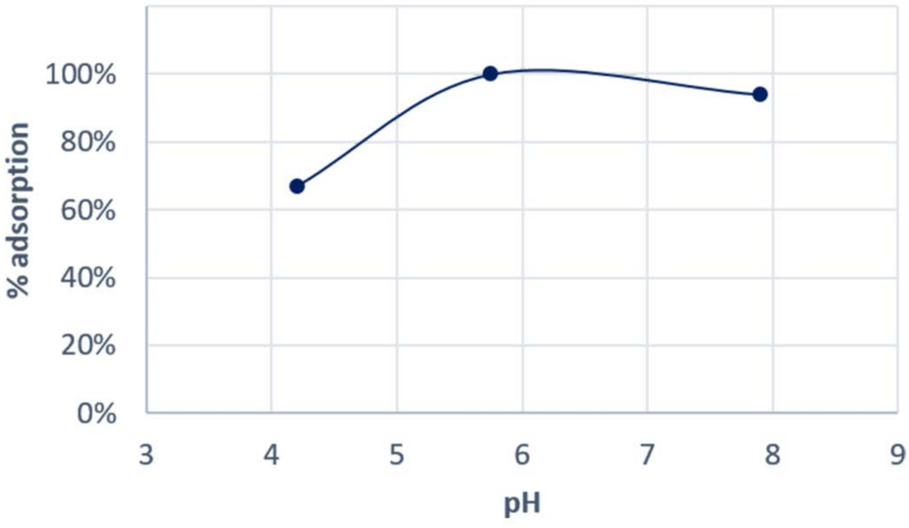

Fig. 3 Maximum percentage of adsorbed Cd^{2+} varying metal solution pH

Then, the optimal analysis condition was pH = 5.75, considering that at pH equal to 7.9, part of metal could precipitate as hydroxide [26] and did not get adsorbed.

For adsorbing cadmium tests, columns with internal diameter of 4 and 5 cm and solutions with 25, 10, 5 ppm of cadmium concentration were used. The bed length was maintained equal to 40 cm and the initial pH of the solution, measured around 5.60, value verified to be close to the optimal (5.75), was not varied.

The graphs in figures 4A and 4B showed the results for the tests carried out on the 4 cm and 5 cm diameter column, respectively.

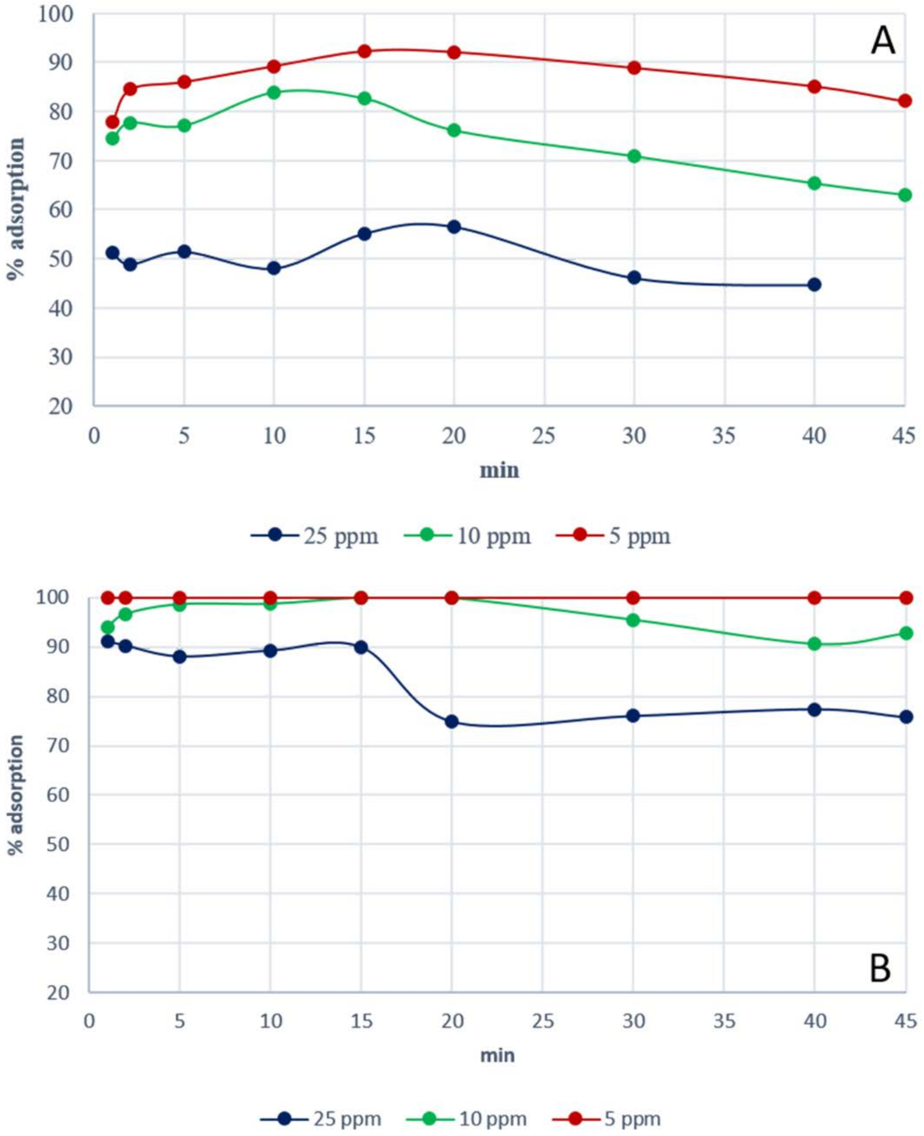

Fig. 4 Percentage of adsorbed cadmium vs. time in columns with diameter equal to 4 cm (A) and 5 cm (B), starting with solution at different metal concentration

It can be noted for both columns that the percentage of adsorption increased as the concentration decreased, much more clearly for the 4 cm column. In particular for the tests 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, cadmium was removed with a more constant pattern, with a total absorption concentration equal to about 50%.

Increasing the diameter, and therefore the quantity of adsorbent material available, metal removal reached higher values. In particular, in the column with 5 cm diameter (Fig. 4B), cadmium present in the initial solution containing 5 ppm was completely removed, and abatement higher than 96% was obtained increasing concentration to 10 ppm. The most important results, however, were related to the 25 ppm concentration, as, increasing column diameter, Cd^{2+} removal reached about 90% in the first 15 min and then it was maintained around 75%.

Subsequently, similar tests were carried out for evaluate Cr^{3+} abatement capacity.

Firstly, pH value was varied and results are shown in Fig. 5. Best absorbing conditions appeared for pH higher than 5, but, as known [27] chromium (III) at pH equal o higher to 6 precipitated in the form of hydroxide, so the best operating condition was considered pH equal to 5-5.5.

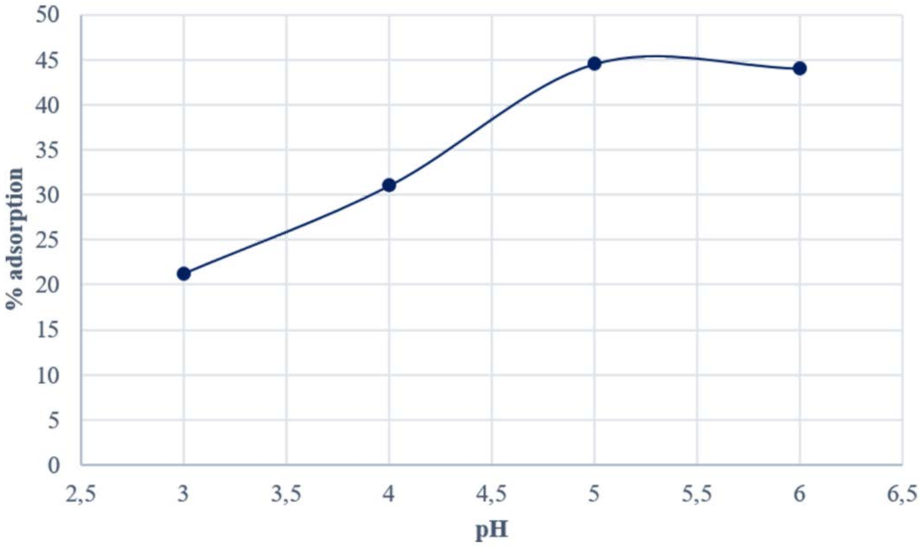

Fig. 5 Maximum percentage of adsorbed Cr^{3+} varying metal solution pH

Absorption tests were again performed in the two columns with diameter equal to 4 and 5 cm and initial concentrations of analysed solution were 5, 10 and 25 ppm of chromium (III).

When Cr3+ initial concentration was equal to 5 ppm (Fig. 6A), in the first minutes the trend of the concentration was approximately equal in both the columns, but after about 15 minutes the smaller adsorbing bed allowed higher adsorption (≈ 55%). Not considering minor variations probably due to the flow instability, rice husk bed contained in the lower diameter column guaranteed a nearly constant reduction of Cr(III) around 50%.

By increasing chromium concentration to 10 ppm (Fig. 6B), the trend of the abatement curves appeared more regular and, again, the best performances were achieved with the smallest absorbent bed with a reduction of around 50% for the duration of the test. The test carried out with the higher Cr(III) concentration shown results (Fig. 6C) similar to those obtained for concentration equal to 5 ppm, with oscillating trend in the first 15 minutes and subsequently a slightly better result for the 4 cm diameter column (≈ 45%).

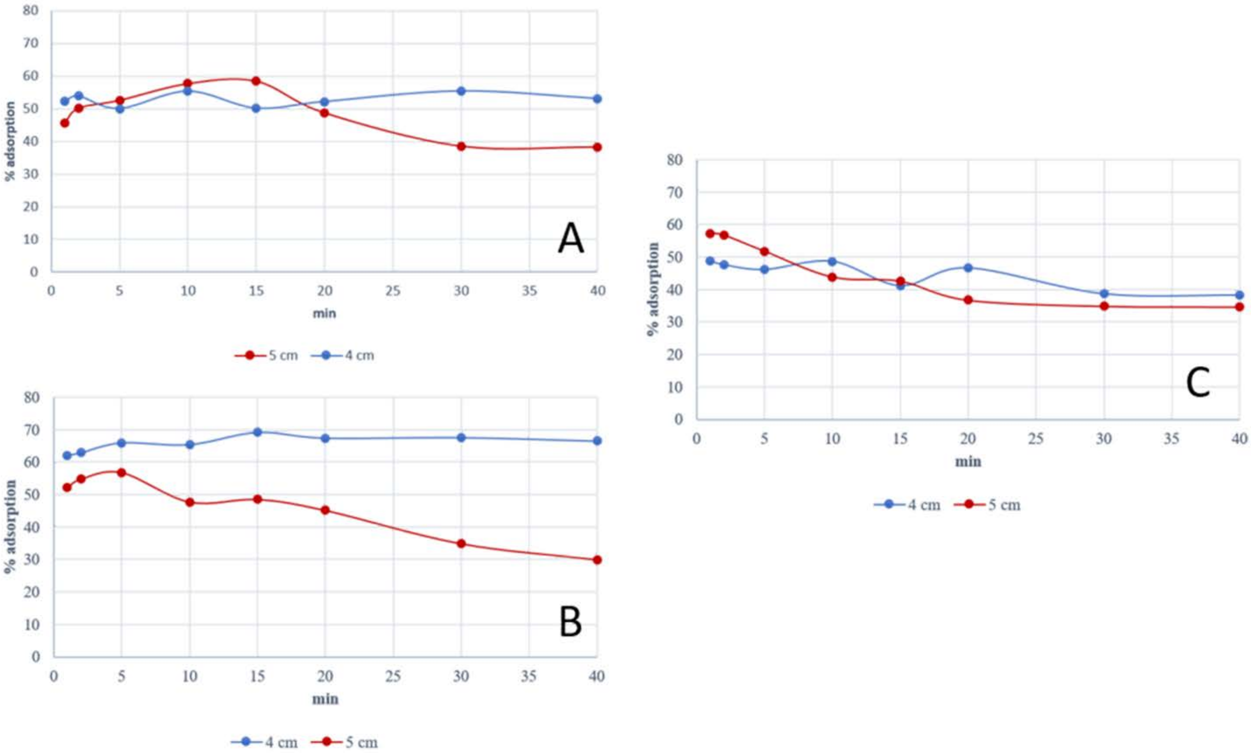

Fig. 6 Percentage of adsorbed chromium vs. time in columns with diameter equal to 4 cm and 5 cm, starting with solution at different metal concentration: 5 ppm (A), 10 ppm (B) and 25 ppm (C)

The adsorbent showed a very different behavior when the solution containing chromium was fluxed, as there was no total exploitation of the bed but there were still wet areas. This could explain the less linear and promising results. Moreover, proportionality between the column size and the adsorbent capacity was not demonstrated, in fact the best performances were obtained for the intermediate concentration (10 ppm) and with the smallest adsorbing bed (diameter equal 4 cm).

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.

In conclusion, the rice husk showed a greater affinity with cadmium and proved to be a promising adsorbent towards this heavy metal.

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