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BIOSORPTION OF Mn (II) IONS FROM AQUEOUS SOLUTION BY JERUSALEM ARTICHOKE (*HELIANTHUS TUBEROSUS* L.) STALKS

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Abstract: *The purpose of this paper is to tested Jerusalem artichoke stalks as a cheap biosorbent for its ability to remove Mn (II) ions from aqueous solution. Batch experiments were carried out to evaluate the effects of pH, biosorbent particle size, dosage, initial metal concentration and contact time. The maximum removal efficiency of about 97.0 % was reached at pH 8.0 by using of biosorbent particle size 530-850 μm, adsorbent dosage 30 g/L, initial metal concentration 10 mg/L, temperature 20 °C, agitation speed 120 rpm and contact time 90 min. Pseudo-first order and pseudo-second order models were applied to describe the obtained kinetic data. The pseudo-second order model provided the best fit for experimental data with coefficient of determination R^2 > 0.99. Freundlich and Langmuir isotherm models were used to describe metal adsorption. Equilibrium data agreed well with Langmuir isotherm with R^2 = 0.993.*

Keywords: *removal, manganese, water, biosorbent.*

1. Introduction

Environmental pollution with industrial wastewaters contaminated with various metals has become one of the major ecological problems nowadays. The raw and wastewaters that consist of heavy metals ought to be treated, because it will be harm the ecosystems and public health. Heavy metals are non-degradable and causing various diseases and disorders [1].
The existing methods used for metal removal from the water could be classified in three main groups such as physical, chemical and biological. Adsorption is one of the successful methods of physicochemical treatment process to remove heavy metals from aqueous solution [2].
Recently, there has been a tendency to shift conventional adsorbents with natural sorbents, especially waste materials, because of its low price, large availability, high efficiency, biodegradability and safety. The ability of the large number of microbial and plant waste materials to bind heavy metals have been reported in the literature. Most of the adsorption studies focused on using plant waste materials, such as leaf powder, rice husks, sunflower stalks, peanut hull pellets, marine algae, etc. [3].
The Jerusalem artichoke stalks have been applied as cheap biosorbent for removal of

Cu (II) and Fe (III) ions from aqueous solutions [4, 5].

Bio-sorption may be defined as a process of removing the metal or metalloid components from the aqueous solution by biological materials. The mechanisms involved in the process of bio-sorption include chemical sorption, complex formation, surface adsorption, inner porous adsorption, ion exchange, etc. It has been found that in the cellular and tissue materials exist a large number of groups (-COOH, -OH, -SH, =NH, $-NH_2$, etc.) which have ability to bind metal and therefore they are ionic functional groups of the biomass [6].

Numerous empirical models for single solute systems have been employed to describe the bio-sorption equilibrium, namely Langmuir, Freundlich, Brunauer-Emmet-Teller, Sips, Dubinin-Redishkevich, Temkin and Toth models. In kinetic modelling the pseudo-first and pseudo-second order equations are considered as the most celebrated models [7].

Manganese is common constituent in waters. It is known that Mn (II) exposure causes neurotoxicity, low hemoglobin levels and gastrointestinal accumulation [8-10].

The WHO set a maximum acceptable drinking water concentration for manganese of 0.05 mg/L. Therefore, it is necessary to treat the manganese contaminated water in order to reduce the environmental and human health risks.

Many studies have been conducted recently on the bio-sorption of Mn (II) from water. As adsorbents usually are used bacteria, corncob biomass, green tomato husks, sewage activated sludge, white rice husk ash, yields and spent mushroom compost [11-17].

To the best of our knowledge, absorbent prepared from Jerusalem artichoke had not been used for the removal of Mn (II) ions from aqueous solution. Therefore, this study examines the performance of Jeruslalem artichoke stalks, as cheap bio-sorbent, for its ability to remove Mn (II) ions from aqueous solution. The effects of different process parameters, such as pH, adsorbent dosage, adsorbent particle size, contact time and initial metal concentration on manganese removal efficiency were determined. The Mn (II) ions biosorption equilibrium and kinetic modeling were carried out.

2. Matherials and methods

Matherials. In the present study the powder obtained from stalks of Jerusalem artichoke by cutting, drying (40^{o}C), milling and sieving was used. For the removal of certain interfering components (pigments, etc.) the plant material was extracted twice with distillated water (1:7) for 45 min at 25^{o}C under continuously stirring. After that the material was dried at 40^{o}C. The particle size distribution was determined by mechanical sifting of dried fractions of powder. Sieves with standard light openings: 1 (2000-3000 μm), 2 (1250-2000 μm), 3 (850-1250 μm), 4 (530-850 μm), 5 (400-530 μm), 6 (250-400 μm), 7 (150-250 μm) and 8 (0-150 μm) were used. The sifting was performed on a laboratory sifting machine. The function of the density distribution was calculated [18,19].

All reagents used in the experiments were of analytical grade. Stock solution of Mn (II) was prepared by dissolving of $MnSO_4.5H_2O$ (Merk) in distillated water. This solution was diluted with distillated water to obtain desired concentrations of working solutions for the batch experiments study. The pH value of the samples was adjusted by adding 0.1 M NaOH or HCl solutions.

Biosorption batch experiments.

Biosorption experiments were carried out in 250 ml Erlenmeyer glass flasks with 100 mL volume of manganese solution. Batch experiments were conducted by varying the pH value (3, 4, 5, 6, 7, 8 and 9), initial Mn (II) concentration (5, 10, 30 and 40 mg/L) and biosorbent dosage (from 1.0 to 35.0 g/L). Experiments were carried out at contact time of 24 h in order to reach equilibrium, agitation speed 120 rpm and ambient temperature 20.0±0.5ºC. All experiments were performed in duplicate.

Analytical methods.

For determination of Mn(II) concentration in the solutions before and after bio-sorption, 10 mL of samples were withdrawn, filtered (Wathman No. 42) and filtrate was analyzed spectrophotometrically according to standard formaldoxim spectrometric method [20-21].

The metal uptake q (mg/g) was determined by employing the mass balance. If C_0 and C_e are the initial and final metal concentration (mg/L), respectively; V (L) is the initial volume of Mn (II) solution and m (g) is the mass of biosorbent material, the equilibrium metal uptake q_e (mg/g) can be calculated as:

$$q_e = \frac{(C_0 - C_e).V}{m} \qquad (1)$$

The performance of biosorption was evaluated in terms of its removal efficiency as RE (%), estimated by the following equation:

$$RE = \frac{(C_0 - C_t)}{C_0}.100 \qquad (2)$$

where C_t is the Mn (II) concentration at time t.

Kinetic experiments.

Batch kinetic experiments were carried out. For this purpose, 3.0 g of biosorbent were contacted with 100 mL of Mn (II) aqueous solution with initial metal concentrations 5, 10, 30 and 40 mg/L in 250 mL Erlenmeyer glass flasks on a magnetic stirrer at 120 rpm, pH 8.0 and temperature 20.0±0.5ºC. At different time intervals ranging from 5 to 180 min the concentrations of Mn (II) in the treated solutions were determined as described in analytical methods.

Kinetic modeling.

The Lagergren model was employed due to its simplicity and good fit. Two different kinetic models were used to model experimental data.

The pseudo-first-order model is expressed as:

$$\frac{dq}{dt} = K_{1,ads}(q_e - q) \qquad (3)$$

where q_e (mg/g) and q are amounts of adsorbed metal ions on the biosorbent at the equilibrium and any time t, respectively; and $K_{1,ads}$ is the Lagergren rate constant of the first-order biosorption (min^{-1}). The model is based on the assumption that the rate is proportional to the number of free site [7, 22].

Integrating Eq. (3) between the limits, $t=0$ to $t=t$ and $q=0$ to $q=q$ yields the linearized version of this model:

$$log(q_e - q) = log\, q_e - \frac{K_{1,ads}.t}{2.303} \qquad (4)$$

Linear plots of $log(q_e\text{-}q)$ versus t were plotted to evaluate this kinetic model and to determine rate constant and q_e from the slope and intercept, respectively.

The pseudo-second-order model is based on the assumption that biosorption follows a second-order mechanism, whereby the rate of sorption is proportional to the squire of the number of unoccupied sites [7, 22]:

$$\frac{dq}{dt} = K_{2,ads}(q_e - q)^2 \qquad (5)$$

where $K_{2,ads}$ is the rate constant of second-order biosorption (g/mg.min). Integrating Eq. (5) from $t=0$ to $t=t$ and $q=0$ to $q=q$ and linearization yields:

$$\frac{t}{q} = \frac{1}{K_{2,ads} \cdot q_e^2} + \frac{t}{q_e} \qquad (6)$$

The parameters q_e and $K_{2,ads}$ are calculated from the slope and the intercept of the plot *t/q* versus *t*. It is not necessary to independently determine q_e to apply this model.

Isotherm experiments.

Equilibrium sorption experiments were performed as follow. Biosorbent (3 g) were exposed to 100 mL Mn (II) solution with an initial concentrations 5, 10, 30 and 40 mg/L at constant pH 8.0, agitation speed 120 rpm and ambient temperature 20.0±0.5ºC for 24 h in order to rich equilibrium. Sorption isotherm is plotted of the sorbate uptake (q_e) versus the equilibrium concentration of the residual sorbate remaining in the solution (C_e).

Sorption isotherm modeling.

The *Freundlich isotherm* which has been widely used in correlating equilibrium data can be expressed by the following linearized logarithmic form:

$$lg\, q_e = lg\, K_F + \frac{1}{n} lg\, C_e \qquad (7)$$

where q_e (mg/g) is the amount of Mn (II) removed per unit mass of the adsorbent, C_e (mg/L) is the residual Mn(II) concentration of the aqueous solution, K_F and *n* are Freundlich constants and measures of adsorption capacity and adsorption intensity, respectively. A higher *n* value (lower value of *1/n*) implies stronger sorbent-pollutant interaction whereas *1/n* equal to 1 indicates linear adsorption leading to identical adsorption energies for all sites [7].

The *Langmuir isotherm is* based on three assumptions: namely adsorption is limited to monolayer coverage, all surface sites are alike and only can accommodate one adsorbed atom and the ability of a molecule to be adsorbed on a given site is independent of its neighboring sites occupancy [7].

This isotherm can be described by the following linearized form:

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{max}}\right)\frac{1}{C_e} + \frac{1}{q_{max}} \qquad (8)$$

where q_e (mg/g) is the equilibrium amount of Mn (II) adsorbed, C_e (mg/L) is the equilibrium concentration of Mn (II) in the solution, q_{max} (mg/g) and K_L (L/mg) are Langmuir constants representing the maximum monolayer adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption, respectively.

For the Langmuir isotherm analysis, the separation factor (R_L) value is of special importance:

$$R_L = \frac{1}{1 + K_L C_0} \qquad (9)$$

where C_0 (mg/L) is the initial Mn (II) concentration in the solution.

Four possibilities for the separation factor values which determine the isotherm type: $R_L = 0$ (irreversible isotherm), $R_L = 1$ (linear isotherm), $R_L>1$ (unfavorable isotherm) and $R_L<1$ (favorable isotherm) have been reported [23].

3. Results and discussion

Effect of pH.

Hydrogen ion concentration (pH) of the aqueous solutions is an important parameter since it affects the surface charge of sorbent and the degree of speciation and ionization of sorbent during adsorption [1].

From the practical point of view, the most important was to be determined the optimal pH at which the investigated system could reach its maximum removal efficiency [15].

The effect of pH on the Mn (II) removal efficiency from the aqueous solution by studied biosorbent is illustrated in figure 1.

It was found that the maximum removal efficiency (81.3 %) was reached at pH 8.0, than it sharply decreased probably due to formation of $Mn(OH)_2$.

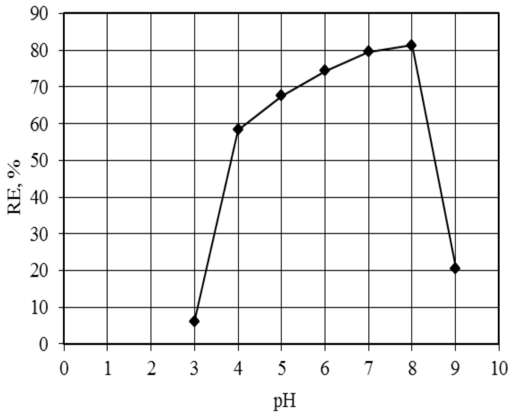

Fig. 1. Effect of pH on the removal efficiency of Mn (II) from aqueous solution by powder of Jerusalem artichoke stalks (initial metal concentration 10 mg/L, biosorbent dosage 1 g/L, 20ºC, 24 h, agitation speed 120 rpm)

Effect of adsorbent particle size and dosage.

The biosorbent particle size and dosage are other two major factors affect the biosorption efficiency. For the evaluation of particle size effect on Mn (II) biosorption, batch experiments were carried out with eight size ranges of bioserbent particle and dosage of 1 g/L. To investigate the effect of biosorbent dosage on biosorption, the experiments were conducted with constant manganese concentration of 10 mg/L and samples with different biosorbent dosage ranging from 1.0 to 35.0 g/L were used under the constant temperature 20ºC and pH 8.0. Data are given in figures 2 and 3. Regarding to the influence of the biosorbent particle size on Mn (II) removal efficiency, the results in figure 2 indicate that the optimal particle size yielded the maximum metal removal of 81.3% was from the range 530-850 μm.

The Mn (II) removal efficiency was found to increase from 81.3% to 97.0% with the increase of the biosorbent dosage from 1.0 to 30.0 g/L (figure 3), which can be explained by an increase of the contact surface available for adsorption and the presence of a larger number of groups, binding the Mn (II) ions. Application of higher biosorbent dosage above 30.0 g/L did not lead to significant increase ($p < 0.05$) in metal removal efficiency due to possible aggregation of the biomass particles and disturbing of the mass transfer of the metal ions from the liquid to solid phase of the system. Similar results have been reported by other researchers [12, 15, 24, 25].

Effect of initial metal concentration.

The initial metal concentration is essential for the duration of biosorption and the rate of metal removal from aqueous solutions. Results for the influence of the initial Mn (II) concentration in the solution on metal removal efficiency are presented in figure 4.

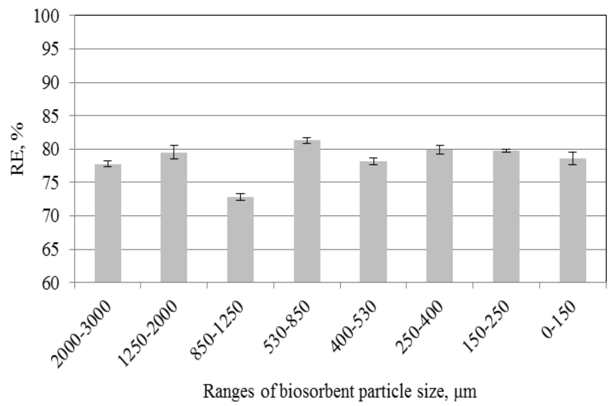

Fig. 2. Effect of biosorbent particle size on the removal efficiency of Mn (II) from aqueous solution by powder of Jerusalem artichoke stalks (initial metal concentration 10 mg/L, pH 8.0, 20ºC, biosorbent dosage 1 g/L, 24 h, agitation speed 120 rpm)

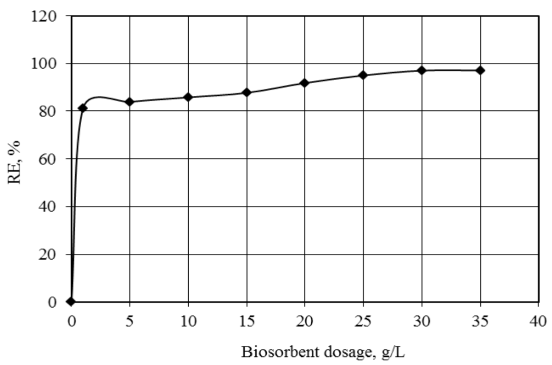

Fig. 3. Effect of biosorbent dosage on the removal efficiency of Mn (II) from aqueous solution by powder of Jerusalem artichoke stalks (initial metal concentration 10 mg/L, pH 8.0, 20°C, 24 h, agitation speed 120 rpm)

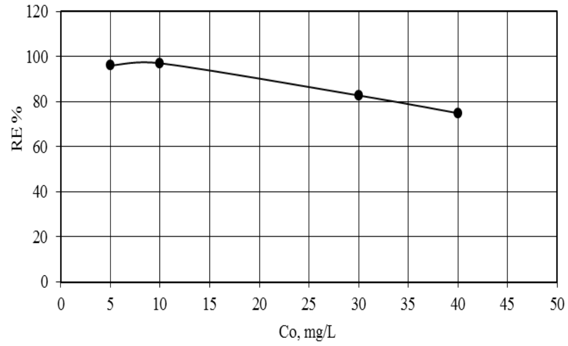

Fig. 4. Effect of initial metal concentration (C_0, mg/L) on the removal efficiency of Mn (II) from aqueous solution by powder of Jerusalem artichoke stalks (biosorbent dosage 30 mg/L, pH 8.0, 20°C, 24 h, agitation speed 120 rpm)

As shown in figure 4, the removal efficiency of Mn (II) ions from aqueous solutions by used biosorbent was found to decrease with the increase of the initial metal concentration, probably due to the restriction or saturation of the biosorbent active groups. The highest level of removal efficiency (97.0%) was established at an initial metal concentration of 10 mg/L. Similar results have been reported for biosorption of Mn (II) ions from aqueous solutions by corncob biomass [12].

Adsorption kinetics data. The contact time of the biosorbent and sorbate also has a significant impact on the biosorption efficiency. Biosorption kinetics of Mn (II) ions on powder of Jerusalem artichoke stalks at four different initial metal concentrations in the aqueous solution are presented in figure 5. The results indicated that the biosorption process can be divided into two main stages. The initial rapid stage where biosorption was fast and second slow stage which refers to gradual biosorption before manganese uptake reached equilibrium. A similar phenomenon was observed by others also [12, 26, 27].

The established times taken to reached equilibrium for Mn(II) concentrations of 5, 10, 30 and 40 mg/L were 30, 90, 150 and 120 min, respectively.

Kinetic data were fitted onto two kinetic models of pseudo-first and pseudo-second order with acquired parameters listed in table 1. By comparing the fitting results the pseudo-second model seems to give better representation of the experimental data. Moreover, calculated values of equilibrium metal uptake (q_e^{cal}, mg/g) from pseudo-second model agree quite well with experimentally obtained values (q_e^{exp}, mg/g).

Equilibrium isotherms data. Equilibrium adsorption isotherms study is of fundamental importance in the design of adsorption systems, since it provides the basic physicochemical data to evaluate the suitability of the sorption process for removal of different pollutants, incl. heavy metals, from aqueous solutions. Adsorption equilibrium is usually described by an isothermal equation whose parameters express the surface properties and the affinity of the adsorbent at a given temperature and pH of the solution. Therefore, an adequate mathematical description of the experimentally obtained equilibrium isotherm is essential for the efficient design of the system. In this work, two of the most frequently used model were tested [7].

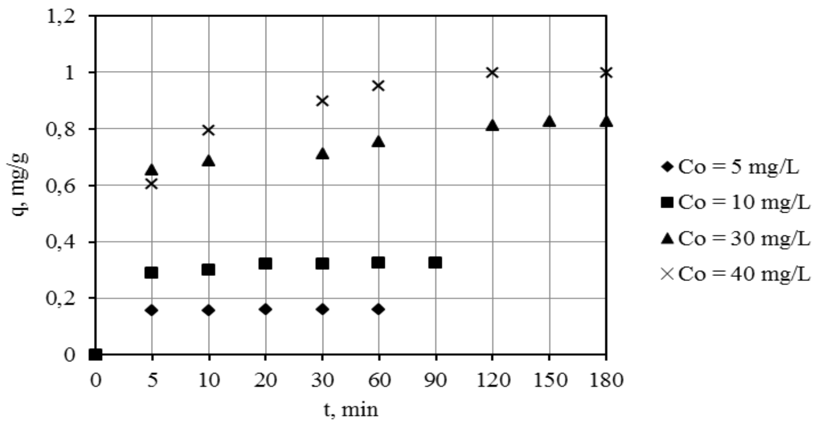

Fig. 5. Biosorption kinetics of Mn (II) ions on powder of Jerusalem artichoke stalks (biosorbent dosage 30 mg/L, pH 8.0, 20°C, agitation speed 120 rpm)

Table 1.
Kinetic parameters for the biosorption of Mn (II) ions onto powder of Jerusalem artichoke stalks

Initial Mn(II) ions concentration (C_0), mg/L	Experimental metal uptake (q_e^{exp}), mg/g	Pseudo-first order model			Pseudo-second order model		
		q_e^{cal}, mg/g	K_{1ads}, min^{-1}	R^2	q_e^{cal}, mg/g	K_{2ads}, g/mg.min	R^2
5	0.1600	0.0122	0.126	0.999	0.1614	21.58	1.0
10	0.3233	0.0227	0.044	0.615	0.3253	4.98	1.0
30	0.8270	0.2003	0.021	0.976	0.8378	0.336	0.999
40	0.9983	0.3525	0.035	0.928	1.0188	0.275	0.999

The results of the application of Langmuir and Freundlich linearized models to the experimental data for biosorption of Mn (II) ions from aqueous solutions by the investigated biosorbent under equilibrium conditions are presented in figures 6 and 7. Model parameters were determined using linear regression toolbox in Microsoft Excel software and are summarized in table 2.

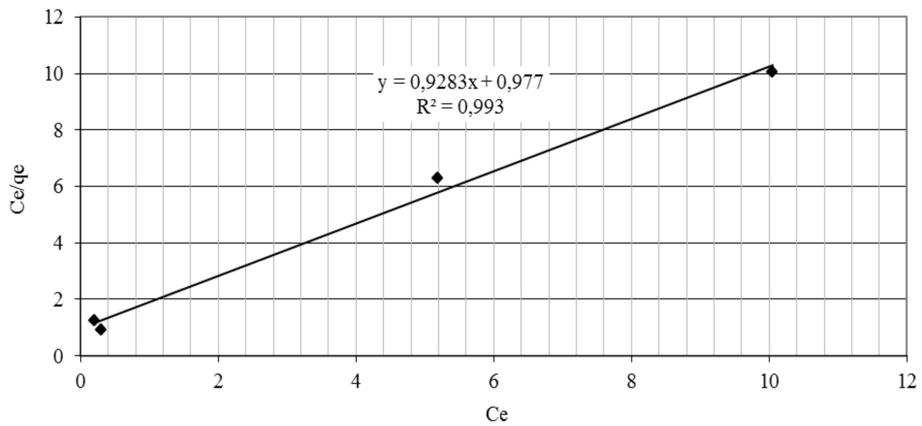

Fig. 6. **Linearized Langmuir isotherm for biosorption of Mn (II) ions on powder of Jerusalem artichoke stalks (biosorbent dosage 30 mg/L, pH 8.0, 20°C, 24 h, agitation speed 120 rpm)**

Table 2.
Isotherm parameters of Langmuir and Freundlich models for biosorption of Mn (II) ions onto powder of Jerusalem artichoke stalks

Langmuir isotherm model			Freundlich isotherm model		
q_{max}, mg/g	K_L, L/mg	R^2	1/n	K_F, mg/g	R^2
1.08	0.95	0.993	0.4163	0.404	0.933

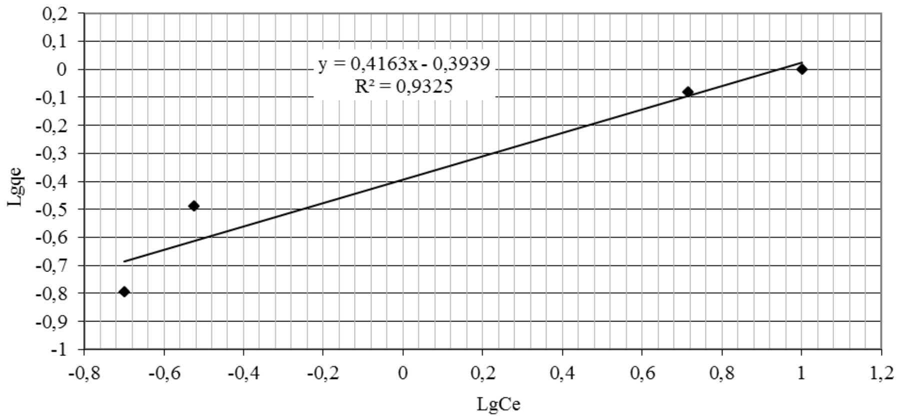

Fig. 7. Linearized Freundlich isotherm for biosorption of Mn (II) ions on powder of Jerusalem artichoke stalks (biosorbent dosage 30 mg/L, pH 8.0, 20°C, 24 h, agitation speed 120 rpm)

The regression parameters and coefficients of determination (R^2) presented in table 2 indicate that the Langmuir and Freundlich models fitted very well the experimental data with the calculated coefficients of determination (R^2) of 0.993 and 0.933, respectively. Similar results were reported for Mn (II) biosorption by corncob biomass [12].

The value of the R^2 for Langmuir model is slightly higher than that for Freundlich model and the Langmuir adsorption capacity (q_{max}) is larger than that obtained by application of Freundlich model (K_F). The Langmuir R_L values were found to be between 0 and 1, which confirmed that the biosorbent prepared from the Jerusalem artichoke stalks is favourable for biosorption of Mn (II) ion under conditions used in this study.

4. Conclusion

Present research showed that powder of Jerusalem artichoke stalks is a potential biosorbent for removal of Mn (II) ions from aqueous solution. The batch study parameters, such as pH of solution, biosorbent particle size, biosorbent dosage, contact time and initial manganese concentration were found to be important on the biosorption process. Finally, the experimental results of present study indicated that maximum removal efficiency of Mn (II) ions of 97.0% was obtained at pH 8.0, biosorbent particle size 530-850 μm, adsorbent dosage 30 g/L, initial metal concentration 10 mg/L, temperature 20 °C, agitation speed 120 rpm and contact time 90 min. The pseudo-second order kinetic model was found to fit well experimental data with $R^2 > 0.99$ and the adsorption isotherm followed Langmuir model ($R^2 = 0.993$).

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