

Utilization of Sawdust Waste Biomass as an Eco-Friendly Biosorbent for Bioremediation of Manganese Pollution in Aqueous Environment

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Abstract

In this study, the sawdust waste biomass was used as an eco-friendly biosorbent material for the bioremediation of manganese pollution in aqueous environment. The effects of various environmental variables such as pH, biosorbent amount, metal concentration and contact time on the manganese biosorption were studied in batch operating conditions. The kinetic and equilibrium studies were performed to elucidate the biosorption behavior of biosorbent material. The biosorption capacity of biosorbent was strongly influenced by the operating parameters. The experimental data were more successfully modeled by the pseudo-second-order kinetic model and Langmuir isotherm model compared to other models applied in the study. The maximum manganese removal capacity of biosorbent was found to be 25.655 mg g⁻¹. These findings showed that the sawdust waste biomass can be used as an eco-friendly biosorbent material for the bioremediation of manganese pollution in aqueous environment.

Key words: Sawdust, Waste biomass, Manganese pollution, Bioremediation

1. Introduction

Heavy metal pollution is a serious global environmental problem. As a significant heavy metal manganese is a commonly used element in various human industrial activities and is usually found in large quantities in the effluents of these industries. Manganese is an essential metal for human health at low concentration. However, its excess concentration causes many health problems including neurotoxicity, low hemoglobin levels, reproductive and respiratory disorders. In addition, it badly affects the taste, odor and appearance of water resource and also causes various problems in the water treatment and distribution systems [1, 2]. The effluents including excess manganese must be properly treated before being discharged into the receiving medium. In the present study, the sawdust as a forest industry waste biomass was explored as a potential biosorbent material for the bioremoval of manganese ions from aqueous medium.

2. Materials and Method

2.1. Biosorbent material

The waste sawdust biomass of *Pinus brutia* Ten. tree was collected from a local sawmill

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(Gaziantep, Turkey). The waste biomaterial was washed with tap water, followed by several washings with double distilled water to remove extraneous materials. It was dried in an oven until a constant weight was achieved. The material was crushed in a laboratory grinder, sieved through a 0.5 mm standard sieve and then modified NaOH chemical (0.3 mol L^{-1}). The obtained final product was kept in a glass bottle for the biosorption assays.

2.2. Manganese solution

A stock solution of manganese (1 g L^{-1}) was prepared from $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ dissolution in distilled water. Necessary dilutions were made from the stock solution to prepare the working solutions. The initial pH of each solution was adjusted to the desired value with HCl and NaOH solutions (0.1 mol L^{-1}) before mixing the biosorbent. All chemicals used were of analytical reagent grade and were purchased from Merck.

2.3. Biosorption experiments

Biosorption experiments were conducted by a set of conical flasks containing 100 mL of manganese solutions using the batch experiment technique. The flasks were agitated at a constant speed of 150 rpm using an orbital shaker for the desired contact times at room temperature. Afterwards, the required amount of aqueous sample was collected from the experiment medium and centrifuged. The residual manganese ion concentrations in the solutions were analyzed by the manganese test kit (Spectroquant, Merck). The amount of manganese bound by the biosorbent (q_t , mg g^{-1}) was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{M}$$

where C_0 and C_t (mg L^{-1}) are the concentrations of heavy metal at the initial, and a t time, respectively. V (L) is the volume of aqueous solution and M (g) is the mass of biosorbent.

2.4. Biosorption system modeling

The biosorption kinetic data were modeled using the pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion kinetic models while the biosorption equilibrium data were modeled by the isotherm models of Freundlich, Langmuir and Dubinin-Radushkevich.

3. Results and Discussion

3.1. Effect of contact time

Fig. 1 shows the effect of contact time on the biosorption of manganese onto the biosorbent. During the first period of biosorption process, the removal yield of biosorbent for manganese ions increased with increasing reaction time rapidly. Thereafter, the heavy metal biosorption proceeded at a lower rate and finally attained equilibrium. The biosorption equilibrium was reached within 120 min. The fast manganese biosorption at the initial stage could be attributed to the availability

of high number of vacant binding sites on the external surface of biosorbent material [3].

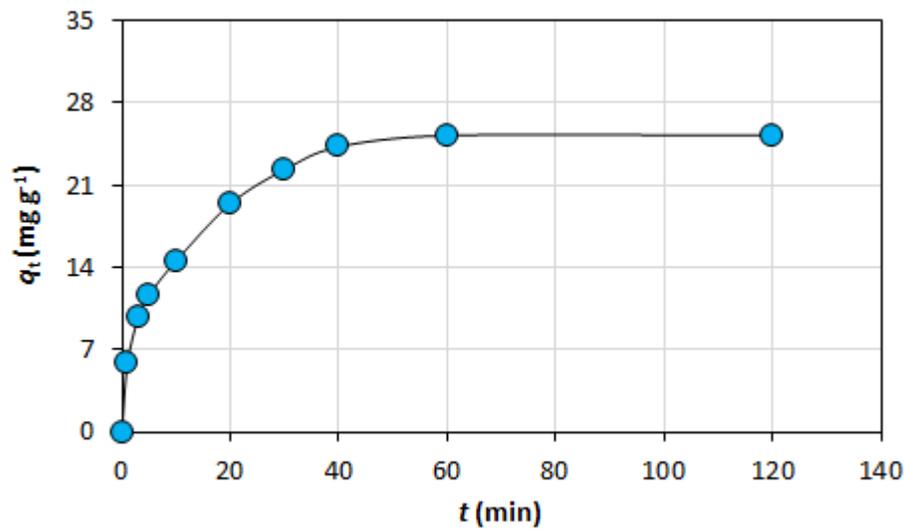


Fig. 1. Effect of contact time

3.2. Effect of pH

The effect of pH on the manganese removal efficiency of biosorbent is displayed in Fig. 2. As pH increased, the biosorption capacity of biosorbent material increased and reached maximum level at pH 6. The experimental studies were not conducted beyond this pH value, as there was a possibility of insoluble heavy metal hydroxide formation which would complicate the biosorption process. At lower pH, the surface charge of biosorbent became positive and this inhibited the approach of positively charged heavy metal cations. Conversely, at higher pH, these repulsive forces between the protons and heavy metal ions decreased and this trend enhanced the biosorption of manganese ions on the binding sites of biosorbent [4, 5].

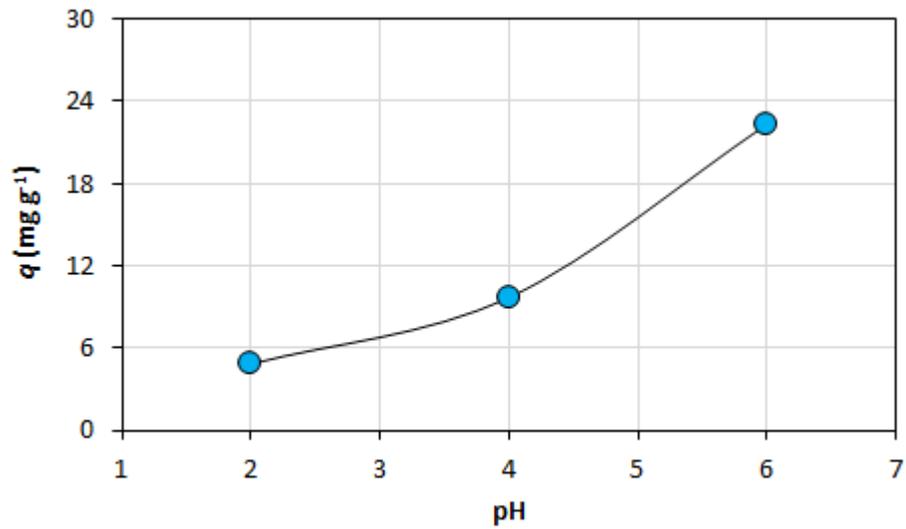


Fig. 2. Effect of pH

3.3. Effect of manganese concentration

As seen in Fig. 3, the heavy metal removal potential of biosorbent increased with increasing concentration of manganese. This is because the higher heavy metal concentration provides a greater driving force to overcome the mass transfer resistance of heavy metal ions between the biosorption medium and biosorbent [6].

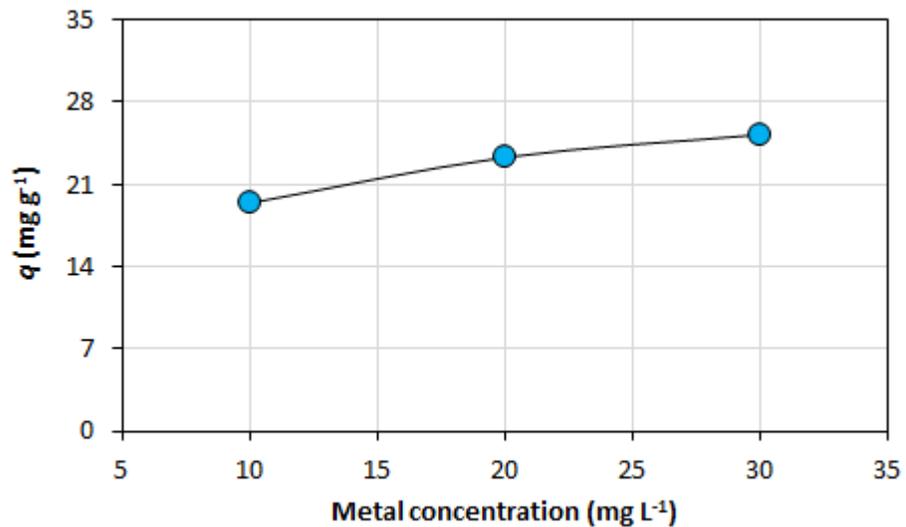


Fig. 3. Effect of manganese concentration

3.4. Effect of biosorbent amount

The biosorption yield of biosorbent material as a function of its amount is demonstrated in Fig. 4. The biosorption capacity decreased with increasing amount of biosorbent. The reduction in the manganese removal potential of biosorbent could be attributed to the unsaturation of biosorption sites and/or the particle aggregation of biosorbent [7].

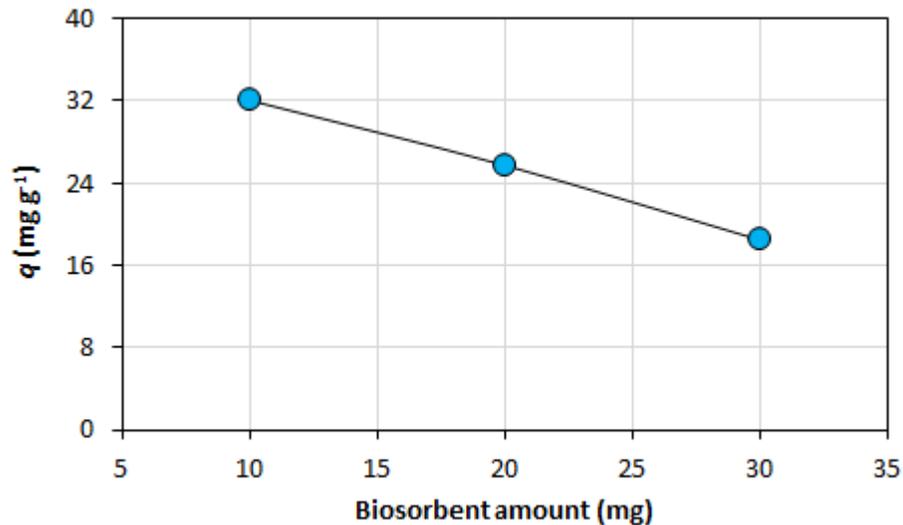


Fig. 4. Effect of biosorbent amount

3.5. System modeling studies

The pseudo-first-order [8], pseudo-second-order [9], Elovich [10] and intra-particle diffusion [11] kinetic models were employed for the modeling of dynamic behavior of biosorption system and the parameters of these models and statistical data are presented in Table 1. Considering its high R^2 value and also low SE value, the pseudo-second-order model provided the best fit to the experimental data of heavy metal biosorption. This model suggests a biosorption process based on the chemical surface reaction. Besides, the intra-particle mass transfer model showed that the biosorption process might be governed by multi-step mechanisms [12].

Table 1. Biosorption kinetic modeling data

Model	Parameter	Value
Pseudo-first-order	q_e (mg g ⁻¹)	24.068
	k_1 (min ⁻¹)	0.116
	R^2	0.9560
	SE	1.978
Pseudo-second-order	q_e (mg g ⁻¹)	26.985
	k_2 (g mg ⁻¹ min ⁻¹)	0.005789
	R^2	0.9824
	SE	1.251
Elovich	α (mg g ⁻¹ min ⁻¹)	4.682
	β (g mg ⁻¹)	0.214
	R^2	0.9789
	SE	1.371
Intra-particle diffusion	C (mg g ⁻¹)	5.496
	k_p (mg g ⁻¹ min ^{-1/2})	2.396
	R^2	0.8338
	SE	3.843

The equilibrium data of biosorption process were modeled using the isotherm models of Freundlich [13], Langmuir [14] and Dubinin-Radushkevich [15]. The parameters of these isotherm models are presented in Table 2. According to the statistical evaluation results, Langmuir model showed the best fit to the biosorption equilibrium data. This isotherm model suggests that the biosorption of heavy metal takes place on the homogeneous surface of biosorbent and the treatment of manganese follows a monolayer biosorption process. The values of n_F lying in the range of 1 and 10 and the values of R_L lying in the range of 0 and 1 indicate that this biosorption system is a favorable treatment process. On the other hand, the mean free energy of biosorption value (E) less than 8 kJ mol⁻¹ shows that the biosorption process might be controlled by means of physical mechanisms [16].

Table 2. Biosorption isotherm modeling data

Model	Parameter	Value
Freundlich	K_F ($\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n_F}$)	12.294
	n_F (-)	4.564
	R^2	0.9733
	SE	0.685
Langmuir	q_m (mg g^{-1})	25.655
	K_L (L mg^{-1})	0.034
	R_L (-)	0.494
	R^2	0.9987
	SE	0.149
Dubinin-Radushkevich	q_m (mg g^{-1})	25.685
	E (kJ mol^{-1})	0.360
	R^2	0.9862
	SE	0.493

4. Conclusion

The sawdust waste biomass was explored as a sustainable alternative biosorbent material for the bioremediation of manganese pollution in aqueous environment. The biosorption capacity of biosorbent was strongly influenced by the operating parameters. The biosorption data were successfully modeled by the pseudo-second-order and Langmuir models. The maximum manganese removal capacity of biosorbent was found to be 25.655 mg g^{-1} . These results showed that the sawdust waste biomass can be used as an eco-friendly biosorbent material for the bioremoval of manganese from aqueous medium.

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