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Conference Paper

Cleaning polluted waters from ions Mn(II) with rice hulk as a biosorbent

Mahi Latifi[1], Jeton Kuçi[2], Ejup Latifi[2], Kiril Lisichkov[1], Mirko Marinkovski[1], Stefan Kuvendiev[1]

[1]*Faculty of technology and Metallurgy – Skopje*
[2]*Ministry of Economy-Skopje*
Corresponding Author: mahi.ljatifi@zellerag.ch

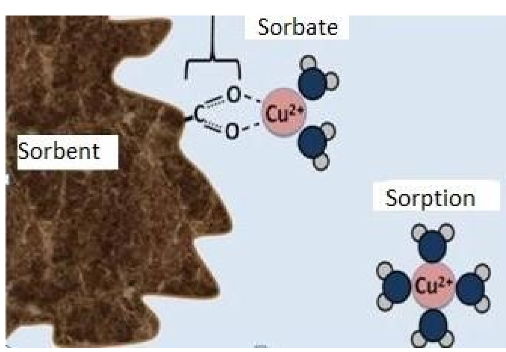
Abstract

Water pollution with heavy metals happens through a wide segment of processes and paths like natural resources and those anthropogenic. The pollution with heavy metals is slow but endless, as metallic toxic ions are not biodegrading. Loading the environmental with heavy metals is a very serious matter that we have to be worried about. Immediate development of industry and environmental overloading contributes a lot on the increase of pollution of water sources with heavy metals which represent a serious risk for the health and the life of all people. Therefore, it is very important to find a manner and a form to eliminate and remove heavy metals from water sources. Different types of agriculture remains may have using potential as absorbents of heavy metals, these have a low cost because they are not useful precipitates, available in high amounts but not harmful for the environment. For this reason, in this research, it is analyzed the ability of natural rice husk, as a natural agricultural by-product, in order to remove Mn(II) ions from water solutions.

Key words: Adsorption, rice husk, biosorption, isotherms

1. Adsorption

Conventional methods for water usage and eliminating heavy metals which are based mainly on precipitation (i.e. oxidation/precipitation, concentration/precipitation, etc.), but are not always sufficient for eliminating heavy metals from polluted waters. The reason of researching new methods for eliminating heavy metals from polluted waters is based on that with precipitation may be eliminated only those metals which are solvent in water, and is often insufficient to fulfill requirements of the newest standards of allowed amount of heavy metals. Therefore, it is necessary to do an additional cleaning process. On the other hand, low concentration of metals, makes the process very expensive, so all these problems open a new opportunity to explore new and innovative methods such as adsorption, separation with the help of membrane as well as bioconversion for usage of polluted contaminated waters with heavy metals. Adsorption has a substantial advantage as it requires lower investments, the simplicity of the process and realization of the process without any side effects.



2 Types of Adsorption

On the molecular level, the adsorption happens as a result of interaction between molecules in the surface of solid and liquid stage.

Physic adsorption happens as a result of intermolecular force attraction between adsorbent molecules and the absorbing material. This type of reaction happens under the influence of physical forces known as Van der Waals forces which happen between the absorbing material and the adsorbent and it is a reversible process. The interaction energy between adsorbent and adsorbed material are reactions of the same range, which is usually bigger than the energy of adsorbent condensation. In order to perform these reactions, it is not required any activation energy, which is necessary in chemistry.

Chemical adsorption is a result of a chemical interaction between solid adsorbent and the adsorbed substance. This is known as an activated adsorption and it is irreversible process. Chemical adsorption is especially important in the catalytic process; therefore, the energy of chemical adsorption is considered as the energy of a chemical reaction that may have an exothermic or endothermic process.

2.1 Adsorption isotherms and equilibrium

There are usually used four types of adsorption isotherms: Langmuir, Freudlich, combined with Langmuir-Freudlich and Ridlich-Peterson.

Many scientists have examined the equilibrium according to Langmuir, and the others have examined the same according to Langmuir and Freundlich about the reaction of the first, second n – level Parameters of isotherm equilibrium are reached when the information about equilibrium correspond during the absorption with the appropriate isotherm. Some scientists have studied only the maximum capacity of adsorbent by using Langmuir isotherm, and the others have examined the Freunlich isotherm, simply to show some kinetic models.

2.2 Parameters that influence the process of biosorption

-Biomass, type and properties

-Specific surface

-pH

-Temperature

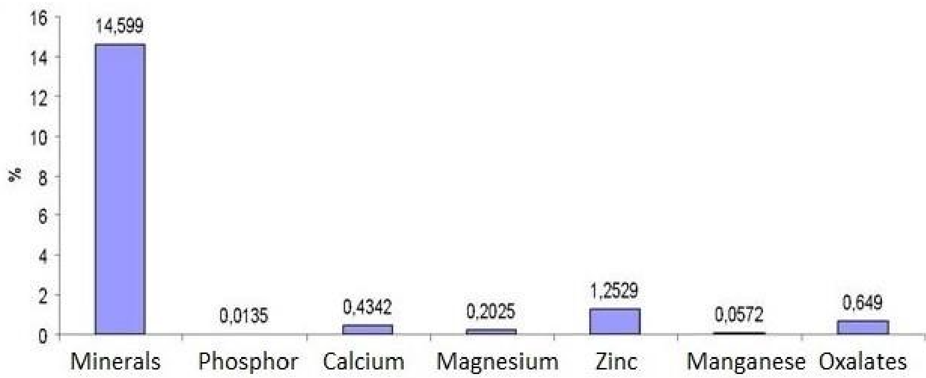
-Ione combination

-other cation

3. Rice husk

It is the orange peel which is indeed the rigid part which covers and protects the whole body of rice. Except the protection of the rice during its growth, the rice husk can be used as a construction material, fertilizer, isolation material, carburant, etc. The orange peel is a protection layer of the rice grain. The husk is made by hard materials, including silicium and lignin, for protection of the rice grain during its growth.

3.1 Structure of the rice husk

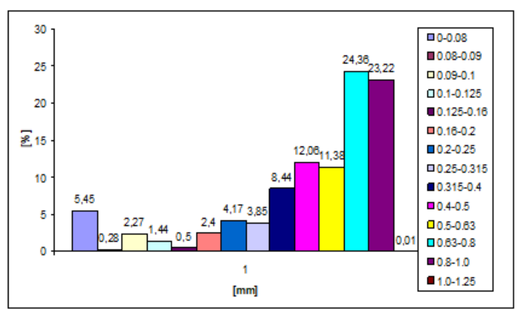


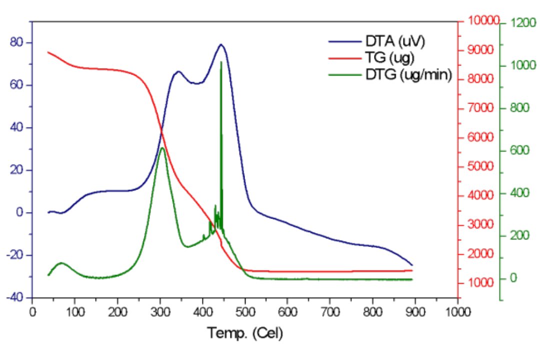
It can be stated that the rice husk contains more minerals comparing to other elements.

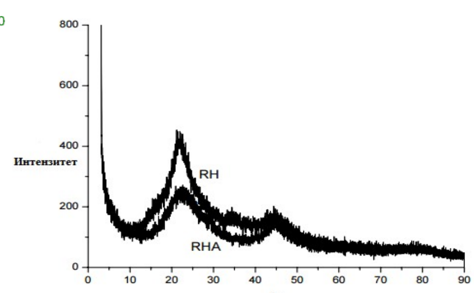
Structure of the rice husk (chemical analysis)

Structure	[%]
Mineral matter	14.599
Phosphor	0.0135
Calcium	0.4342
Magnesium	0.2025
Zinc	1.2529
Manganese	0.0572
Other	0.6490

Gravimetric analysis of rice husk

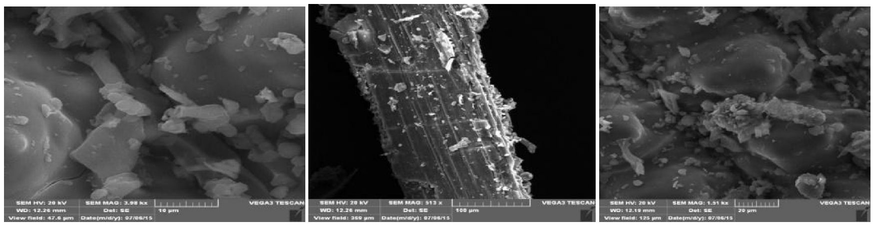






Thermic and thermo-gravimetric analysis of rice husk

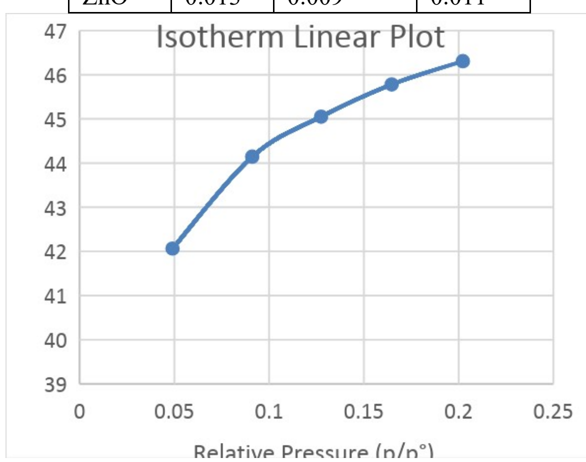
X-ray Graphical analysis of rice husk



SEM analysis of rise husk

In order to determine the quantity of several oxides at rice husk, it is made XRF analysis, which structure can be seen in the chart below:

Sample	Natural	Carbonated	Activted
SiO_2	85.196	0.137	13.170
Al_2O_3	0.17	0.151	3.473
CaO	0.613	0.186	0
Cr_2O_3	0.018	0.074	0.835
Fe_2O_3	0.185	0.576	0.051
K_2O	3.235	0.189	0.881
MgO	3.529	0.114	0.064
Mn_2O_3	0.190	0.011	0.544
Na_2O	3.778	0.201	0
P_2O_5	5.791	0.014	0
SO_3	0.090	91.156	77.9
SrO	0.009	0.009	0.065
TiO_2	0.013	0.007	0.143
ZnO	0.013	0.009	0.011

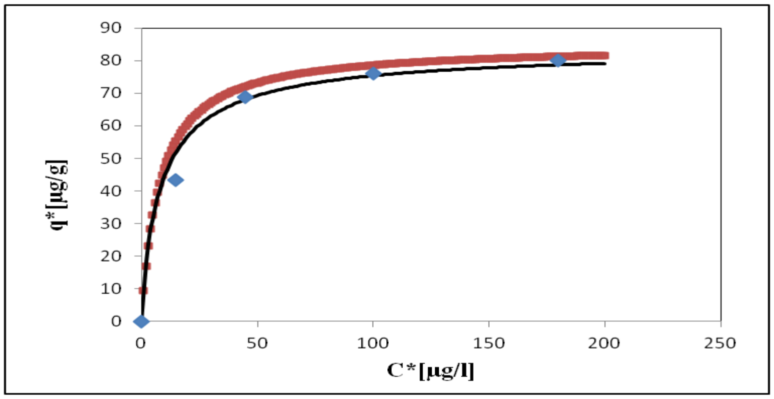


BET Analisys

Determining the specific surface of rice husk

Sample Mass	0.0947 g
Temperature of degassing	77.300 K
Specific surface for one drop	160.8197 m²/g
BET specific surface	158.3804 m²/g

4. Reaching the equilibrium according to Langmuir and Langmuir-Freundlich isotherms

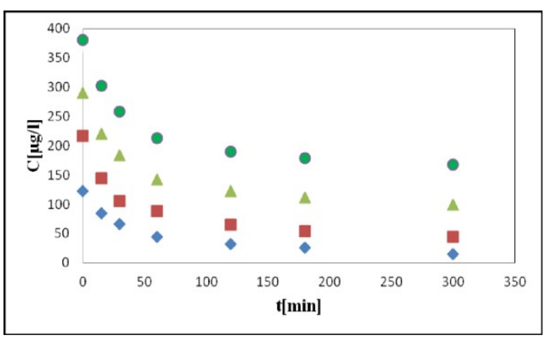


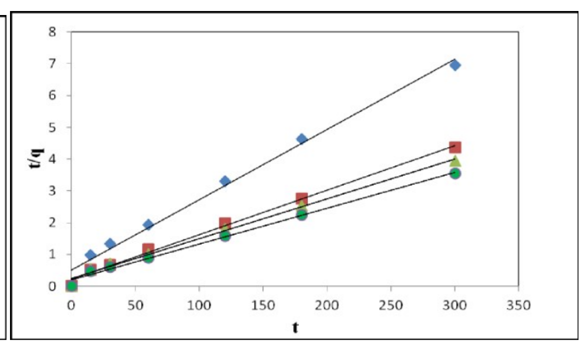
Experimental results; Langmuir - Langmuir-Freundlich

4.1 Parameters of equilibrium of analyzed isotherms

	Langmuir	Langmuir-Freundlich
R^2	0,9956	0,9986
q_m(μg/g)	112,96	117,239
K_L(dm^3/μg)	0,125	
K_C(dm^3/μg)$^{1/n}$		0,1514
N		1,143

The correlation coefficient R, is taken as an index to find with which isotherms we could have better results. At Mn(II)ions – Natural rice husk, better results are reached with the Langmuir-Freundlich isotherms, but we have chosen Langmuir isotherm to design the equilibrium system, due to the physical importance, as further in kinetic calculations of the adsorption process, it is important the coefficient K_L as well as maximum capacity of absorbent q_m reached with the Langmuir isotherm.





Concentration of adsorbent depending on the time for the Mn(II) system Natural rice husk V=2 dm^3, m=5g, T=25^{0}C

- C_0=400 μg/dm^3; - C_0=300 μg/dm^3; - C_0=200 μg/dm^3; - C_0=100 μg/dm^3;

From the experimental results we take information that show how are reduced the initial concentrations of adsorbant in relative systems depending on the time. The whole process is developed within e period of 300 minutes, by mixing continuously by a magnetic mixer with a speed of 400 rotations per minute at a room temperature 25 ± 2 0C, normal atmospheric pression and a constant mass of 5 g biosorbent.

	Reaction of the first stage		**Reaction of second stage**	
Mn	R^2	k (min^{-1})	R^2	k ($g{\cdot}\mu g^{-1}\, min^{-1}$)
100	0.886	-0.44207	0.99	$20{\cdot}10^{-5}$
200	0.859	-0.34474	0.9364	$6{\cdot}10^{-5}$
300	0.887	-0.52003	0.8566	$2{\cdot}10^{-5}$
400	0.89	-0.5727	0.7091	$0.9{\cdot}10^{-5}$

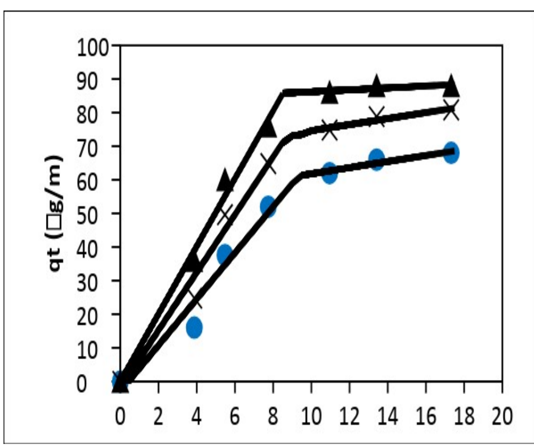
4.2 Biosortion chinetics for pseudo reaction of the second range for Mn(II) ion system
V=2 dm^3, m=5g, T=25^{0}C

	Preudo reaction of the first range		Pseudo reaction of the second range	
Mn	R^2	k (min^{-1})	R^2	k ($g{\cdot}\mu g^{-1}\, min^{-1}$)
100	0.8601	-0.0082	0.9886	$24{\cdot}10^{-5}$
200	0.8864	-0.0105	0.9944	$4{,}47{\cdot}10^{-5}$
300	0.8656	-0.0099	0.9923	$3{,}79{\cdot}10^{-5}$
400	0.8652	-0.0106	0.9931	$2{,}57{\cdot}10^{-5}$

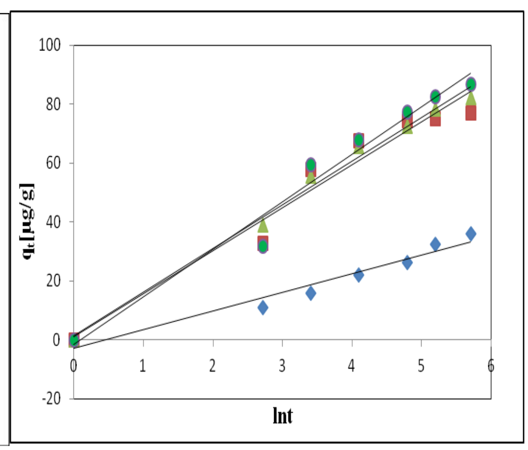
For the Mn(II) ion system – reaction of the first range with the help of biosorbent the natural rice husk, the correlation coefficient is over 0,8, a satisfying value, but it does not have to be that the kinetic reaction is developed according to this mechanism.

During the reaction of the pseudo-second range, there are reached excellent results that are based on the R correlation coefficient. All the coefficient values have a value over 0,9, by showing that reaction kinetics for the shown system is developed according to this mechanism.

Kinetics of rect. Accord to Moris Weber-midgranular diffusion



Kinetics of reaction according to Elovich model



- Kinetic model of midgranular diffution according to Moris Weber end Elovich for Mn**(II) ions**

  - C_0=400 µg/dm^3; - C_0=300 µg/dm^3; - C_0=200 µg/dm^3; - C_0=100 µg/dm^3;

Moris Weber				
First stage of react. From 0-60 min			Second stage of react from 120-300 min	
Mn	R^2	**k**	R^2	**K**
100	0.95	6.8701	0.9009	0.9033
200	0.973	8.6035	0.9009	0.9033
300	0.989	10.073	0.6302	0.2856
400	0.95	6.8701	0.9009	0.9033

Using the kinetics model of Webber – Morris for the interstitial diffusion for the bisorption process, shows that the process can be devided into two stages: the first stage where there is a diffusion of metalic ions through the absorbing mass at the outer surface of biosorbent, passing the limit through diffusion layer and gradual adsorption of metalic ions at the inner surface of the adsorbent. This process, the inner intergranular diffusion is a determined rule for the speed of the process, this stage may also be called the stage of a fast adsorption which is developed until the minute 60 of biosorption process and the second stage, otherwise called slow adsorption which corresponds to a definition of a dynamic equilibrium between the concentration of metalic ions in solution and biosorbent.

Mn	α (µg g^{-1} min^{-1})
100	7.8286
200	12.548
300	14.102
400	15.846

5. Conclusion

-The rice husk represents a very good biosorbent for elimination of Mn from polluted waters
-The absorption process has biosorption coefficient with a very high value-over 0.9
-The experimental results correspond totally with adsorption isotherms
-By increasing the concentration of the initial mass of the metal in solution, the coefficient of adsorption increases as well.
-The more suitable value of pH for the Mn(II) system is pH=6
-The length of biosorption process is max. 300 min.
-The process is very cheap, no high costs, ecological, and the process does not have side effects.

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