

## The study of nonlinear isotherms for Mn(II) adsorption from aqueous solution

Maryam Saleh Mohammadnia<sup>a\*</sup>, Peyman Salaryan<sup>b</sup>, Nahid Ghasemi<sup>a,c</sup>

<sup>a</sup>Department of Chemistry, Sciences Faculty, Arak Branch, Islamic Azad University, Arak, Iran

<sup>b</sup>Young Researchers Club, I.A.U, Kazerun branch, Kazerun, P.O.Box 168 / 73135, Iran

<sup>c</sup>Process Systems Engineering Center (PROSPECT), Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

### Abstract

The pollution of heavy metal is considered due to recent industrial activities. These pollutants must be removed from wastewater because of environmental damages. The adsorption process is a new method for this purpose. In the present work, the adsorption of manganese ions from aqueous solution was studied as environmental pollutants. Black carbon derived from rice straw one of the agricultural wastes, is used as adsorbent, and three parameters to determine the adsorption isotherms such as pH, adsorbent dosage and contact time were optimized for initial concentration (100mg L<sup>-1</sup>) and volume of solution (100ml). Optimal values, were obtained (pH=6, adsorbent dosage (0.3g) and contact time at 60 minutes. Three nonlinear isotherms such as Langmuir, Redlich-Peterson and Sips models were investigated. Chi-square analysis by using solver add in excel were used to obtaining the best fit of the experimental data in the cases of predicated isotherm models. Experimental results showed that adsorption of Mn(II) on black carbon followed by Sips isotherm.

**Key words:** Adsorption, isotherm, Mn(II), pollutant, Chi-square analysis

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\*Corresponding Author, e-mail: maryamsaleh4@gmail.com, Tel.: +98 8633670017; fax: +988633670017

### 1. Introduction

One of today's environmental challenges is the excessive use of heavy metals for industrial and domestic practices contaminates ground and surface water [1], before these pollutants discharge to the environment, it is important to remove from water and wastewater [2]. The high Mn(II) concentrations also caused gastrointestinal accumulation, low haemoglobin levels and neurotoxicity. Industries such as those involved in the production of fertilizer, petrochemicals, electroplating, tanneries, metal processing, and mining industries are released Mn(II) into the environment. [3-5]. Activated carbon has been used as an adsorbent in wastewater treatment application throughout the world, but because of its cost in efficiency it is no longer attractive to be widely used in small-scale industries. In recent years research interest into the production of adsorbents to replace the costly activated carbon has intensified [6]. Several studies related to wastewater treatment were carried out using low-cost materials such as: rice husk (RH), that has interesting properties such as hydrophilic, porous, and high surface area, is promised as adsorbent [7], wheat barn is used as adsorbent because of its easily available, economically viable, and biodegradable [8], and also Jordanian Pottery materials was chosen as

adsorbent due to its low cost, its granular structure, insolubility in water, chemical stability and local availability [9]. Adsorption isotherms are used to evaluate the adsorption mechanism. Yuh-Shan Ho compared the linear least-squares method and a non-linear method of three widely used isotherms, the Langmuir, Freundlich and Redlich-Peterson in an experiment examining lead ion sorption onto peat. A trial-and-error procedure for the non-linear method using the solver add-in with Microsoft's spreadsheet, Microsoft Excel was used [10]. The heavy metal biosorption capacities of the non-living *U. lactuca* alga was investigated by Zakhama S, Dhaouadi H, et al. and they were using the most common kinetic and equilibrium models in their nonlinear method to evaluate the biosorption mechanism and performance of this algal biomass for lead, copper, cadmium and nickel [11]. In this study, a non-linear method of three widely used isotherms, the Langmuir, Redlich-Peterson and Sips were compared for manganese ion sorption onto rice-straw black carbon.

### 2. Material and Methods

#### 2.1. Materials

Manganese (II) solution were prepared from manganese nitrate (II). Rice straw black carbon that sieved to

pass through a 60-mesh (ASTM) were used as adsorbent. HCl and NaOH were used to adjusted the initial pH of solution. All solutions in this experiment were used in a volume of 100 ml.

## 2.2. Adsorption experiments

100 mg L<sup>-1</sup> of Mn (II) solution were used to determine optimum pH in the experiments. The effect of pH was investigated in the range of 3.0-8.0 and 0.2 g of adsorbent were added to each solution and agitated on a shaking bath at 250 rpm for 30min. 100 mgL<sup>-1</sup> of solutions were prepared to determine the effect of adsorbent dosage on the adsorption efficiency. 0.1 to 0.6 g of adsorbent were added to each solution and agitated on a shaking bath at 250 rpm for 30 min. The initial pH was adjusted at 6.

Solutions of 100 mg L<sup>-1</sup> were prepared to determine the optimum contact time and 0.3 g of adsorbent were added into each solution and the initial of pH value were adjusted (pH=6) and contact time between 30 to 75 minutes were studied.

Four solution with concentration 20,40,60 and 80 mgL<sup>-1</sup> were prepared to investigated the isotherm adsorption .Each solution was added by 0.3 g of adsorption and were stirred at 250 rpm for 60 minutes. The initial pH was adjusted at 6.

## 3. Results and Discussion

### 3.1. Determine the optimum pH

Experimental results for the effect of pH on adsorption of Mn (II) in the study area is shown in Fig.1. As seen from Fig .1 the optimum pH in the range of Mn(II) adsorption is 6. The range of chemical precipitation of Mn(II) is at pH above 6 and also maximum adsorption is occur at pH above 6 .

### 3.2. Determine the optimum adsorbent

Effect of amount of adsorbent on the Mn (II) adsorption is shown in Fig.2. removal rate were increased with increase in the amount of adsorbent and reaches to maximum value with 0.3 g of adsorbent.

After this value removal rate does not change much, therefore the optimum amount of adsorbent was determined on 0.3g.

### 3.3. Determine the optimum contact time

Contact time is an important factor in adsorption. Adsorption is an equilibrium process and determining the equilibrium time is important .The effect of contact time on removal of manganese (II) is shown in Fig .3. With increasing contact time to equilibrium time , removal percentage was increased after equilibrium time, removal percentage does not have much effect, therefore the 60 minutes, was selected as the optimum time.

### 3.4. Adsorption isotherm

To study adsorption isotherms, Chi-square(X<sup>2</sup>) analysis was used to fit experimental data with adsorption isotherm. In this study solver add in is used to fit the data in Excel .The X<sup>2</sup> value is determined by Eq.1.

$$\chi^2 = \sum ((q_e - q_{e,m})^2 / q_{e,m}) \quad (1)$$

Where q<sub>e</sub> (mg g<sup>-1</sup>) is equilibrium capacity from the experimental data (mgL<sup>-1</sup>) and q<sub>e,m</sub> is equilibrium from model.

The experimental data are in good agreement with model data. Langmuir ,Redlich-Peterson and sips models were used in the present work. The expressed mathematical models are shown in table1. The value of isotherm parameters that were studied in this work are shown in table 2. The values of X<sup>2</sup> is compared and between isotherms models ,Sips isotherm were shown lower value than other isotherms. Therefore it can be concluded that the experimental data were fitted with Sips isotherm.

## 4. Conclusion

The following conclusions were drawn from study of adsorption of Mn(II) on carbon black.

1. The optimum adsorption of Mn(II) were occurred at pH6.
2. 0.3g of adsorbent was selected as optimum adsorbent.
3. The adsorption of Mn(II) on black carbon is rapidly equilibrated within 60 minutes.
4. From various adsorption isotherms investigated, only Sips model was found to be in good agreement with the experimental.

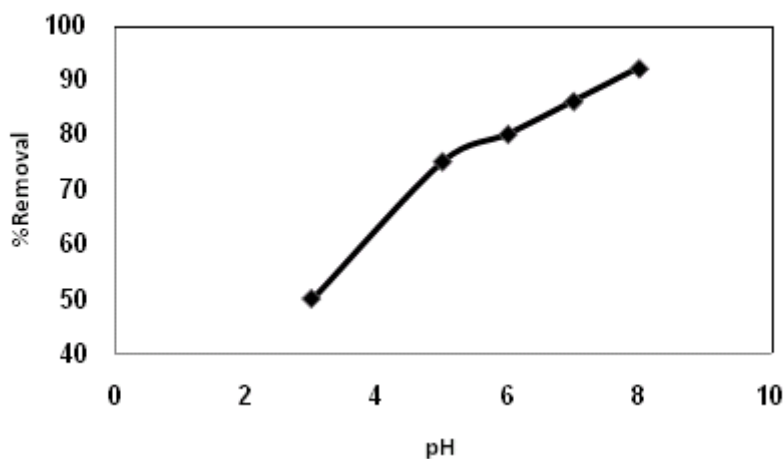


Fig.1. Effect of pH on percentage removal of Mn(II)

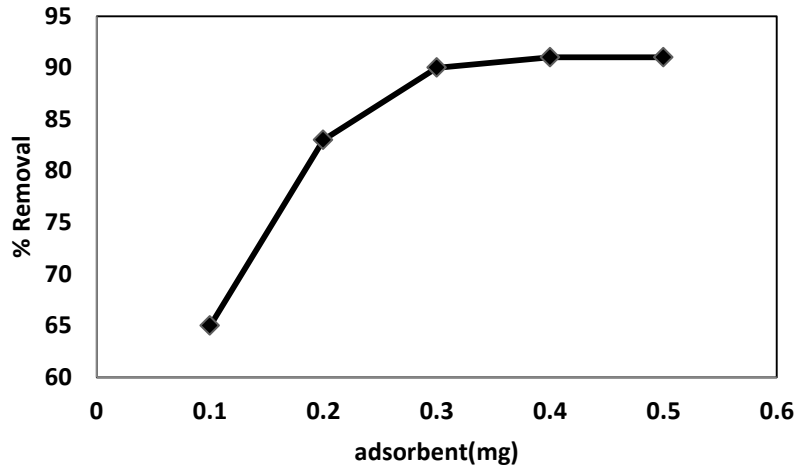


Fig.2. Effect of adsorbent dosage on percentage removal of Mn(II)

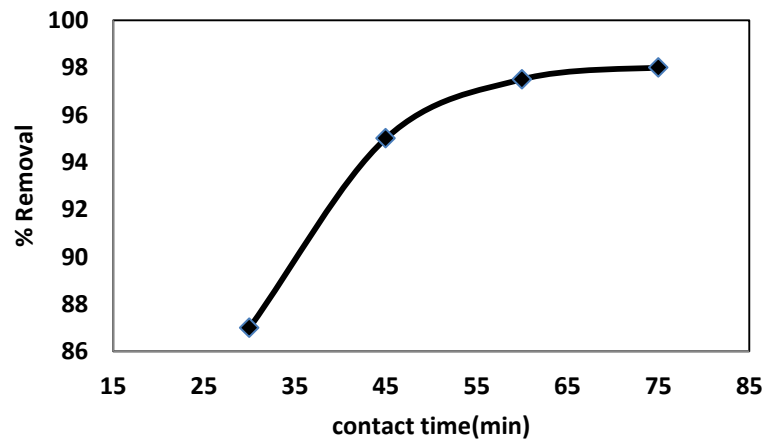


Fig.3. Effect of contact time on percentage removal of Mn(II)

Table 1. Isotherms and their linear forms

Isotherm models	Linear form
langmuir	$q_e = q_{max} K_L C_e / (1 + K_L C_e)$
Redlich-Peterson	$q_e = K_{RP} C_e / (1 + a C_e^b)$
Sips	$q_e = q_{max} (K_s C_e)^{\gamma} / (1 + (K_s C_e)^{\gamma})$

**Table 2.** Comparison of isotherm parameters and Chi-square test analysis ( $\chi^2$ )

<b>Langmuir model</b>		
$q_{\max}$ (mg /g)		79.56
$K_1$ (L/mg)	0.023	
$\chi^2$	0.55	
<b>Redlich-Peterson model</b>		
K	1.74	
a	0.054	
$\beta$	-0.429	
$\chi^2$	0.546	
<b>Sips model</b>		
$q_{\max}$	9.56	
$K_s$	0.38	
$\gamma$	2.09	
$\chi^2$	0.26	

## References

- [1] Y.P. Teoh., M.A. Khan and T.S.Y. Choong. (2013). Kinetic and isotherm studies for lead adsorption from aqueous phase on carbon coated monolith. *Chemical Engineering Journal*.217.248-255.
- [2] H.B. Bardl. (2005). Heavy metal in environment. first edition, Elsevier, Netherlands.
- [3] H.A. Hasan., S.R.S. Abdullah., N.T. Kofli and S.K. Kamarudin.(2012). Isotherm equilibria of  $Mn^{2+}$  biosorption in drinking water treatment by locally isolated *Bacillus* species and sewage activated sludge. *Journal of Environmental Management*.111.34-43.
- [4] H.A Hasan., S.R.S. Abdullah., S.K. Kamarudin and N.T. Kofli. (2011a). Ammonia and manganese problems in Malaysian drinking water treatment. *World Applied Science Journal*. 12 (10). 1890-1896.
- [5] K. Parvathi., R. Nareshkumar and R. Nagendran. (2007). Biosorption of manganese by *Aspergillus niger* and *Saccharomyces cerevisiae*. *World Journal of Microbiology and Biotechnology* .23. 671-676.
- [6] S. Babel and T.A. Kurniawan. (2003). Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials*. B97.219-243.
- [7] E. Pehlivan., T.H. Tran., W.K.I. Ouédraogo., C. Schmidt., D. Zachmann and M. Bahadir.(2013). Removal of As(V) from aqueous solutions by iron coated rice husk. *Fuel Processing Technology*.106:511-517
- [8] K.K. Singa., S.H. Hasan., M. Talat., V.K. Singh and S.K. Gangwar.(2009). Removal of Cr (VI) from aqueous solutions using wheat bran. *Chemical Engineering Journal*.151.113-121.
- [9] K.A. Souod. (2012). Adsorption Isotherm Studies of Chromium (VI) from Aqueous Solutions Using Jordanian Pottery Materials. *APCBEE Procedia*.1:116-125
- [10] Y.S.Ho. (2006). Isotherms for the Sorption of Lead onto Peat: Comparison of Linear and Non-Linear Methods. *Polish Journal of Environmental Studies*. 15:81-86.
- [11] S. Zakhama, H. Dhaouadi and F. M'Henni. (2011). Nonlinear modelisation of heavy metal removal from aqueous solution using *Ulva lactuca* algae. *Bioresource Technology*.102.786-796.