RAWTRAP
Nano-traps from rice ashes to purify water

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- **Summary**

Water is the most precious commodity for every nation today. The main objective is to have it available in sufficient quantity and with the right purity for the intended use. In our territory, surface water is mainly contaminated with traces of pesticides and heavy metals. The project was born out of concern for our territory and the need to concretely implement a path of environmental sustainability by valorising local raw materials. Novara in fact has a vast agricultural area almost completely dedicated to rice cultivation, but about 20% of all rice production is waste called chaff. In our work, we evaluated the possibility of using the combustion ashes of rice husk, which is very rich in silica, for further processing into functionalized materials type (MCM-41) suitable for capturing pollutants in water. The molecular sieve MCM-41 is a crystalline solid with a highly defined hexagonal structure, a surface area of more than 700 $[m^2/g]$, excellent thermal stability and a structure that can be modified in a variety of ways. The pore size of MCM-41 can be controlled from 2 to 10 [nm] using an appropriate surfactant as a model. By using rice husk as a source of silica in the synthesis of MCM-41, the production costs of adsorbent materials have been significantly reduced as well as helping to overcome environmental pollution. We have focused our research on the adsorption of a specific dye called Rhodamine B, primarily used in the textile industry.

- **List of acronyms**
1. MCM-41= Mobile Composition of Matter
2. RHANs/RHANo/RHANn= Rice Husk Ashes of Novara (south, west, north)
3. FTIR= Fourier Transform Infrared Spectroscopy
4. EDX= Energy Dispersive X-ray Analysis
5. DLS= Dynamic Light Scattering
6. UV-VISIBLE= Ultraviolet Visible Spectroscopy
7. CTAB= Cetyltrimethylammonium bromide
8. RhB= Rhodamine B

- **Acknowledgements**

INDEX:

- **Analysis of the problem:**

Water is the most precious resource for any nation today. The possibility of having enough of it, with the right purity for the type of use (agriculture or human consumption), is the main objective. In our area, surface water is mainly contaminated with traces of pesticides and heavy metals. The project was born from the need to a path towards environmental sustainability by reducing waste and promoting the reuse of water. There are approximately 1.5 billion cubic kilometres of water on Earth, 97% of which is salt water from the oceans and the remaining 3% fresh water in the form of lakes, rivers, glaciers and groundwater.

One of the biggest challenges is to find an efficient way to remove harmful contaminants from water to prevent its quality from deteriorating dramatically. In addition to the many methods already used to reduce their diffusion in water, particular attention should be paid to adsorption. Adsorption is an efficient and inexpensive mass-transfer process in which a solid material can capture dissolved components from the aqueous phase by exploiting specific physical-chemical interactions.

- **Local rice production**

The outer husk of rice is called CHAFF. Graphs 1 and 2 illustrate local and national rice production by analysing product crop and waste percentages for the different types and varieties of rice.
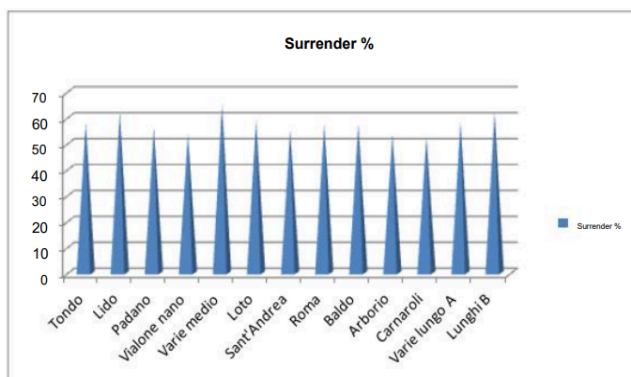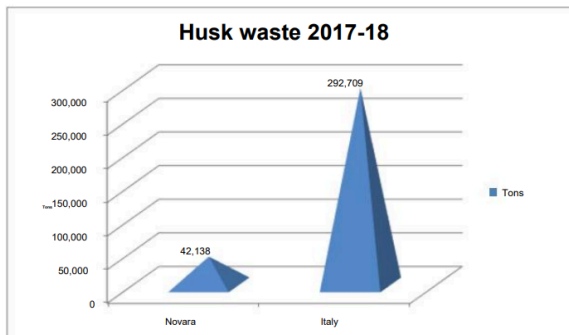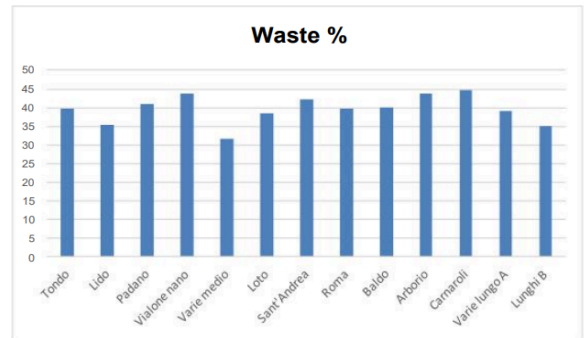

Graph 1
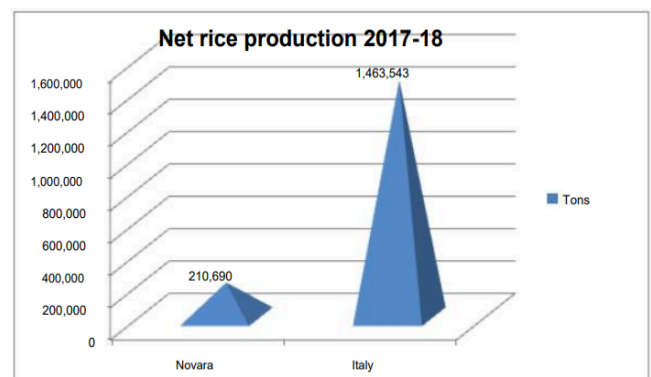
Graph 2

The Graphs 3 and 4 compare the waste of the different rice varieties and the husk waste in the province of Novara.
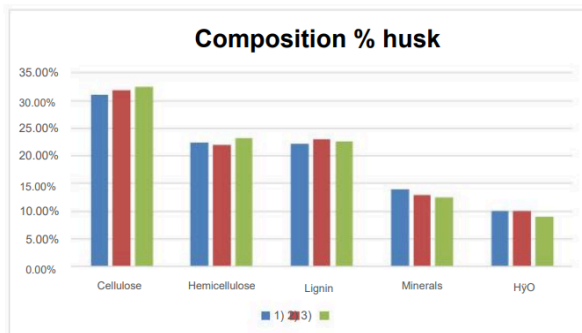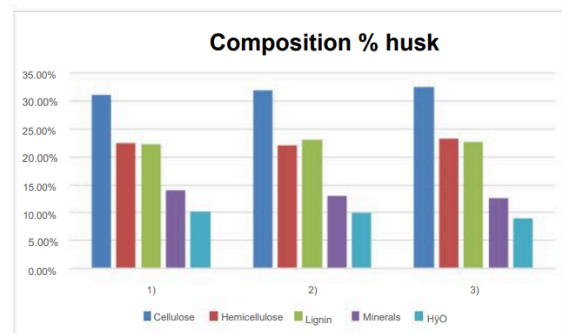

Graph 3

Graph 4

Of the different percentages of waste, the husk represents about 20%. In the province of Novara, about 43,000 tonnes of chaff are produced every year, and their combustion produces heat (P.C.I. 15.2 Mj/Kg s.s.) can crop 8400 tonnes of ashes which are rich in silica. The latest information from the Chamber of Commerce puts the price of the chaff at 25 euros per tonne. The composition of the chaff for the three samples that were analysed (sample 1: RHANn, sample 2: RHANs, sample 3: RHANo) are shown in Graphs 5 and 6.

Graph 5

Graph 6

Rice husk is a by-product of rice milling that is used as an energy source in many sectors, such as biomass power plants. The combustion of rice husk produces rice husk ashes (RHA), which is rich in silica and can be an economically valuable raw material for the production of natural silica.

● **Our Project**

The project was born from the attention to our territory and the need to concretely implement a path of environmental sustainability by increasing the use of local raw materials. Novara has a vast agricultural area almost completely dedicated to rice cultivation. Approximately 20% of all rice production is a waste product called '**husk**', which is already used in a variety of ways, including: zootechnical litter in stables, riding stables, cattle and poultry farms, agricultural soil improver in floriculture and horticulture, simple vegetable soil improver in the chemical industry for composting, fluidifying agent in the oilseed and feed industry, fuel in the energy industry, support for chemical substances or fertilisers in the pharmaceutical industry, biological thermal insulation in the brick industry. The idea for the project came about by evaluating the possibility of using the combustion ash of rice husk, which is very rich in silicon, for subsequent processing into functionalized materials suitable for capturing pollutants in water. Three different types of husks from three different rice-growing areas in Novara (north, south, west, referred to as RHANn, RHANs and RHANo) were used, all of which are dedicated to the same type of rice cultivation. The combustion processes were

carried out at three different temperatures (500, 600 and 700 ° [C]) for different times (3 , 6 hours) in the presence of air and in a modified atmosphere. In addition to the ash produced in the laboratory, ash from a plant that generates energy by burning husks was also used. The different types of ash were then used to create the MCM-41 molecular sieve.

- **MCM 41 nanoparticles from the ashes of rice**

Due to its high Silica content, the rice husk has become a source for the preparation of numerous silicon compounds such as mesoporous MCM-41. By using rice husks as a source of silica in the synthesis of MCM-41, the production costs were considerably reduced as well as helping to overcome environmental pollution. The sodium silicate solution was obtained by refluxing the rice husk ash in a 2 [M] NaOH aqueous solution (1 [g] RHA: 50 [mL] NaOH) for 24 hours (at 70 ° [C]), in order to carry out the following reaction $SiO_2 + NaOH \rightarrow Na_2SiO_3$. The surfactant silica mixture resulted from the addition, under stirring at room temperature, of 7.6 [g] of the silicate solution obtained to 6 [g] hexadecyltrimethylammonium bromide (CTAB) dissolved in 60 [mL] ultrapure water. The pH was then adjusted to 10.5 and the mixture was further stirred for a further 12 hours. Finally, the mixture was subjected to hydrothermal treatment (at 100° [C], for 72 hours) in a Teflon acid digestion vessel. After this period, the solid was vacuum-filtered, rinsed with ultrapure water, dried and calcined (at 550°[C], for 6 hours) to obtainedMCM-41. obtain the MCM-41 product (Fig 1-2)
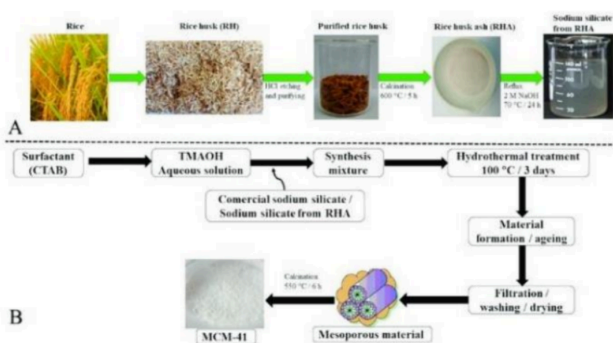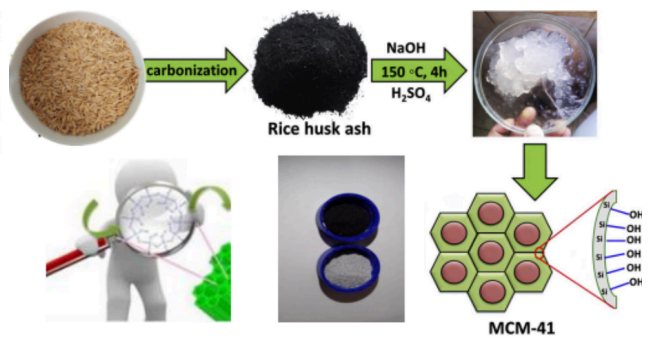

Figure 1

Figure 2

The molecular sieve MCM-41 is a crystalline solid with a highly defined hexagonal structure, a surface area of over 700 [m²/g], excellent thermal stability and a structure that can be modified in various ways. The pore size of MCM-41 can be controlled from 2 to 10 [nm] using an appropriate surfactant as a template (Fig. 3-4).
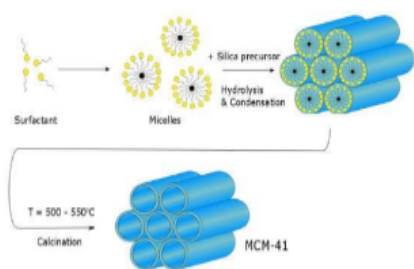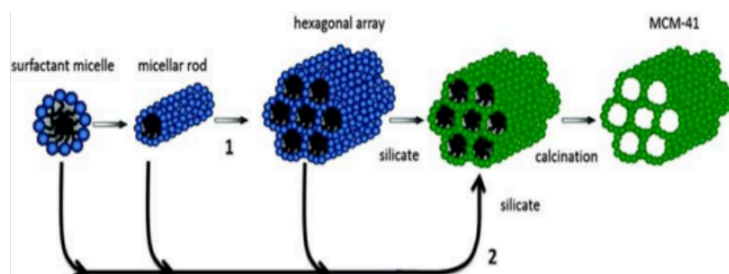

Figure 3

Figure 4

- **Analysis FTIR EDX DLS UV-VISIBLE**

FTIR measurements were performed on the calcined and non-calcined MCM41 samples. The samples were analysed using KB tablets (Figure 6-7-8-9-10 and Graph 7).
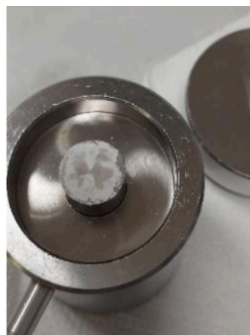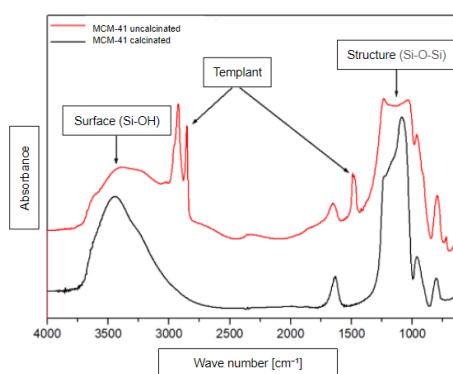

Figure 6   **Figure 7**   **Figure 8**   **Figure 9**

Figure 10   **Graph 7**

As can be seen from the two superimposed IR spectra, the typical groups of the templating agent used (hexadecyltrimethylammonium bromide CTAB) are still present on the uncalcined MCM-41 sample, these groups disappear on the calcined MCM-41 sample because the organic compound is destroyed. The surface stretching of the Si-OH groups and the Si-O-Si structure stretching are also visible. In order to highlight the crystallographic planes of the prepared material, EDX measurements were also performed on the MCM-41 sample (Figure 12-13 Graph 8).
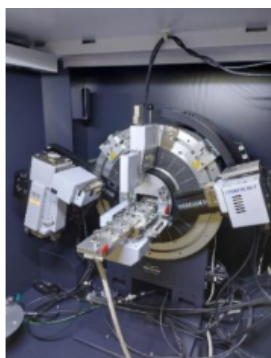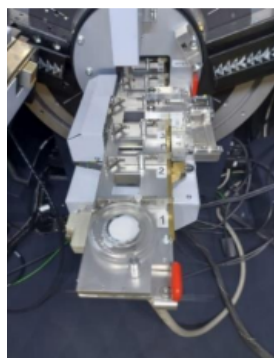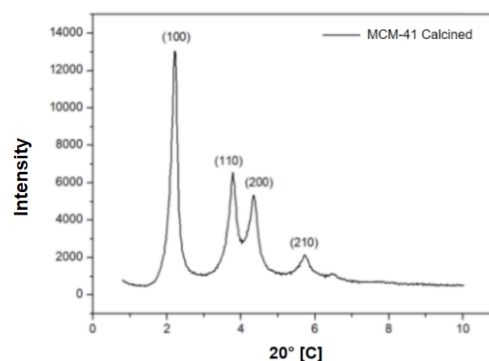

Figure 12   **Figure 13**   **Graph 8**

As can be seen from the graphs, crystallographic planes (100), (110), (200) and (210) are evident on the calcined MCM-41 sample. Finally, DLS (Dynamic Light Scattering) analyses were performed to study the dimensions of MCM-41. Measurements were conducted at 20°[C] on MCM-41 particles using a Malvern Zetasizer NanoZS (Malvern Panalytical, Malvern, UK) equipped with a He-Ne laser (λ = 633 [nm]). In detail, 4 [mg] of MCM-41
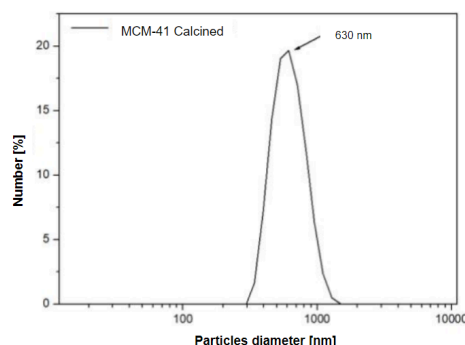
powder was dispersed in 40 [mL] of deionised water, and sonicated for 30 minutes to reduce the number of water molecules adsorbed on the surface (Fig. 15-16 Graphs 9-10).
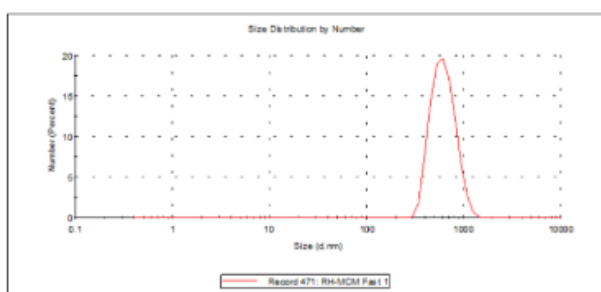

| Figure 15 | Figure 16 | Graph 9 |

As can be seen from the graphs, the MCM-41 particles all have a size (hydrodynamic radius) around 600 [nm].

Graph 10

The adsorption of rhodamine B from the aqueous phase was studied by UV-visible spectroscopy. Prior to the experiments, a calibration line was constructed using five different rhodamine B standard solutions: 2×10^{-2}, 1×10^{-2}, 6.6×10^{-3}, 5×10^{-3} and 3.3×10^{-3} [mmol×L^{-1}]. The equation of the calibration line is shown in the figure (at 554 [nm]) (Graphs 11-12).
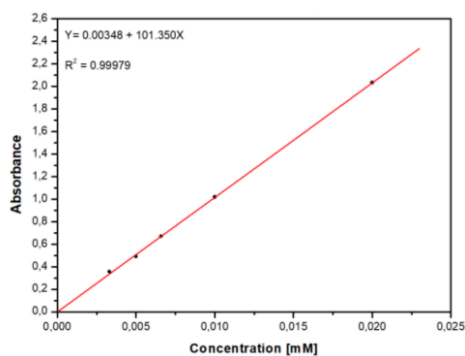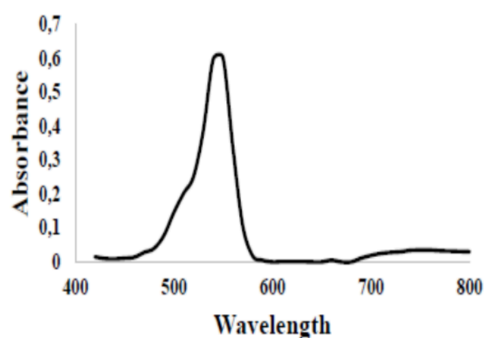
| Graph 11 | Graph 12 |

- **Pollution from dyes**

Pollution from dye effluents has become a major environmental problem in the last decade due to the increasing use of dyes in various applications. The global textile industry is the main source of these effluents. Dyes are organic compounds used to colour various substrates and are raw materials used in many production processes such as textiles, paper, plastics, leather, food and chemicals, paper, plastics, leather, food and pharmaceuticals. RhB is a basic reddish dye of the xanthene class and is highly soluble in water. Xanthene dyes tend to fluoresce and produce bright colours ranging from pinkish yellow to bluish red. RhB is widely used as a dye in textiles, food, medicine (for animals) and for staining biological

samples. It is also a fluorescent marker for water. Improper disposal of this dye prevents sunlight from penetrating the water, causing serious environmental problems, and is toxic and carcinogenic. It is toxic and carcinogenic to living organisms. It is therefore essential to remove it from aquatic wastewater. Adsorption technology removes organic dyes from aqueous solution using efficient materials such as MCM-41 (Figures 17-18-19).
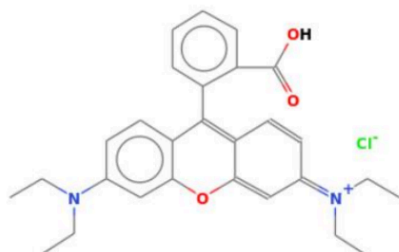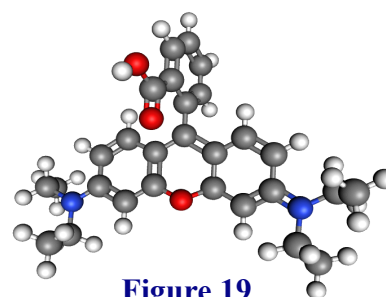

Figure 17   **Figure 18**   **Figure 19**

● Rhodamine B adsorption

Experiments were conducted at room temperature by placing 100 [mg] of MCM-41 in 20 [mL] of a 2×10^{-1} [mmol·L^{-1}] rhodamine B solution into 50 [mL] conical bottom polypropylene centrifugation tubes with caps. The suspension was then stirred at 300 RPM using a magnetic stirrer. Before recording the UV spectra, the test tubes were centrifuged at 8000 RPM for 5 minutes, in order to collect approximately 3 [mL] of clear solution to be introduced into a cuvette and analysed by UV-Visible spectroscopy. After each measurement, the aliquots taken were returned to the centrifuge tube. To follow the entire adsorption process, via UV-Visible spectrophotometry, the spectra were recorded at different times (10, 20, 60, 120, 180, 240, 300 and 360 minutes) and the results were reported as [mg] of rhodamine B adsorbed on [g] of absorbent material (Graph 13 Figure 20).
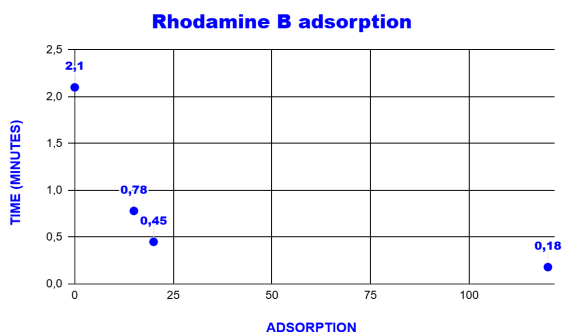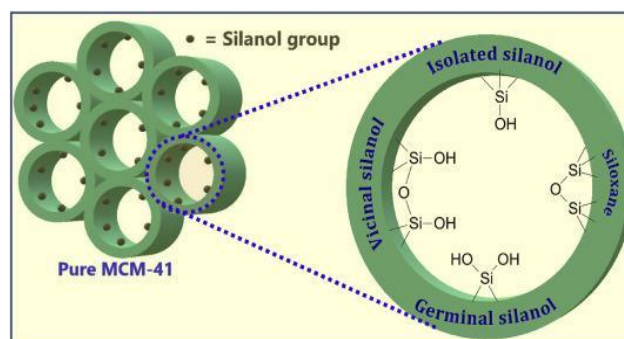
Graph 13   **Figure 20**

At the end of the adsorption measurements, to recover the adsorbent, the sample was centrifuged to remove the supernatant. The remaining powder was then dried at room temperature for 12 hours and finally the solid was transferred to a ceramic crucible to be calcined at 600° [C] for 6 hours. The regenerated MCM-41 particles were used for a new adsorption kinetics with a fresh rhodamine B solution. In the adsorption test, at a pH of about 4.8, the zeta potential (i.e. the surface charge of the silica particles) was negative, while the dye Rhodamine B is mainly present as a zwitterion. Therefore, the positively charged groups ($-C=N^+$) of Rhodamine B tend to interact with the Si-O$^-$ silano groups present in the silica materials through electrostatic forces. In addition, the residual surface hydroxyl groups in the porous material can act as centres for the adsorption of rhodamine B through H-bonding interactions with the COO$^-$ group present in the rhodamine B molecules.

- **Effect of the reaction parameters**

The pH of the dye solution is a parameter of significant influence in determining adsorption capacity. The pH of the solution influences the degree of ionisation and speciation of various dyes, which subsequently change the reaction kinetics and equilibrium characteristics of the adsorption process. The influence of the pH of the RhB dye solution on the adsorption capacity of each sample was tested with a concentration of 15 [mg/L] dye, adjusted to different pH levels. For each sample, 30 [mL] of dye with a mass of MCM-41 of 0.3 g was used. Samples were prepared with a pH between 1 and 14 (at various intervals), for a total of seven samples. The samples were acidified and made alkaline using 1 [M] hydrochloric acid and 1 [M] sodium hydroxide solutions. The experimental results for RhB adsorption on both samples (calcined MCM-41 and uncalcined MCM-41) are shown in graph 14.
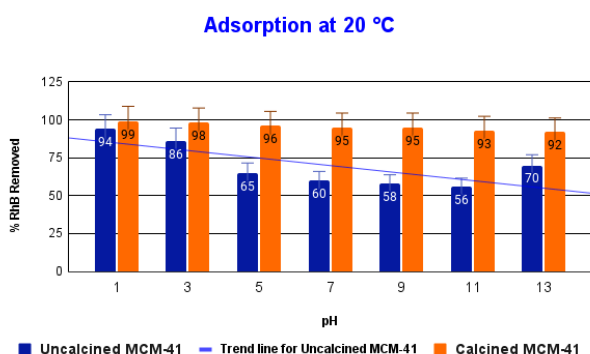
Graph 14

By uncalcined MCM-41, we mean the nanotrap with the presence of the templant, which can only adsorb on the surface and not within the pores. Uncalcified MCM-41 showed low adsorption, mainly at pH 7, 9 and 11. It was noted that the most favourable adsorption of the RhB dye occurs at acidic pH levels. The results for calcined MCM- 41 indicate that the effect of pH was not as evident. As can be seen, calcined MCM-41 adsorbs and removes high percentages of RhB dye at almost all pH levels, from acidic to basic. This can be attributed to the fact that adsorption occurred both on the surface of the calcined MCM-41 and in the inner pore region, due to the greater number of active sites. It should be noted that the surface of the MCM-41 adsorbent changes its polarisation depending on the pH value of the solution and the isoelectric point (IEP) of the solid. The pH chosen for the tests was lower than the isoelectric point of the MCM-41, i.e. 1. When the solution pH is lower than the isoelectric point pH, the surface of the material is positively charged.

The opposite occurs at higher pH values, when the decrease in dye adsorption levels can be attributed to OH competition with dye ions for adsorption sites on the material. Increasing the number of hydroxyl groups decreases the number of positively charged sites and reduces the attraction between the dye and the adsorbent surface. Adsorption experiments were conducted in pH-controlled (1.0) Erlenmeyer flasks. Aliquots of the solution were collected at time intervals (20 minutes) between 0 and 180 minutes. Subsequently, the solutions were centrifuged and analysed for residual dye concentration with a UV vis spectrophotometer.

The RhB dye concentration was determined using a UV-VIS spectrometer with a wavelength of 554 [nm]. The removal percentage (R%) and the amount of adsorbed RhB (q) were obtained using the equations respectively:

$$R\% = \left(\frac{C_i - C}{C_i}\right) * 100$$

$$q = \frac{V}{m}(C_i - C)$$

R% = removal percentage; q= amount of RhB adsorbed (mg RhB/g adsorbent); V = volume of dye solution(L); m= mass of adsorbent(g); Ci = initial concentration of dye solution (mg/L); and C= final concentration remaining after the process (mg/L).
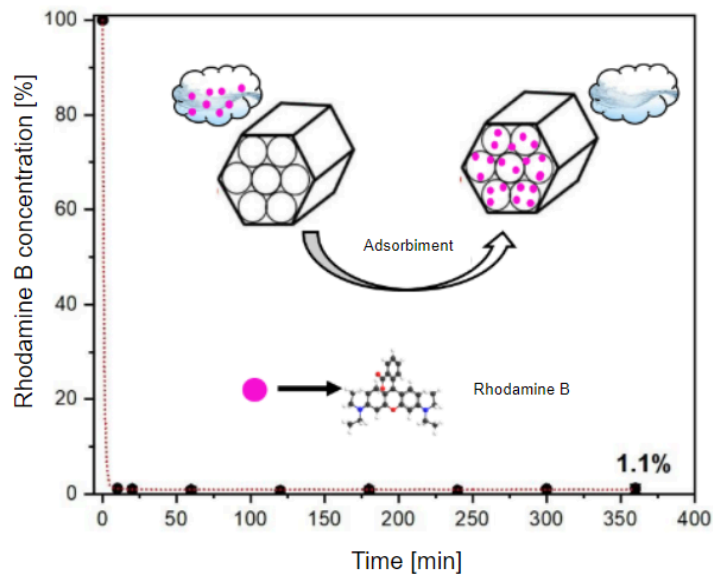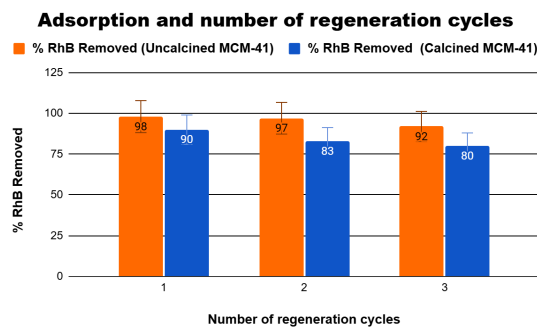

Graph 15

For the calcined MCM-41 samples, a rapid adsorption was observed during the first 10 minutes of contact time between the RhB dye solution and the material, after which adsorption equilibrium was established, with little change in adsorption capacity until the final contact time of 180 minutes. MCM-41 showed a maximum adsorption capacity of 1.50 [mg/g] in 20 minutes (graph 15).

- **Regeneration of the MCM-41**

The ability of an adsorbent material to be regenerated and reused is crucial to its ability to be used in wastewater treatment. In order to verify the reusability of MCM-41, repeated tests were carried out under the optimum conditions found. Each run consisted of a 1.0 [g] sample with 100 [mL] of dye at pH 1, shaken for 30 minutes. Regeneration was performed by washing each sample with 100 [mL] of deionised water and 50 [mL] of methyl alcohol (MeOH). After washing, the samples were filtered and dried at 60° [C] for 24 hours. The graph 16 shows the removal rate data in each adsorption cycle.

Another method for regeneration MCM-41 is by using high temperatures in such a way as to destroy the pollutant molecule; this is possible due to the strong thermal resistance of the MCM-41.

Graph 16

- **Results obtained**

From the results obtained and reported in the various graphs produced, it can be concluded that water purification water according to the principles of green chemistry using MCM-41 is good in the case of coloured contaminant molecules such as Rhodamine B. The removal of rhodamine B is strictly dependent on pH, contact time, concentration of the dye and the working temperature. The optimum values for the above-mentioned operating variables are proved to be: contact times greater than 15 minutes, reaction temperatures of 20-30° [C], Rhodamine B concentrations of 2.5×10^{-3} [M] and acid pH. Furthermore, the realisation by means of green chemistry of an MCM-41 structure to be used as an adsorbent material for the adsorption simultaneous absorption of dyes such as methylene blue and crystal violet gave satisfactory results.

- **Cost analysis**

The ability of an adsorbent material to be regenerated and reused is crucial to its ability to be used in wastewater treatment. In order to verify the reusability of MCM-41, repeated tests were carried out under the optimum conditions found. Each run consisted of a 1.0 [g] sample with 100 [mL] of dye at pH 1, shaken for 30 minutes. Regeneration was performed by washing each sample with 100 [mL] of deionised water and 50 [mL] of methyl alcohol (MeOH). After washing, the samples were filtered and dried at 60° [C] for 24 hours. The graph below shows the removal rate data in each adsorption cycle.

- **Conclusion**

From the results obtained and shown in the various graphs, it can be concluded that the production of MCM-41-type absorber materials according to green chemistry principles from local raw materials to be used for the purification of wastewater from the textile dyeing industry is promising. The best results were obtained with calcined MCM-41 samples.

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