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Research Article

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Biosorption of Fe^{+3} and Mn^{+2} ions from aqueous solution by a *Pleurotus mutilus* fungal biomass

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ABSTRACT

The biosorption properties of the Pleurotus mutilus fungal biomass waste collected from an antibiotic production plant to remove Mn^{+2} and Fe^{+3} from the ground water were investigated. The residue was characterised by IR analysis. These showed that amino and carboxyl were the main functional groups present in the biosorbent. The structural and morphological characteristics of Pleurotus mutilus fungal biomass were determined by scanning electron microscopic (SEM) analysis. Batch biosorption experiments were performed at different pH to find optimum pH. Langmuir, Freundlich, Redlich-Peterson, Dubinin-Radushkevich (D-R) and Temkin models were applied to describe a single biosorption equilibrium data. The Langmuir model gave the best fit for the data of single component. Maximum biosorption capacities of 26.7 mg Fe^{+3}/g biomass and 18.5 mg Mn^{+2}/g biomass were obtained. HNO_3 was selected as desorption agent. 92% of Fe^{+3} and 95% Mn^{+2} were obtained after regeneration.

Keywords: Isotherm model, Mn^{2+} biosorption, Fe^{3+} biosorption, Drinking water treatment, *Pleurotus mutilus*

INTRODUCTION

In recent years, research attention has been focused on biological methods for the treatment of effluents containing heavy metal ions. In this study, the biosorption process was investigated, as an alternative method for the removal of Mn^{2+} and Fe^{3+} due to its technical and economical feasibility [1].

Manganese and iron are common constituents of ground waters. These metals cause several problems such as water coloration, metallic taste, odor, turbidity, corrosion, hardness, and staining of laundry. The World Health Organisation sets a maximum acceptable drinking water concentration for iron and manganese of 0.3 and 0.1 mg/L respectively.

The presence of manganese Mn^{2+} in water will primarily be problematic for water treatment systems. The high concentration of Mn^{2+} in drinking water will become toxic to both the environment and living organisms, causing gastrointestinal accumulation [2], low haemoglobins levels[3], and neurotoxicity[4].

Recently, the removal of iron or manganese from aqueous solution by several types of biomass was investigated by different authors[5,6,7].
Therefore, this study aimed to investigate the use of a low cost sorbent (*Pleurotus mutilus* fungal biomass) to the sorption of Fe^{+3} and Mn^{+2} ions from a ground water.

Biosorption isotherms:
Biosorption isotherms characterised by certain constant values express the surface properties and affinity of the biosorbents [8], and can be used for comparing biomass biosorptive capacity for various heavy metals. Metal uptake

by biomass has been shown to occur in two successive stages, the first being rapid (passive uptake) followed by a much slower process (active uptake)[9]. The biosorption isotherms of Fe^{+3} and Mn^{2+} were investigated using five isotherm models: the Langmuir, Freundlich, Dubinin-Radushkevich (D-R), Temkin, and Redlich-Peterson (R-P) isotherm models.

2.1 Langmuir isotherm:

The isotherm has been successfully applied to many pollutant biosorption processes and has been the most widely used isotherm for the biosorption of solutes from a liquid solutions. However, one should point out that the Langmuir isotherm offers no insights into the mechanistic aspects of biosorption [10]. This model can be written in nonlinear Langmuir isotherm form as in equation (1) [10, 11]:

$$q_e = q_{\max} K_d C_e / (1 + K_d C_e) \tag{1}$$

where q_e is the biosorption capacity at equilibrium (mg/g), q_{max} is the maximum specific uptake (mg/g) and K_d represents the equilibrium constant of the biosorption process. The model was linearized as equation (2) and equation (3) in order to obtain q_{max} and K_d values.

$$C_e/q_e = \quad C_e/q_{\max} + \quad 1/q_{\max}K_d \tag{2}$$

$$1/q_e = 1/q_{\max} K_d C_e \quad + 1/q_{\max} \tag{3}$$

Temkin isotherm:

The Temkin isotherm is based on the assumption that the heat of biosorption decreases linearly with an increase in biosorbent coverage [10]. The model is represented by equation (4):

$$q_e = (RT/B)\ln(K_T C_e) \tag{4}$$

where (K_T) is the Temkin isotherm constant and (B) is the constant related to the heat of biosorption.

2.3 Redlich-Peterson:

The R-P isotherm [10,12] is expressed as follows:

$$q_e = K_R C_e / (1 + a_R C_e^{B_R}) \tag{5}$$

where K_R is the R-P isotherm constant as $K_R = q_{max} K_d$ (L/g), a_R is the R-P isotherm constant (L/mg) and B_R is an exponent that lies between 0 and 1. For high concentrations, equation (5) reduces to the Freundlich isotherm. In the case, that $B_R=1$ it will reduce to the Langmuir equation moreover for $B_R=0$, equation reduces to Henry's equation as expressed in equation (6):

$$q_e = K_R C_e / (1 + a_R) \tag{6}$$

The R-P isotherm incorporates three parameters and can be applied either in homogeneous or heterogeneous systems. The linearized version of equation (5) can be written as equation (7):

$$\ln[K_R (C_e/q_e) - 1] = \ln a_R + B_R \ln C_e \tag{7}$$

Freundlich isotherm :

The Freundlich isotherm is applied under the assumption of a heterogeneous adsorption surface and active sites with different energies involved. The model is represented as follows:

$$qe = k_f C_e^{1/n} \tag{8}$$

where k_f is the Freundlich constant relating to the binding capacity and (1/n) is an empirical parameter relating to the biosorption intensity which varies with the heterogeneity of the biosorbent. The parameters can be determined through the linearization of equation (8) as follows:

$$\ln q_e = (1/n)\times \quad LnC_e + Lnk_f \qquad (9)$$

2.5 Dubinin –Radushkevich isotherm:

The D-R isotherm was developed to account for the effect of the porous structure of a biosorbent [10,13]. The model can also be used to determinate whether the Mn^{2+} and Fe^{3+} biosorption process is physical or chemical in nature. The linearized D-R isotherm is expressed as follows:

$$Ln(q_e) = Ln(q_{\max}) - \beta\varepsilon^2 \qquad (10)$$

where β is the activity coefficient related to biosorption mean free energy and Ɛ is the Polanyi potential which can be determined from equation (11):

$$\varepsilon = RT\ln(1 + 1/C_e) \qquad (11)$$

The plot of (ln qe) versus (ε^2) results in a straight line, and its slope is equal to (–ß). Thus, the mean biosorption energy (E) can be calculated using equation (12):

$$E = 1/\sqrt{-2\times slope} \qquad (12)$$

The obtained E values provide useful information to assess whether biosorption is subject to a physical or chemical process [10, 14].

EXPERIMENTAL SECTION

3.1 Source of biosorbents:

The *Pleurotus mutilus* fungal biomass was collected from a pharmaceutical plant producing an antibacterial drug (*Pleuromutilin*). This pharmaceutical waste is generally destined for incineration. It was investigated for removal of Fe^{3+} and Mn^{2+} ions from a ground water treatment system.

3.2 Characterisation of biosorbents:

The characterization of the biosorbent was achieved using FTIR 4800S (PerkinElmer), to determine the functional groups on the biosorbent. Adsorption sites responsible for the biosorption process are due to the chemical functional groups such as the carboxyl (-C=O), amine ($-NH_2$) and hydroxyl (-OH) groups. A SEM (scanning /electron/microscopy) was also used to study the biosorbent surface morphology (PHILIPS ESEM XL 30FEG).

3.3 Preparation of biosorbents:

The *Pleurotus mutilus* fungal biomass was washed several times with distilled water to remove undesired solid materials and dissolved heavy metals, dried at 100°C until constant weight (24h). The dry sludge was crushed using a jaw crusher and sieved by successive sieves.

3.4 Mn^{2+}, Fe^{3+} biosorption study:

Sorption studies were performed in batch mode to obtain both rate and equilibrium data. Mn^{2+}, Fe^{3+} biosorption studies were carried out using 500 mL conical flasks containing 500 mL of the 0- 300 mg(Fe^{3+}, Mn^{2+})/L solution at initial concentration .

Mn^{2+} stock solution was prepared using ($MnCl_2$, $2H_2O$) and Fe^{3+} stock solution was prepared using ($FeCl_3$, $6H_2O$). The biosorbents were suspended in the Mn^{2+}, Fe^{3+} solutions and were centrifuged at 250 rpm for 3 hours. Experimental measured parameters are listed in Table 1. The pH was varied from 1 to 8.5 using dilute solution of Hcl and NaOH. The metal concentrations in the samples were determinated using an AAS Perkin Elmer A600 at 248.3 nm (Fe) and 280.1 nm (Mn).

Table1. Experimental data for Mn^{2+} and Fe^{3+} biosorption

Parameter	Concentration
Fe^{+3}	0-300 (mg/L)
Mn^{+2}	0-300 (mg/L)
Biomass	3g/L
pH	1 – 8.5

Mn^{2+}, Fe^{3+} uptake by the biomass was calculated using the following equation (13):

$$q_e = \frac{(C_i - C_e)V}{X} \tag{13}$$

where (q_e) is the manganese or iron (mg Mn^{2+}/g biomass, mgFe^{3+}/g biomass) , (V) is the volume of the Mn^{2+}, Fe^{3+} solutions (mL) , C_i is the initial concentration of Mn^{2+} or Fe^{3+} in their solutions (mg Mn^{2+}/L , mgFe^{3+}/L) , (C_e) is the final concentration of Mn^{2+} or Fe^{3+} in their solutions (mg Mn^{2+}/L, mgFe^{3+}/L) and X is the dry weight of the biomass (g).

RESULTS AND DISCUSSION

4.1 FTIR and SEM analysis:

FTIR analysis was conducted on *Pleurotus mutilus* fungal biomass in order to obtain information regarding the presence of negatively charged functional groups such as carboxyl (-C=O), amine ($-NH_2$), alcohol (-C-O) and hydroxyl (-OH). Table 2 show the FTIR spectra *of Pleurotus mutilus* fungal biomass in the wave number range of 400-4000 cm^{-1}.

Table2. IR absorption bands and corresponding possible groups

Wavenumber (cm^{-1})	Bonds	Functional groups
3425	O-H (stretch)	Hydroxyl
	N-H (stretch)	Amine,amide
	O-H (stretch)	Acid
2924	C-H (stretch	Alkane
	C=O (stretch)	Amide
1645	N-H (stretch)	Amine
	C=C (stretch)	Alkene
1087	C-O (stretch)	Ether,alcohol,ester
<800	P=O (stretch)	Phosphate

The FTIR spectra of *Pleurotus mutilus* fungal biomass (Fig.1) shows broad stretching vibrations at 3438cm^{-1}, 1640cm^{-1} and 1085 cm^{-1} which indicates the presence of the ($-OH,-NH_2$); (-C=O); (-C-O) respectively.

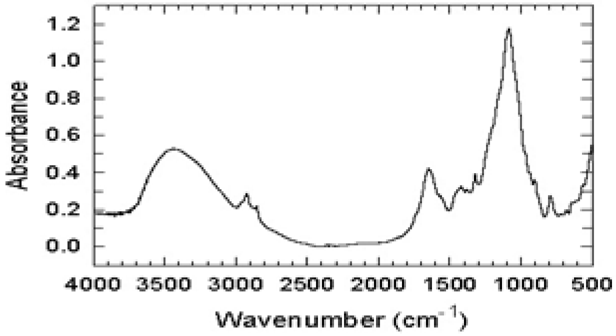

Fig.1. FT-IR spectra of the *Pleurotus mutilus* fungal biomass before biosorption

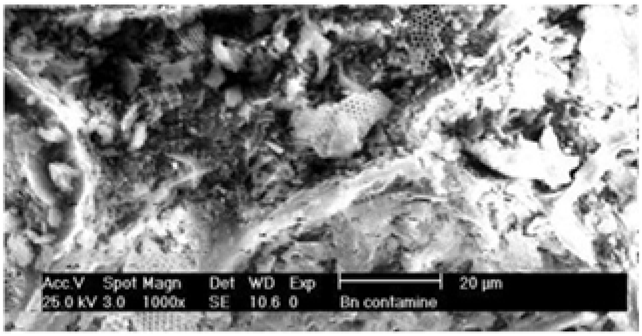

Fig.2. SEM image of the *Pleurotus mutilus* fungal biomass before biosorption

SEM micrographs of dried biosorbent particles (Fig.2) showed fairly regular spherical structures with an external surface which, although rather smooth, displayed a number of cracks likely to favor solute adsorption through enhanced diffusion to active sites.

4.2 Effect of pH

The removal of Fe^{3+} and Mn^{2+} at different pH is shown in Fig.3. The removal of Fe^{3+}, Mn^{2+} ions on *Pleurotus mutilus* fungal biomass increase with the increase in pH. For sorption studies, the pH must be less than the pH for precipitation of respective metal ions.

The Fe^{3+} sorption increase in pH range 2-3 and Ferric ions Fe^{3+} hydrolyse much more readily. For pH>3 precipitation as well as sorption takes place. Polynuclear species such as $Fe_2(OH)_2^{4+}$, mononuclear species $FeOH^{2+}$, and $Fe(OH)_2^+$ are formed in acidic medium, while $Fe(OH)_4^-$ and $Fe(OH)_3$ (aq) are formed in neutral and basic medium. For pH<3, the elimination of Fe^{3+} ions, $Fe(OH)_4^{+\ 2}$, $Fe(OH)^{2+}$ occurs by electrostatic attraction with the –COOH and $–NH_2$ groups present on the biomass surface. For a pH>3, Fe^{3+} is largely removed by precipitation as $Fe(OH)_3$ and $Fe(OH)_4^-$ was removed by electrostatic attraction with the biomass. Thus to correlate removal with sorption, the pH chosen was around 2.6.

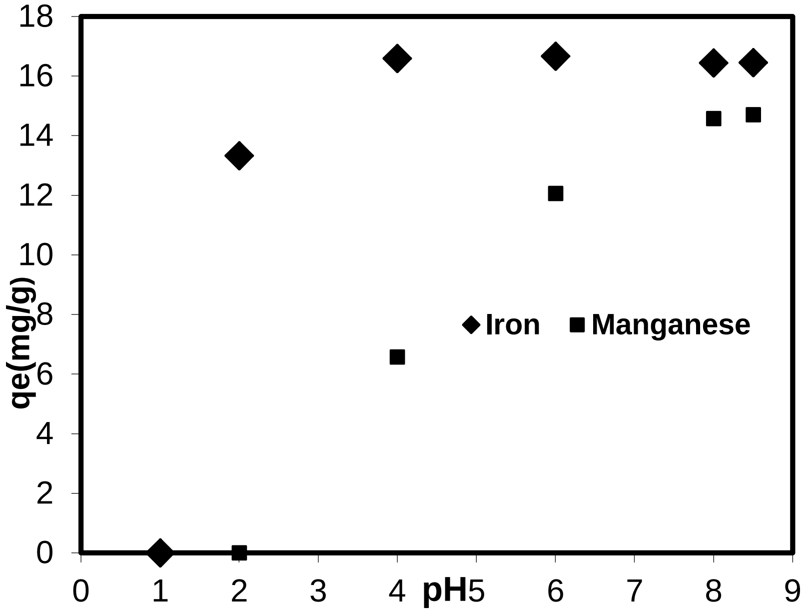

Fig.3. Effect of pH on the biosorption of Fe^{3+} and Mn^{2+} (Co= 50mg/L for Fe^{3+} and Mn^{2+}, biomass dose 3g/L) on the *Pleurotus Mutilus* fungal biomass

Mn^{2+} at ordinary concentrations hydrolyzes negligibly at pH<8 but it forms different species at pH>8. Thus under acidic conditions soluble Mn^{2+} predominates. At more alkaline pH values, a number of oxyhydroxides and oxides ($Mn_2(OH)^{3+}$ and $Mn(OH)_2$) exist in which manganese has an oxidation state between +2 and +4. The removal of Mn^{2+} ions is negligible at low pH<2 and it increases with increased pH (sorption process), at pH>8 precipitation and sorption occurs.

For a pH<8, Mn^{2+} ions are removed by electrostatic attraction with the –COOH and $–NH_2$ groups present on the biomass.

For pH>8, the $Mn_2(OH)^{3+}$ are removed by electrostatic attraction with the negatively charged biomass [15] and Mn^{2+} ions can be removed by precipitation as $Mn(OH)_2$.

4.3 Fe^{+3} and Mn^{+2} biosorption kinetics

As can be seen from Fig.4, Fe^{+3} and Mn^{+2} biosorption kinetics is very fast suggesting very active surface phenomena of the biomass.

The metal biosorption depends strongly on the protonation or unprotonation of the functional groups on the cell wall, i.e., carboxylic, hydroxyl and amino groups [5,8,9,11]. The ionic forms of the metal in solution and the electrical charge of the biomass depend of the solution pH. For Fe^{+3} and Mn^{+2} sorption studies, the pH chosen were 2.6 and 8 respectively.

After a contact time of 10 min, the quantity of Fe^{+3} fixed on the biomass was around 16.5 mg/g, and after a contact time of 30 min, the quantity of Mn^{+2} fixed on the biomass was around 12.3 mg/g.

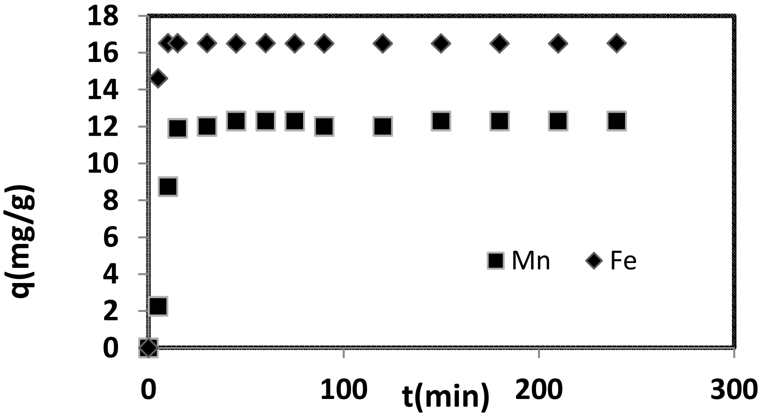

Fig. 4. Time evolution of the biosorption capacity of Mn^{2+} and Fe^{3+} during the experiments. (*$T=20°C$, $\omega=250$ rpm, $C_o(Fe^{+3})=50$ mg/L, $C_o(Mn^{+2})=50$ mg/L, $C_{biomass}=3$g/L, pH of solution (metal+biomass)=2.6 (Fe^{+3}), pH of solution (metal+biomass)= 8 (Mn^{+2}), PS: 250-315µm*)

4.4 Adsorption isotherm:

Langmuir, Freundlich, Dubinin-Radushkevich and Temkin adsorption isotherms were used to fit the experimental data. Plot for Langmuir, Redlich-Peterson, Freundlich, Dubinin–Radushkuvich and Temkin equations gives the values of the isotherm constants and are shown in Table 3 and Table 4.

Five correlation isotherms were used to model the experimental data for Fe^{3+} and Mn^{2+} biosorption on the *Pleurotus mutilus* fungal biomass. However regarding the correlation coefficient R^2 for the Fe^{3+} ions adsorption Langmuir ($R^2=0.98$) and Redlich –Peterson ($R^2=0.98$) isotherms were found to represent the equilibrium adsorption data. For Mn^{+2} biosorption Langmuir isotherm ($R^2=0.98$) was found to represent the equilibrium adsorption data.

Table 3. Parameters of iron biosorption isotherm

Isotherm	Equation	constant	value	R^2
Langmuir	$q_e = q_{max} K_d C_e / (1 + K_d C_e)$	K_d	0.689	0.980
		q_{max}	8.064	
Freundlich	$\ln q_e = 1/n \quad Ln C_e + Ln k_f$	k_f	8.759	0.95
		n	2.811	
Dubinin-Radushkevich	$Ln(q_e) = Ln(q_{max}) - \quad \beta\varepsilon^2$	q_{max}	17.864	0.830
		β	2.969	
Temkin	$q_e = (RT/B)\ln(K_T C_e)$	B	684.383	0.955
		K_T	34.982	
Redlich-Peterson	$\ln(K_R C_e / q_e - 1) = \ln a_R + \beta_R \ln C_e$	β_R	1.219	0.983
		a_R	0.084	

Table 4. Parameters of manganese biosorption isotherm

Isotherm	Equation	constant	value	R^2
Langmuir	$q_e = q_{max} K_d C_e / (1 + K_d C_e)$	K_d	0.066	0.982
		q_{max}	20.24	
Freundlich	$\ln q_e = (1/n) \quad LnC_e + Lnk_f$	k_f	2.113	0.633
		n	1.984	
Dubinin-Radushkevich	$Ln(q_e) = Ln(q_{max}) - \quad \beta\varepsilon^2$	q_{max}	14.667	0.942
		β	3.039	
Temkin	$q_e = (RT/B)\ln(K_T C_e)$	B	0.002	0.841
		K_T	1	
Redlich-Peterson	$\ln[K_R (C_e/q_e) - 1] = \ln a_R + \beta_R \ln C_e$	β_R	0.835	0.684
		α_R	0.117	

4.5 Mn^{2+} and Fe^{3+} desorption study

The metals desorption from biosorbent was achieved with HNO_3, EDTA, and H_3PO_4. In real application the desorption of metal allows the biosorbent to be reused for further cycle, which may decrease the overall cost of process and also reduce the dependency of the process on a continuous biosorbent supply. In this study, HNO_3 was selected as desorption agent as it appeared to have the best desorption efficiency among other agents, the pH of the solution containing Mn^{2+}, Fe^{3+} loaded biomass was adjusted to pH=1 using an appropriate volume of HNO_3 . 92% of Fe^{+3} and 95% Mn^{+2} were obtained after regeneration.

CONCLUSION

The present results indicate that *Pleurotus mutilus* fungal biomass (a low-cost sorbent) may be a suitable material for the removal of Mn^{+2} and Fe^{+3} from ground waters.

The Langmuir and Redlich-Peterson isotherms models are found to describe fairly well the sorption of Fe^{+3} onto the dried *Pleurotus mutilus* fungal biomass. As for the manganese adsorption, only Langmuir isotherm model was found to describe the experimental data.

These metallic ions are known to cause adverse problems for the classic water treatment. Several methods have been employed to remove iron and manganese from water. However, the biosorption may be applied for the removal of Mn^{+2} and Fe^{+3} from dilute solutions due to its technical and economical feasibility.

Furthermore, in view of practical application of this waste biomass to the treatment of metal charged effluents, this preliminary study needs obviously to be completed by additional experiments concerning the influence of ionic strength and other constituents that are frequently found in actual surface ground waters.

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