# REMOVAL OF MANGANESE(II) IONS FROM AQUEOUS SOLUTIONS. II. THERMODYNAMICS

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## ABSTRACT

The adsorption of Mn(II) ions from water solutions was investigated at 288, 298 and 308 K using white rice husks ash as an adsorbent. The obtained results showed that the removal of Mn(II) ions from aqueous solutions using WRHA is a chemisorption process. In this process the OH-groups of $SiO_2$ take part, releasing $H^+$ ions in the solution. The adsorption process was well described with the Langmuir isotherm. On its basis the values of $\Delta G^o$, $\Delta H^o$ and $\Delta S^o$ for adsorption of Mn(II) ions onto WRHA were calculated. From the data analysis and the obtained results it was concluded that WRHA is an effective and very cheap adsorbent for removing Mn(II) ions from water solutions.

*Keywords: Adsorption, Manganese(II) ions, Rice husk ash; Batch study, Adsorption isotherms.*

## INTRODUCTION

Water pollution by heavy metals, through the discharge of industrial effluents, is a global environmental problem. The presence of heavy metal ions in municipal and industrial wastewater and their negative effect on the environment and human health have been a subject of scientific research for a long time because of their extreme toxicity even at low concentrations, and their tendency to accumulate in the food chain. The removal of metal ions from aqueous solutions, Mn(II) ions in particular, is a serious problem in many countries. Manganese is one of the elements that are most difficult to be eliminated from surface water. [1-3]. Manganese is an oligo-element, which is necessary for human survival, but becomes toxic when the concentration in the human body is too high. According to World Human Organization, the maximum concentration of manganese admissible in drinking water is 0.05 mg $L^{-1}$ [4]. Excess manganese in drinking water can cause problems in the nervous and respiratory systems and retards the intellectual development and normal growth of infants. Manganese can also provoke the illness of Parkinson, pulmonary disorder and bronchitis. Prolonged exposure to high manganese concentrations can lead to impotence in men [1]. For these reasons it is necessary to treat the water contaminated by excess manganese so as to reduce its impact on the environment and human health. Several processes are used for water purification: coagulation-flocculation, adsorption on activated carbon, electro coagulation, ions exchange, inverse osmosis, extreme filtration, etc. [5-7]. These techniques are highly effective, but very expensive in most cases. In recent years the studies have been oriented towards physicochemical methods for water purification using natural materials like clays, agricultural waste (wood saw dust, activated carbon, etc.). There are a number of studies, which indicate that the white rice husks ash (WRHA) and the black rice husk ash (BRHA) can be excellent adsorbents, because they are inert, cheap and have good porous structure and pore size distribution.

The aim of the present work is to study the adsorption thermodynamics of Mn(II) ions from aqueous solutions onto white rice husks ash at different temperatures.

## EXPERIMENTAL

All the reagents used in the experiments were of analytical grade. The initial stock solution of Mn(II) ions (1000 mg $L^{-1}$) was prepared by dissolving the required amount of manganese acetate $Mn(CH_3COO)_2 \cdot 4H_2O$ (Merck). A series of six solutions were prepared by diluting aliquots of the initial solution in double distilled water. The concentration of Mn(II) ions was determined by measuring the absorbance at the characteristic wavelength using a spectrophotometer JENWAY

6300 (UK). Manganese is oxidized to permanganate with potassium periodate in an acid medium, according to the following reaction:

$$2Mn^{2+} + 5IO_4^- + 3H_2O \leftrightarrow 2MnO_4^- + 5IO_3^- + 6H^+ \tag{I}$$

A standard curve of absorption at wavelength 525 nm versus concentration was generated. Once the permanganate was formed, the concentration of Mn(II) was determined using the standard curve.

### Preparation of the adsorbent

A batch of white rice husk ash (WRHA) has been produced via pyrolysis of raw rice husks in a pilot plant fluidized-bed reactor with a capacity of 100 kg $h^{-1}$. The WRHA is almost pure amorphous silica ($SiO_2 > 94$ mass %), highly porous and has a specific surface of 228 $m^2$ $g^{-1}$. The surface of WRHA is polar, because it contains surface OH-groups, which makes this adsorbent suitable for adsorption of ions. Detailed physicochemical characteristics of the WRHA have been presented previously [8]. The obtained product was used without any pretreatment for the removal of Mn(II) ions from model aqueous solutions in batch experiments.

### Batch experiment

For the thermodynamic study, six Mn(II) solutions were prepared with concentrations 10, 20, 40, 60, 80, and 100 mg $L^{-1}$. 0.25 g of WRHA were added to 100 mL of each solution in a 150 mL glass container equipped with a water jacket for maintaining constant temperature (288, 298 or 308 $\pm$ 0.5 K) with a continuous stirring at 300 rpm by an electromagnetic stirrer. Two parameters were varied – initial Mn(II) ions concentration and temperature, in order to investigate their effect on the adsorption process. For the determination of pH influence on the adsorption process, 0.1 M HCl and 0.1 M NaOH were used to adjust the desired initial pH of the solutions.

The percent removal of Mn(II) ions by WRHA, %, and the amount of ions adsorbed per unit weight of adsorbent at time $t$, mg $g^{-1}$, were calculated using the following equations:

$$\% \text{ removal Mn(II) ions} = \frac{C_0 - C_t}{C_0} \times 100, \tag{1}$$

$$Q_t = \frac{C_0 - C_t}{m} \times V, \tag{2}$$

where $C_0$ and $C_t$ are the initial concentration of Mn(II) ions and their respective concentration at any time $t$, mg $L^{-1}$, $V$ is the solution volume, L, and $m$ is the weight of the adsorbent, g.

### Mathematical apparatus

In the literature are presented different equations describing the adsorption processes according to their specificity [9].

### Freundlich isotherm

The empirical Freundlich adsorption isotherm is based on adsorption on a heterogeneous surface and is expressed by the following equation:

$$Q_{eq} = K_F C_{eq}^{1/n}, \tag{3}$$

where $K_F$ is a rough indicator of the adsorption capacity, (mg $g^{-1}$)(L $mg^{-1}$)$^{1/n}$, and $1/n$ is the adsorption intensity. $C_{eq}$ is the equilibrium concentration of Mn(II) ions, mg $L^{-1}$, and $Q_{eq}$ is the amount of Mn(II) ions adsorbed per unit weight of the adsorbent at equilibrium, mg $g^{-1}$. The values of $K_F$ and $n$ were obtained by plotting $\ln Q_{eq}$ versus $\ln C_{eq}$ according to the linear form of the Freundlich equation:

$$\ln Q_{eq} = \ln K_F + \frac{1}{n} \ln C_{eq} \tag{4}$$

In general, as the $K_F$ values increase, the adsorption capacity of the adsorbent for a given sorbate increases. The higher numerical values of $K_F$ confirm the significant affinity of the corresponding adsorbent for the given metal ions. The magnitude of the exponent $1/n$ gives an indication of the favorability of adsorption. Values of $n > 1$ represent favorable adsorption condition.

*Langmuir isotherm*

The Langmuir isotherm model is based on the assumptions that the surface is energetically homogeneous and there is no interaction between the neighboring adsorbed species, the uptake occurs on homogeneous surface by monolayer sorption and the adsorbed layer is unimolecular. The maximum adsorption occurs when the surface is covered by a monolayer of sorbate. For solid-liquid systems Langmuir adsorption isotherm can be expressed as:

$$Q_{eq} = \frac{Q_{max} K_L C_{eq}}{1 + K_L C_{eq}}, \tag{5}$$

where: $Q_{eq}$ is the equilibrium amount of sorbate per unit weight of adsorbent, mg g$^{-1}$, $C_{eq}$ is the equilibrium concentration of the sorbate in the solution, mg L$^{-1}$, $Q_{max}$ and $K_L$ are the Langmuir coefficients related to the monolayer adsorption capacity, mg g$^{-1}$, and the adsorption energy, L mg$^{-1}$, respectively. A linear form of the Langmuir adsorption isotherm can be obtained after some rearrangements:

$$\frac{1}{Q_{eq}} = \frac{1}{Q_{max} K_L C_{eq}} + \frac{1}{Q_{max}} \tag{6}$$

It is one of the ideal limiting-condition type models. The equation is valid for monolayer sorption onto a homogeneous surface with a finite number of energetically identical sites. The Langmuir adsorption parameters $Q_{max}$ and $K_L$ can be determined from the intercept and the slope of the plot $1/Q_{eq}$ versus $1/C_{eq}$.

*Estimation of the thermodynamic parameters $\Delta G^o$, $\Delta H^o$ and $\Delta S^o$*

The thermodynamic studies play an important role in order to fully understand the nature of the adsorption. Therefore the adsorption isotherm data obtained at different temperatures were used to calculate the thermodynamic parameters associated with the adsorption process. Based on the Van't Hoff equation, Langmuir constants $K_L$ were used to determine the change of the standard Gibbs free energy $\Delta G^o$, standard enthalpy change $\Delta H^o$ and standard entropy change $\Delta S^o$ using the following equations [9]:

$$\Delta G^o = -RT \ln K_L \tag{7}$$

$$\ln K_L = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{8}$$

The values of $\Delta H^o$, kJ mol$^{-1}$, and $\Delta S^o$, J mol$^{-1}$ K$^{-1}$, can be calculated from the slope and intercept using the plotted graph of $\ln K_L$ versus $1/T$. The value of the change of standard Gibbs energy $\Delta G^o$, kJ mol$^{-1}$, can be calculated using the next relationship:

$$\Delta G^o = \Delta H^o - T \Delta S^o \tag{9}$$

Negative values of $\Delta G^o$ and $\Delta H^o$ show that the adsorption process is spontaneous and exothermic. Such values of $\Delta H^o$ correspond to an isosteric heat of adsorption with zero surface coverage (i.e. $Q_{eq} = 0$). Positive values of $\Delta S^o$ indicate the affinity between adsorbent-adsorbate and suggest an increased randomness at the solid-solution interface during the adsorption process. This may occur, for example, at the liberation of water molecules from the hydrated shells of the adsorbed species. As the sorbed molecules have two degrees of transitional freedom on the surface at the most and in

view of this fact, the rotational freedom of sorbed species must always be less than that of gas phase molecules, the entropy change on sorption $\Delta S = S_{ads} - S_{gas}$ is inevitably negative. The negative values of $\Delta S^{o}$ suggest the probability of favorable sorption with no structural change at solid-liquid interface. In order a significant sorption to occur, the change of Gibbs free energy $\Delta G^{o}$ must also be negative, which requires negative $\Delta H^{o}$ or exothermic sorption. This is generally true for sorption from liquid phase, although exceptions are possible.

### RESULTS AND DISCUSSION

In Fig. 1 are presented the adsorption isotherms of Mn(II) ions at 288, 298 and 308 K onto WRHA.
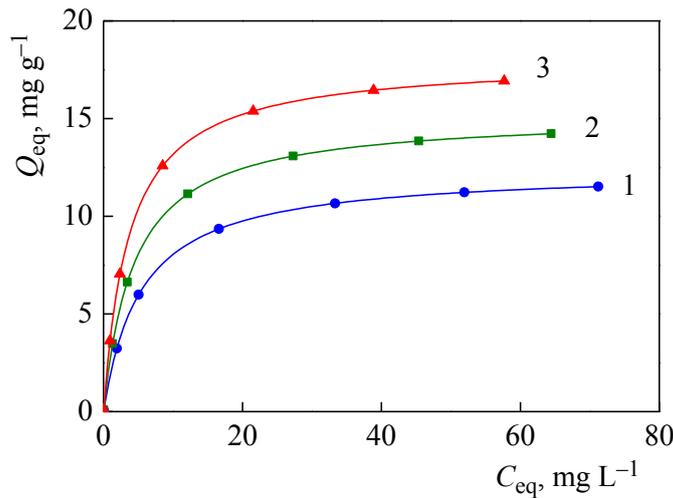


**Fig. 1.** Adsorption isotherms of Mn(II) ions at 288 – 1, 298 – 2 and 308 K – 3 onto WRHA.

As can be seen from Fig. 1 with the temperature increase, the adsorption isotherms curves lie progressively higher. This is evidence that the sorption process was endothermic, and the adsorption was a chemical process. The corresponding plots were drawn on the basis of these data and Eqs. (4) and (6). The obtained results showed that the most appropriate adsorption isotherm was Langmuir equation. For this reason Fig. 2 presents solely the Langmuir adsorption isotherms at 288, 298 and 308 K.
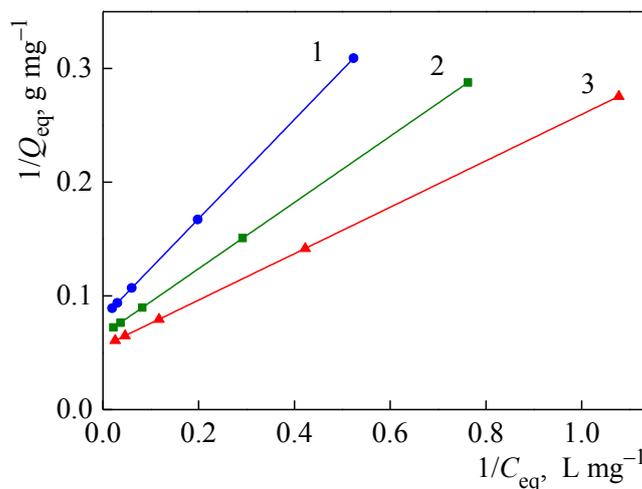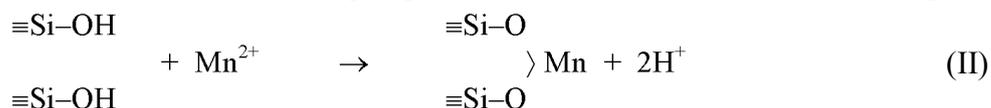


**Fig. 2**. Plots of $1/Q_{eq}$ versus $1/C_{eq}$ at 288 – 1, 298 – 2 and 308 K – 3.

Pursuant to Eq. (6) the values of the Langmuir constants $K_{L}$ and $Q_{max}$ were calculated for the corresponding temperatures and presented in Table 1. Using Eqs. (7), (8) and (9) the values of $\Delta G^{o}$, $\Delta H^{o}$ and $\Delta S^{o}$ were calculated for the adsorption of Mn(II) ions onto WRHA.

**Table 1.** Adsorption characteristics of Mn(II) ions onto WRHA.

| $T$, K | $K_L$, L mg$^{-1}$ | $Q_{max}$, mg g$^{-1}$ | $\Delta G^o$, kJ mol$^{-1}$ | $\Delta H^o$, kJ mol$^{-1}$ | $\Delta S^o$, J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|---|
| 288 | 0.185 | 12.39 | 4.047 | | |
| 298 | 0.226 | 15.20 | 3.685 | 14.49 | 36.25 |
| 308 | 0.272 | 18.01 | 3.324 | | |

As can be seen from Table 1, the adsorption process was endothermic and this may be explained with a chemical reaction between the surface OH-groups of $SiO_2$ and the Mn(II) ions, for example:

$$\begin{array}{ccc} \equiv Si\text{--}OH & & \equiv Si\text{--}O \\ & + \ Mn^{2+} \quad \rightarrow & \rangle Mn \ + \ 2H^+ \qquad \text{(II)} \\ \equiv Si\text{--}OH & & \equiv Si\text{--}O \end{array}$$

The values of $\Delta G^o$ were positive in the entire studied temperature range, proving that the adsorption process was not spontaneous. The positive values of $\Delta S^o$ showed that entropy had increased in the process, because the adsorption of every one $Mn^{2+}$ ion was accompanied by the release of two $H^+$ ions in the solution.

**CONCLUSIONS**

The obtained results showed that the elimination of Mn(II) ions from aqueous solutions using WRHA as an adsorbent is a chemisorption process, in which OH-groups of $SiO_2$ participate, releasing $H^+$ ions in the solution. The adsorption process was well described with Langmuir isotherm. On the basis of that thermodynamic model the values of $\Delta G^o$, $\Delta H^o$ and $\Delta S^o$ for Mn(II) adsorption onto WRHA were calculated. The WRHA was set as an effective and very cheap adsorbent proposed to be chosen when it is necessary to remove Mn(II) ions from waste water.

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