

Biosorption of Mn(II) ions from water solutions by natural sorbent: equilibrium study

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Abstract

In the modern society, the problem of the treatment of natural and wastewater resources and their management, is becoming very important.

Of particular interest is the definition of adequate and sophisticated procedures for the treatment of natural and wastewater resources, regardless of whether the source of pollution is of geogenic or anthropogenic origin.

Sustainable development of separation processes has recently been increasingly imposed by the need to develop modern, non-conventional bioseparation processes for the elimination of toxic metals from wastewater, by applying low cost unconventional sorbents.

The purpose of this paper is to remove Mn (II) ions from aqueous solutions by applying a natural adsorbent (grape branches - agricultural waste). To accomplish the established goal, the experiments were carried out with model solutions with known initial concentrations of Mn(II) ions in a laboratory batch reactor, with the purpose of studying the effect of adsorption time on adsorbate concentration and on the adsorbed amount of Mn(II) ions.

The raw material was characterized in terms of its chemical composition and particle size distribution.

The obtained results were applied to model the adsorption equilibrium using several adsorption isotherms such as Langmuir, Freundlich, Langmuir-Freundlich and Redlich-Peterson, using the MATLAB/Curve fitting toolbox software package.

Key words: adsorption, toxic metals, biosorbent, grape branches, wastewater

1. Introduction

The world today is faced with the largest evidenced water supply crisis. Apart from reducing the quantities of available water resources, the world is also threatened with long-term pollution of existing reserves.. Present in higher concentrations than prescribed, heavy metal ions are highly toxic and endanger living organisms and humans in the polluted environment. Therefore there is a growing concern for the development and improvement of more accessible

wastewater treatment methods for the reduction of heavy metals to an acceptable level (Rahul 2013, Ghormi et al., 2013).The adsorption is the most commonly applied method as it is considered to be an efficient and economic which provides flexibility in design and course of the process and gives an effluent with high quality. Many materials, such as clay, zeolites, activated carbon, perlite, metal oxides, waste by-products from the agricultural and food industry, biosorbents, nanomaterials, can be used as adsorbents for removal of heavy metal ions from aqueous solutions (Al-Jlil 2014, Liang and Zhijun 2014, Sarifah et al., 2015).The adsorption properties of grape branches for removal of Mn(II) ions from water resources are presented in this study.

2. Materials and Methods

2.1. Natural sorbent preparation

The applied grape branches are with a diameter of 0.5-1.0 cm and a length of 1.0-2.0 cm. The resulting biomass is immersed in heated, de-ionized, water (70-80 ° C) for 4-5 hours to remove dust and other impurities. After this treatment the biosorbent is treated with 70% ethanol solution and it is dried at 40°C. The dried working material is granulated with a laboratory mill.

2.2. Adsorption experiment

Adsorption experiments were carried out using batch adsorption method (laboratory glass reactor of 2l, 2.5 g/l biosorbent, pH-6, magnetic stirring at 400 rpm, room temperature, 3h) to obtain equilibrium data for different initial Mn(II) ions concentrations of 0.2, 0.3, 0.4 and 0.5 mg/l. Experimental data were processed by Langmuir, Freundlich, Langmuir-Freundlich and Redlich-Peterson isotherms, by using MATLAB/Curve fitting toolbox.

3. Results and Discussion

3.1. Material characterization

The chemical composition of grape branches is given in Tab.1. As typical for biomass the majority of composition includes cellulose, hemicelluloses and lignin.

Table1. Chemical composition of grape branches

Comp.	cellulose	hemicellulose	lignin	tannin	proteins	moisture
wt%	30	21	18	16	6	9

The results obtained by sieve analyses are shown on Tab.2. The biosorbent has the highest percentage of particles with size over 1mm.

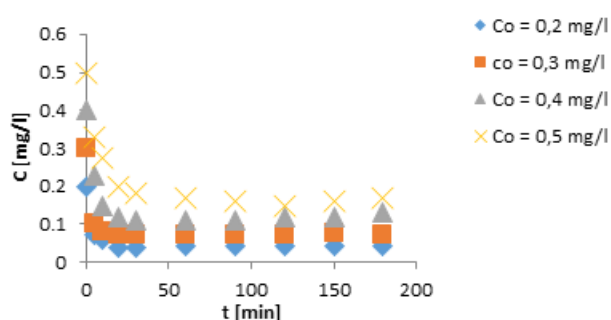
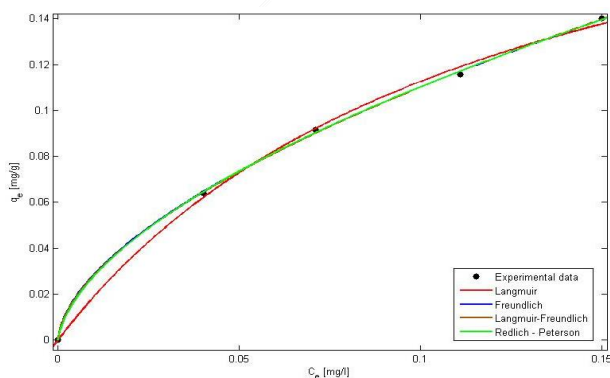
Table 2. Particle size distribution of grape branches

Fraction (mm)	wt%
>1.000	42.94
0.500 -1.000	31.96
0.250-0.500	12.18
0.125-0.250	11.92
0.063-0.125	0.80
<0.063	0.06

Table 3. Parameters and correlation coefficients of equilibrium isotherm models

Isotherm	Langmuir	Freundlich	Lang.-Freu.	Redl.-Peters.
Parameters and correlation coefficients	q_m [mg g ⁻¹] 0.2477 K_L [l mg ⁻¹] 8.336 R^2 0.9981	K_F [l g ⁻¹] 0.4216 n 1.715 R^2 0.999	q_m [mg g ⁻¹] 13.86 K_C [l mg ⁻¹] 0.031 n - 1.69 R^2 -0.9996	K_{RP} [l g ⁻¹] 20.69 A [l mg ⁻¹] 49.19 β -0.4422 R^2 -0.0996

The influence of the time of adsorption on the change of concentration of Mn(II) ions is given in Fig1. It can be seen that the adsorption equilibriums, for all initial concentrations of Mn(II) ions, were attained after 30-60 min.

**Figure 1.** Change of concentration of Mn(II) ions depending on time of adsorption**Figure 2.** Modeling of the experimental data for the system Mn(II) - grape branches

3.2. Effect of time of adsorption

3.3. Adsorption isotherm studies

Experimental data were processed by the four most commonly used isotherms: Langmuir Freundlich, Langmuir-Freundlich and Redlich-Peterson, by using the MATLAB/Curve Fitting Toolbox, Fig.2. Table 3 contains the data of model parameters of the applied adsorption isotherms as well as the coefficients of correlation (R^2) for the adsorption of Mn(II) ions on grape branches. The high values of the coefficients of correlation ($R^2 > 0.99$) reveal that experimental results correspond good to all four utilized isotherm models.

4. Conclusion

In this study, the biosorption of Mn(II) on grape branches was investigated. The steady state of the system for all initial concentrations of Mn(II) was achieved after 30 - 60 min. of adsorption. All applied isotherm models indicate good correspondence to the experimental results. The obtained results suggest that natural grape branches can be successfully used as sorbents for removal of heavy metal ions from water resources.

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