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Biosorption of Manganese by Amended *Aspergillus versicolor* from Polluted Water Sources

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ABSTRACT

This study deals with the adsorption capacity of the powder of Aspergillus versicolor (Ascomycota) as a bioadsorbent for the removal of manganese ion from polluted water samples. The effect of various experimental parameters such as the effect of pH, quantity of the fungus powder, contact time with the manganese (II) ion solution and its concentration on the biosorption capacity was conducted to optimize them. Potato Dextrose Agar (PDA) plates amended with 100 ppm of Mn(II) ions were used for growing the fungus isolates and standard spread plate method was applied. The plates were incubated at 27°C for 4 to 7 days, then the grown fungi were killed by adding 0.5 N NaOH, washed with doubly distilled water, dried out in hot air oven and finally ground into a very fine powder. The results verify that the optimum pH value for manganese biosorption was 6. The rate of adsorption of manganese by Aspergillus versicolor was very fast reaching a maximum within 15 min at 31°C. Maximum removal efficiency occurred on the use of 0.3 g A. versicolor powder. The maximum metal uptake was relatively observed at 90 ppm manganese concentration. Manganese removal process decreased with increasing metal concentration. The desorption study showed that manganese was recovered up to 81.53% using 0.1 N HCl rendering the possibility of the adsorbent regeneration. Experimental results have been analysed using a Langmuir and Freundlich adsorption isotherm models. Surface morphology study of A. versicolor powder using SEM analysis, assured its irregular surface nature.

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INTRODUCTION

Heavy metals in the environment represent a significant and long-term environmental hazard (Saranya et al. 2017), even low concentration of metals can be toxic to organisms, including humans (Ramrakhiani et al. 2011). Industrial wastewater usually contains non-biodegradable heavy metal ions and many of them are soluble in aqueous media thus being available to living organisms (Ashraf 2017). Groundwater is considered as one of the major sources of drinking water especially in rural and semi-urban areas of Egypt (Akl et al. 2013). Manganese is often present in groundwater through natural leaches from soil rocks. The presence of such metal in waste stream and groundwater represents very serious concern since this metal is toxic to various life forms (Garba et al. 2016). Heavy metals and other constituents leach into the soil and damage the flora and fauna on the earth (Gayatri et al. 2017). The administration of water contaminated with heavy metals even in low dose has been found to cause kidney damage, liver damage and anaemia. Manganese is a common metallic element found in the earth's crusts (Kerani & Barbell 2014). According to the World Health Organization (WHO), the maximum acceptable drinking water limit of Mn is 0.05 mg/L. Abnormal concentration of manganese in the brain, especially in the basal ganglia, results in neurological disorders which are similar to Parkinson's disease (Okoniewska et al. 2007). Manganese presence in water may generate organoleptic and operational troubles including discolouration of water, unpleasant metallic taste and odour, increased turbidity and biofouling of pipelines as well (El Nemr et al. 2008, Khaled et al. 2015). Manganese can pollute water from dual sources, natural and manufactured (El-Waked et al. 2015). Manganese must be removed from water and wastewater for many reasons; first of them, it causes corrosion and pipe blockages. Thus, many methods have been developed for manganese removal such as precipitation, ion exchange, membrane technologies, adsorption, electrochemical processes, and also biological methods are commonly used (Shu et al. 2016). However, most of these methods are highly priced and complicated. Others can produce secondary pollution (Emmanuel & Rao 2009). Adsorption is one of the most accessible techniques for heavy metals elimination from wastewater. Diverse physicochemical characteristics like specific surface area,

pore structure, and surface chemistry of adsorbents control the adsorption efficiency, selectivity, equilibrium time, regeneration capability, and their stability in aqueous solutions have been studied (Islam et al. 2015). Microorganisms such as yeasts, fungi, bacteria and algae can adsorb heavy metals and radionuclides from their external environment (Jasmidia et al. 2017). The cell wall of the microorganisms essentially consists of negative surface charge membrane composition and various organic compounds such as carboxyl, acidic polysaccharides, lipid molecules, amino acids and other constituents, extracellular polymeric substances present on the outer surface of some microorganisms also contribute to biosorption of metal ions as those of polymers which retain negatively charged functional groups, such as carboxyl group, phosphate and sulphate. Several studies have been forwarded towards the use of fungal biomass such as Rhizopusarrhizus, Saccharomyces cerevisiae and Aspergillus niger for heavy metals removal (Veglio & Beolchini 1997). Aspergillus niger has been utilized in the biological decolourization of azo dyes from textile wastewater effluent (Salem et al. 2019). Heavy metal removal by fungus Mucorrouxii has been achieved by Khambhaty et al. (2009). Biosorption of hexavalent chromium ions by dead marine Aspergillus niger fungus has been reported by Wang & Chen (2009).

In the present study, *Aspergillus versicolor* powder has been used for Mn removal from polluted water. Aspergillus is defined as a group of conidial fungi, where fungi are in an asexual state. The influences of the experimental parameters such as the effect of pH, contact time, initial concentration, stirring time, adsorbent dosage, the temperature on adsorption were studied.

MATERIALS AND METHODS

Reagents

All reagents were of analytical pure grade. Standard manganese(II) solution (1000 ppm) and Mn(II) stock solutions were prepared by dissolving 0.2846 g of anhydrous MnSO₄ in DDW containing 2 mL conc. H₂SO₄ and accurately diluted to volume in 100 mL volumetric flask by 20% potassium tartrate solution.

1M formaldoxime prepared by dissolving 20.0 g of hydroxylamine hydrochloride in 450 mL of distilled water. Add 10 mL of formaldehyde solution (37%) and made up to 500 mL with distilled water. Doubly distilled water [DDW] was used in all the experiments.

Preparation of Potato Dextrose Broth and Agar Media

Potato dextrose broth and agar media for *Aspergillus versi*color fungus composed of 20 g of potato slices was boiled with 100 mL of doubly distilled water for 30 min, the filtrate was extracted by strain through many layers of cheesecloth and then the cloth was pressed for extracting the remaining liquid. Two g of dextrose was added. The filtrate was made to 100 mL. For agar plates, 1.5 g of agar was added to this mixture, the flask was closed with cotton plug and aluminium foil and this solution was autoclaved for 20 minutes at 121°C.

Preparation of Fungal Biosorbents

A. versicolor was obtained from Assuit University Mycological Centre under the AUMC No. 90. It was grown on Czapek yeast extract agar (CYA). For fungal biosorption examination, Potato Dextrose Agar (PDA) plates were amended with 100 ppm of Mn(II) ions and the standard spread plate method was performed. The fungus was incubated for 4 to 7 days at 27°C (Wang & Chen 2009). After the incubation period, the fully grown fungi (resistant metal fungi) were killed by adding 0.5 N NaOH in a conical flask containing the fungal mat and preserved in a water bath for 15 minutes. The mat was washed with doubly distilled water for about 6-7 times till the pH reaches 7. The mat was then transferred to a sterile Petri dish and put in a hot air oven for 24 hours at 75°C. The dried dead fungal mat was powdered to smallest particle size using mortar and pestle; the smaller the particle size, the larger the surface area. Biomass has been crushed to inhibit particle aggregation for enhancing the biosorption capacity, then stored in a sterile container for further study.

Instruments

UV/Vis spectrophotometer (Shimadzu UV/Vis, Perkin Elmer Lambada 3B spectrophotometer with 1cm Quartz cell) and Flame Atomic Absorption Spectrophotometer (AA 240FS, Agilent Technologies) were used for the determination of the residual manganese ions in the effluents samples after each adsorption processes. The pH measurements were made by the microprocessor pH meter (BT 500 BOECO, Germany), which was calibrated with two standard buffer solutions of pH 4 and 9. The morphology of the prepared samples was studied by Scanning Electron Microscopy (SEM) JEOL JEM-1200 EX.

Adsorption of Manganese

Batch experiments were carried out by shaking stopper flasks containing specific concentration of Mn^{2+} cations solution and specific amount of *Aspergillus versicolor* powder at 120 rpm for desirable time, temperature and initial pH. The suspensions were then filtered and the filtrates were analysed using flame atomic absorption spectrophotometer. The pH values of suspensions were adjusted with dilute HCl or NaOH solution. The experiments were carried out by varying the

initial metal ion concentration, contact time, amount of the adsorbent, and pH of the initial suspension. Removal percentage of the initial concentration was expressed by a specific biosorption q (mg/g), which is calculated by equation (1):

$$q = \frac{c_i - c_f}{w_t} \times V \qquad \dots (1)$$

Where, C_i is the initial manganese concentration (ppm), C_f is the final concentration (ppm), Wt is the dose of sorbents (g) and V is the volume of solution (mL). The equation was applied in the pH range 1-10; the optimum pH was found to be 6 (Fig. 1).

Optimization of the Factors Affecting the Adsorption of Mn from Standard Solutions

Optimization of the pH: To study the effect of pH on the uptake % (adsorption) of manganese from aqueous media by *Aspergillus versicolor* dried powder, aliquots of 25 mL containing 100 ppm of the manganese ion were transferred to a set of 100 mL conical flasks each containing 0.3 g of the fungal powder. The pH of each flask was adjusted to a value in the range of 1-10, respectively, using 0.1M NaOH and 0.1M HCl solutions and stirred for 15 minutes. The contents of each flask were centrifuged and the residual manganese content in the supernatant solution was decanted, then filtered and the concentrations of metal ions were determined using both the spectrophotometric and the flame atomic absorption method.

Optimization of biomass dose: Aliquots equal to 100 ppm manganese were transferred to a set of 100 mL conical flasks. The pH of each flask was adjusted to the optimum value of 6. Varying amounts of *A. versicolor* powder in the range 0.05-0.5 g were added to each flask, respectively. The mixtures were stirred for 15 minutes, the residual manganese content in the supernatant solution separated by centrifugation, was determined by FAAS.

Stirring time: A set of 100 mL conical flasks, each of which loaded with the optimum biomass dose 0.3 g of *A. versicolor* powder and aliquots of 25 mL solution containing 100 ppm of manganese at the optimum pH of 6 were taken, and the incubation time was changed for different intervals of time (5-30 min) for each flask.

Metal ion concentration range: Applying the optimum conditions of the weight of *A. versicolor* powder, pH and stirring time in a group of flasks, aliquots of 25 mL solution containing varying concentrations of manganese in the range of 90-150 ppm were added to the flasks. The same procedure was applied and the residual manganese content was determined from which the uptake per cent was calculated.

The Determination Methods: *The spectrophotometric method:* In a 25 mL volumetric flask, 2 mL of 20% potassium tartarate solution (in case of the presence of traces of Al, Ti, Cr or U), about 10 mg of ascorbic acid (in case of the presence of traces of Fe (III)), and 20 mg of KCN (in case of presence of Ni, Co, Fe(III) or Cu) were added. Next, 1 mL of 1 M formaldoxime was added followed immediately by 1 mL 1 M NaOH more than the volume required for the neutralization. The solution was diluted with DDW and mixed thoroughly. After 10 minutes, the absorbance of the solution was determined at 455 nm against a blank solution as reference.

FAAS method: The Mn lamp was adjusted at current 5.0 mA with optimum work range of 0.02-5 μ g/mL at _{max} equals 279.5 nm, slit width 0.2 nm, using an acetylene-nitrous oxide fuel-oxidant mixture.

Desorption studies: Reusability of the adsorbent was tested by regenerating the spent adsorbent following a modified literature procedure (Chen et al. 2011). The desorption process should yield the metal in a concentrated form, restore the biosorbent close to the original state for effective reuse with undiminished metal uptake and physical changes or damages to the biosorbent (Tella et al. 2014). The adsorbed manganese ions on the adsorbent surface are treated with 25 mL 0.1 M HCl and stirred for 1 h. The amount of manganese ions remained in the solution after filtration or centrifugation is measured using the recommended spectrophotometric and FAAS methods. The percentage desorption was calculated according to equation (2)

Desorption
$$\% = \frac{C_r}{C_i} \times 100$$
 ...(2)

Where C_r is the released metal concentration, and C_i is the initially sorbed metal concentration.

RESULTS AND DISCUSSION

The dried powdered biomasses have been introduced as a new field of bio-treatment technology, as an effective and relatively simple method for heavy metals recovery. Several studies have explained that inactive dried microbial biomass can passively bind metal ions via various physicochemical mechanisms (Dhankhar & Hooda 2011). It has been suggested that the pretreatment by manganese ions stimulates the surface characteristic groups by removing or masking them or by increasing the metal-binding sites (Asheh et al. 2003). The use of fungal biomass has been reported in literature for the removal of different heavy metals from wastewater, e.g. the uptake of chromium by Aspergillus foetidus (Prasenjit & Sumathi 2005), heavy metal biosorption using Aspergillus niger (Kapoor et al. 1999, Ahluwalia & Goyal 2007), heavy metal removal by fungus Mucorrouxii (Khambhaty et al. 2009) biosorption of hexavalent chromium by dead fungal biomass of marine Aspergillus niger (Wang & Chen 2009).

Different factors that affect the adsorption process have been extensively studied to improve the biosorption capacity Q (mg/g) of *A. versicolor* towards manganese ions from the aqueous solutions.

Optimum pH

Earlier studies showed that the pH value has been observed as one of the important parameters which control the heavy metal biosorption (Blázquez et al. 2005, Dogan et al. 2006, Siddiquee et al. 2015). The variation of adsorption rates at different pH values is dependent on both the metal chemistry in solution and the surface chemistry of the sorbent (Iram et al. 2015). Adsorption of manganese by *A. versicolor* powder has been found to increase with the increase in pH value until it attains its maximum at pH 6. The biosorption of dried biomass increased with the solution pH due to the excess amounts of OH⁻ ions within the solution, the binding sites on the fungal cell wall are negatively charged. The cell wall is made up of several components such as carboxyl, carbonyl, alcoholic and amino groups which determines the biosorption ability based on its protonation or unprotonation nature. This exerts an influential attraction between active sites and positively charged ions. Thus, it is most possible that at low pH values, the positively charged surface will not favour the binding with manganese ions due to columbic repulsion. With an increase in pH values, the surface becomes more and more negatively charged and thereby favouring manganese ion binding (Fig. 1, Table 1).

Stirring Time

The kinetics of adsorption describing the shaking time in the removal of manganese is one of the characteristics defining the efficiency of biosorption rate. The results indicate that maximum biosorption capacity occurred after 15 minutes



Fig. 1: Effect of Initial pH on biosorption capacity of manganese by A. versicolor resistant powder.

Fable 1: Effect of initia	al pH on biosorption	capacity of manganese	e by Aspergillus v	ersicolor resistant powder, 1	N=3.
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pH	Std. Deviation	q (mg/g)
1.00	0.051	5.16±0.03
2.00	0.037	9.16±0.02
3.00	0.072	13.25±0.05
4.00	0.080	16.23±0.04
5.00	0.019	20.82±0.07
6.00	0.025	22.83±0.01
7.00	0.105	17.26±0.06
8.00	0.152	12.27±0.08
9.00	0.069	7.23±0.04
10.00	0.090	2.54±0.06

where the uptake was 22.83 mg/g for manganese ions. After this period, the equilibrium is reached (Fig. 2, Table 2).

Biomass Dose

The increase in biosorbent concentration from 0.05g to 0.5g results in an extensive increase in the metal adsorption. The increase of the adsorption surface area and the availability of free adsorption sites help in the removal of manganese. Maximum removal efficiency was observed at the biomass dosage concentration of 0.3 g *A. versicolor*; which achieves manganese removal of 22.83 mg/g, after this concentration equilibrium is reached (Fig. 3, Table 3).

Effect of Initial Metal Ion Concentration

The interest in processes of heavy metal removal by microorganisms has increased considerably in recent years due to the biotechnological potential of microorganisms in metal recovery (Soleimani et al. 2016). The maximum metal uptake was 22.83 mg/L at 90 ppm manganese concentration, which decreases with the increase of manganese concentration. At higher concentration, the available sites for sorption become fewer in comparison with the molecules of solute present. Hence, the removal of metal ions is strongly dependent upon the initial solute concentration, so heavy metal tolerant microorganisms such as *A. versicolor* instinctively use defence mechanisms on exposure to metal stress (Fiol et al. 2006) (Fig. 4, Table 4).

Effect of Temperature

Temperature is an essential and important factor in the biosorption process of metals. Metal adsorption onto the biosorbent is dependent on temperature; the increase in temperature has improved the manganese biosorption rate and decreased the contact time required for heavy metal removal. The temperature of the adsorption medium is con-



Fig. 2: Effect of stirring time on biosorption capacity of manganese by A. versicolor resistant powder.

Table 2: 1	Effect of stirring	time on biosorptic	on capacity of n	nanganese by A	Aspergillus ve	ersicolor resistant r	owder, N=3
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Time of stirring (min)	Std. Deviation	q (mg/g)
3.00	0.105	3.22±0.06
6.00	0.070	6.16±0.04
9.00	0.159	10.22±0.09
12.00	0.020	14.53±0.01
15.00	0.015	22.83±0.08
18.00	0.020	18.15±0.05
21.00	0.095	12.15±0.07
24.00	0.028	6.16±0.02
27.00	0.022	2.53±0.01
30.00	0.018	1.53±0.03



Fig. 3: Effect of biomass dose on biosorption capacity of manganese by A. versicolor resistant powder.er.

Table 3: Effect of biomass dose on biosorption capacity of manganese by Aspergillus versicolor resistant powder, N=3.

	Otd Deviction	- (
Dose (g)	Std. Deviation	q (mg/g)
.050	0.020	8.54±0.01
.100	0.035	12.14±0.02
.150	0.115	15.45±0.06
.200	0.032	18.30±0.02
.250	0.085	21.55±0.05
.300	0.047	22.83±0.03
.350	0.078	22.82±0.04
.400	0.085	22.83±0.01
.450	0.075	22.83±0.06
.500	0.040	22.85±0.02

sidered to be an important parameter for energy-dependent mechanisms in metal removal using the biosorbent. Maximum removal of manganese was found to be 22.93 mg/g at a temperature of 31°C. Temperature affects the cell wall stability components, its configuration and ionization of chemical moieties, and energy-independent mechanisms are likely to be affected due to temperature changes since the processes responsible for removal are largely phys-

icochemical (Bayramo lu et al. 2003). Similar results have been recorded in the bioaccumulation of Cu(II) and Cr(VI) by *Streptococcus equisimilis* and *Aspergillus sp.* (Dehghani et al. 2016, Chen et al. 2011) (Fig. 5, Table 5).

The Morphology of the Prepared Fungi

Scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it



Fig. 4: Effect of metal concentration on biosorption capacity of manganese by A. versicolor resistant powder.

Metal Concentration (ppm)	Std. Deviation	q (mg/g)
90.00	0.030	21.56±0.01
100.00	0.144	19.28±0.08
110.00	0.142	16.57±0.08
120.00	0.305	14.54±0.17
130.00	0.172	12.44±0.09
140.00	0.104	10.30±0.06
150.00	0.025	16.79±0.05

Table 4: Effect of metal concentration on biosorption capacity of manganese by Aspergillus versicolor resistant powder.

with a focused beam of electrons. The micrographs showed that the fungi have an irregular surface (Fig. 6).

Adsorption Isotherm Studies

For the solid-liquid adsorption system, the adsorption behaviour can well be described as adsorption isotherm model (Tella et al. 2014). The adsorption isotherm means the distribution of adsorbate molecules between the solid phase and the liquid phase at equilibrium. Equilibrium is said to be reached when the concentration of adsorbate in bulk solution is in dynamic balance with that on the liquid adsorbate interface.



Fig. 5: Effect of temperature on biosorption capacity of manganese by A. versicolor resistant powder.

Table 5: Effect of temperature on biosorption capacity of manganese by Aspergillus versicolor resistant powder, N=3.

Temperature (°C)	Std. Deviation	q (mg/g)
25.00	0.081	20.22±0.04
27.00	0.061	21.34±0.03
29.00	0.098	22.23±0.07
31.00	0.020	22.93±0.01
33.00	0.026	21.56±0.05
35.00	0.079	20.44±0.06
37.00	0.028	19.54±0.02
39.00	0.115	19.25±0.09
41.00	0.025	18.53±0.01

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Fig. 6: Scanning electron micrograph of Aspergillus versicolor biomass

Table 6: Freundlich, Langmuir adsorption isotherm parameters.

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Langmuir and Freundlich	adsorbiion isoinerm Paran	ieters of manganese for	is dv <i>Asper</i>	guius versicolor.

S. No.	Langmuir isotherm Parameters		Freundlich isotherm para	ameters
1	Q _{max} (mg/g)	22.9	1/n	0.826
2	KL	0.27	KF	1.9
3	R2	0.999	R2	0.999
4	RL	0.045		

Langmuir adsorption isotherm: The equilibrium adsorption data for the concentrations of manganese ions were fitted into the linear form of Langmuir's isotherm equation to determine the distribution of manganese ions between the adsorbent and solution according to equation (3).

$$\frac{c_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{c_e}{Q_e} \qquad \dots (3)$$

Where, C_e is the equilibrium concentration of the manganese ions in solution $(mg.L^{-1})$, Q_e is the equilibrium concentration of manganese ions on *A. versicolor* adsorbent $(mg.g^{-1})$, Q_m and K_L are Langmuir constants related to sorption capacity and the rate of adsorption respectively. Maximum adsorption capacity (Q_m) is the monolayer capacity of the adsorbent $(mg.g^{-1})$ and K_L is the Langmuir adsorption constant. A plot of C_e/Q_e against C_e over the entire concentration range is a straight line with a slope of $1/Q_m$ and the intercept of $1/Q_mK_L$. The correlation coefficient (R^2) values reported were very close to 1 indicating that the adsorption follows the Langmuir adsorption isotherm. The quality of Langmuir isotherm can be determined by the magnitude of a dimensionless constant R_L known as the separation factor expressed in equation (4).

$$R_L = \frac{1}{1 + C_0 K_L} \qquad \dots (4)$$

Where, C_o is the initial concentration of the manganese

ions in mg.L⁻¹ and K_L is the Langmuir constant described earlier. The adsorption process is favourable within the range $0 < R_L < 1$, unfavourable when $R_L > 1$, becomes linear when $R_L = 1$, and the process is irreversible when $R_L = 0$. The value of R_L is 0.045 for *A. versicolor*; hence the adsorption process is favourable (Fig. 7, Table 6).

Freundlich adsorption isotherm: The linear form of the Freundlich adsorption model equation (5) is:

$$\log e Qe = \log e KF + \frac{1}{n} \log e_e \qquad \dots (5)$$

Where, Q_e is the quantity of manganese ions adsorbed at equilibrium per gram of the adsorbent (mg.g⁻¹), C_e is the equilibrium concentration of the manganese ions in the solution (mg.L⁻¹), and K_f and n are the Freundlich adsorption model constants related to the adsorption capacity and adsorption intensity, respectively. Log Q_e was plotted against log C_e and a straight line obtained giving the intercept of log K_f and the slope of 1/n. The reported numerical value of 1/n is less than 1, (Fig. 8, Table 6).

Selectively of the Adsorbent

The spiking of the manganese authentic samples with different concentrations of other metal ions, e.g. Ni(II) and Cu(II) proved that there is no complete selectivity for the resistant *A. versicolor* powder towards manganese ions, but it has an



Fig. 7: Langmuir isotherm plots for the adsorption of manganese ions by A. versicolor.

Table 7: Effect of pH on desorption%, N=3.

pH	Std. Deviation	Desorption %
1.80	0.020	81.53±0.01
2.40	0.147	81.44±0.08
3.00	0.228	77.66±0.13
3.60	0.102	73.19±0.05
4.20	0.245	68.27±0.14
4.80	0.221	64.30±0.11
5.40	0.191	58.35±0.01
6.00	0.147	55.48±0.09
6.60	0.019	52.31±0.02
7.20	0.025	81.53±0.07

increased capacity towards the spiking ion more than the others. However, the resistant *A. versicolor* powder proved as efficient, low cost, available, economic biosorbent for removal of heavy metals, in general.

Desorption Studies

Effect of pH on desorption of iron: In strong acidic media at pH range (1.8-2.4) *A. versicolor* resistant powder showed a high desorption percentage, but on increasing the pH values



Fig. 8: Freundlich isotherm plots for the adsorption of manganese ions by A. versicolor.

Stirring time (min)	Std. Deviation	Desorption %
20.00	0.032	81.54±0.01
25.00	0.075	65.23±0.04
30.00	0.161	52.44±0.09
35.00	0.258	44.41±0.14
40.00	0.158	38.34±0.09
45.00	0.294	34.58±0.17
50.00	0.025	33.55±0.01
55.00	0.133	32.49±0.07
60.00	0.136	32.81±0.08

Table 8: Effect of stirring time on desorption %, N=3



Fig. 9: Effect of pH on desorption (%) of manganese by A. versicolor resistant powder.



Fig. 10: Effect of stirring time on desorption (%) of manganese by A. versicolor resistant powder.

desorption percentage decreases (Fig. 9, Table 7). **Stirring time**: The maximum desorption percentage was found to be 81.54 during the first 20 minutes, but then grad-ually decreased (Fig. 10, Table 8).

Real Samples Analysis

Water samples collected from tap water, Bahr Youssef water, groundwater and Ibrahemia water were subjected to the adsorption procedure as mentioned previously and the residual manganese was analysed by two methods, viz. colourimetry and AAS (Table 9).

CONCLUSION

Biosorption of manganese ion by *A. versicolor* resistant fungus is shown to be an effective bioremoval process. It could retain relatively high quantities of metal ions with increased capacity towards the adsorption of the amending metal ion,

Type of sample	Method of finish	Aspergillus versicolor			
		Measured Concentration	SD	Removal %	
Drinking water	AAS	0.19	0.228	88.24±0.13	
	Colorimety	0.18	0.152	88.16±0.08	
Bahr youssef water	AAS	1.11	0.025	87.97±0.01	
	Colorimety	1.05	0.047	87.84±0.03	
Ground water	AAS	1.22	0.161	87.57±0.09	
	Colorimetry	1.21	0.305	87.53±0.17	
Ibrahimia water	AAS	0.81	0.115	88.15±0.09	
	Colorimetry	0.79	0.080	88.11±0.04	

Table 9: Analysis of real water samples after adsorption on Aspergillus versicolor powder, number of determinations N=3.

although its selective adsorption was not achieved. The kinetics of biosorption has rapidly enhanced with temperature increase and acidic pH. From the obtained statistical results, it can be seen that the models are suitable for predicting biosorption capacity of *A. versicolor* within the range of the studied variables.

REFERENCES

- Ahluwalia, S.S. and Goyal, D. 2007. Microbial and plant derived biomass for removal of heavy metals from wastewater. Journal of Bioresource Technology, 98(12): 2243-2257.
- Akl, M.A., Yousef, A.M. and AbdElnasser, S. 2013. Removal of iron and manganese in water samples using activated carbon derived from local-agro-residues. Journal of Chemical Engineering Process Technology, 4(4): 154.
- Asheh, S.A., Jumah, R., Banat, F. and Hammad, S. 2003. The use of experimental factorial design for analyzing the effect of spray dryer operating variables on the production of tomato powder. Journal of Food and Bioproducts Processing, 12(12): 0960-3085.
- Ashraf, A. 2017. Removal of Mn[II] from water using chemically modified banana peels as efficient adsorbent. Journal of Environmental Nanotechnology, Monitoring & Management, 7(4): 757-763.
- Bayramo lu, G., Bekta, S. and Arica, M.Y. 2003. Biosorption of heavy metal ions on immobilized white-rot fungus *Trametes versicolor*. Journal of Hazardous Mater, 101(3): 285-300.
- Blázquez, G., Hernáinz, F., Calero, M. and Ruiz-Nú⁻nez, L.F. 2005. Removal of cadmium ions with olive stones: The effect of some parameters. Journal of Process Biochemistry, 40(8): 649-654.
- Chen, C.Y., Yang, C.Y. and Chen, A.H. 2011. Biosorption of Cu(II), Zn(II), Ni(II) and Pb(II) ions by cross-linked metal-imprinted chitosans with epichlorohydrin. Journal of Environmental Management, 92(3): 796-802.
- Dehghani, M.H., Sanaei, D., Ali, I. and Bhatnagar, A. 2016. Removal of chromium (VI) from aqueous solution using treated waste newspaper as a low-cost adsorbent: Kinetic modeling and isotherm studies. Journal of Ecological Engineering, 215(1): 671-679.
- Dhankhar, R. and Hooda, A. 2011. Fungal biosorption- An alternative to meet the challenges of heavy metal pollution in aqueous solutions. Journal of Environmental Technology, 32(5): 467-491.
- Dogan, C.E., Turhan, K., Akcin, G. and Aslan, A. 2006. Biosorption of Au(III) and Cu(II) from aqueous solution by a non-living *Cetraria islandica* (L.). Journal of Ach. Analytical Chemistry, 13(2): 229-236.
- El Nemr, C.A., Khaled, A., Abdelwahad, O. and El Eikalily, A. 2008. Treatment of wastewater containing toxic chromium using new activated

carbon developed from date palm seed. Journal of Hazardous Mater, 152(1): 263-275.

- El-Waked, K.Z., El-Sayed, G.O., El-Abo, S.M. and Nassr, E.I. 2015. Removal of ferrous and manganese from water by activated carbon obtained from sugarcane bagasse. Journal of Desalination Water Treatment, 55(2): 179-186.
- Emmanuel, E.A. and Rao, A.V. 2009. Comparative study on adsorption of Mn(II) from aqueous solutions on various activated carbon. Journal of Chemical Engineering, 6(2): 693-704.
- Fiol, N., Villaescusa, I., Martinez, M., Miralles, N., Poch, J. and Serarols, J. 2006. Sorption of Pb(II), Ni(II), Cu(II) and Cd(II) from aqueous solution by olive stone waste. Journal of Separation and Purification Technology, 38(4): 132-140.
- Garba, Z.N., Ugbaga, N.I. and Abdullahi, A.K. 2016. Evaluation of optimum adsorption conditions for Ni(II) and Cd(II) removal from aqueous solution by modified plantain peels (MPP). Journal of Basic and Applied Science, 135(5): 170-179.
- Gayatri, Y., Shailaja, R.M. and Vijayalakshmi, B. 2017. Biosorption of lead by *Bacillus licheniformis* isolated from e-waste landfill, Hyderabad, Telangana, India. Journal of Bioassays, 13(1): 5240-5244.
- Iram, S., Shabbir, R., Zafar, H. and Javaid, M. 2015. Biosorption of copper and lead by heavy metal resistant fungal isolates. International Journal of Scientific and Research Publications, 5(1): 255-266.
- Islam, S. Md., Rahaman, S. Md. and Yeum, J.H. 2015. Phosphine-functionalized electrospun poly (vinyl alcohol)/silica nano fibers as highly effective adsorbent for removal of aqueous manganese and nickel ions, colloids and surfaces. Journal of Physicochemical Engineering Aspects, 484(1): 9-18.
- Jasmidia, Z.M., Kembarenc, A., Sellyd, R. and Silalahie, A. 2017. Biosorption of manganese ions (II) by immobilized biomass on a mixture of silica gel and zeolite. Journal of Basic and Applied Research, 35(2): 102-112.
- Kapoor, A. and Viraraghavan, T. and Roy, C.D. 1999. Heavy metal biosorption using *Aspergillus niger*. Journal of Bioresource Technology, 70(1): 95-104.
- Kerani, D.S.L. and Barbell, B. 2014. Pyrolucite fluidized-bed reactor [PFBR]: A robust and compact process for removing manganese from groundwater. Journal of Water Research, 49(4): 475-483.
- Khaled, Z., Waked, A.I., Abd, H., Monem, E.I, Mostara, M. and Kharil, H. 2015. Removing of divalent manganese from aqueous solution using glycine modified chitosan resin. Journal of Chemical Engineering, 3(4): 179-186.
- Khambhaty, Y., Mody, K., Basha, S. and Jha, B. 2009. Kinetics, equilibrium and thermodynamic studies on biosorption of hexavalent chromium by dead fungal biomass of marine *Aspergillus niger*. Journal of Chemical Engineering, 145(3): 489-495.
- Okoniewska, E., Lach, J., Karperzak, M. and Tveczaj, E. 2007. Removal

of manganese, iron and ammonium nitrogen on impregnated activated carbon. Journal of Desalination, 206(2): 251-258.

- Prasenjit, B. and Sumathi, S. 2005. Uptake of chromium by Aspergillus foetidus. Journal of Mater Cycles Waste Management, 3(2): 88-92.
- Ramrakhiani, L., Majumdel, R. and Khowala, S. 2011. Removal of hexavalent chromium by heat inactivated fungal biomass of *Termitonayces clypeatus*: Surface characterization and mechanism of biosorption. Journal of Chemical Engineering, 171(4): 1060-1068.
- Salem, S.S., Mohamed, A., El-Gamal, M., Talat, M. and Fouda, A. 2019. Biological decolorization and degradation of azo dyes from textile wastewater effluent by *Aspergillus niger*. Egyptian Journal of Chemistry, 62(10): 1799-1813.
- Saranya, A., Sasikala, S. and Muthuraman, G. 2017. Removal of manganese from ground/ drinking water at South Madras using natural adsorbents. International Journal of Recent Scientific Research, 8(6): 0976-3031.
- Shu, J., Liu, R., Liu, Z., Chen, H. and Tao, C. 2016. Simultaneous removal of ammonium and manganese from electrolytic metal manganese residue leachate using phosphate salt. Journal of Cleaner Production,

135(1): 468-475.

- Siddiquee, S., Rovina, K., Azad, S.A, Naher, L. and Suryani, S. 2015. Heavy metal contaminants removal from wastewater using the potential filamentous fungi biomass: A review. Journal of Microbial Biochemistry Technology, 243(6): 384-395.
- Soleimani, N., Fazli, M.M., Ramazani, A and Mehrasbi, M. 2016. Application of live, dead, and dried biomasses of *Aspergillus versicolor* for cadmium biotreatment. Journal of Human Environmental Health Promotion, 6(2): 87-98.
- Tella, A.C., Owalude, S.O., Ojekanmi, C.A. and Oluwafemi, O.S. 2014. Synthesis of copper-isonicotinate metal-organic frameworks simply by mixing solid reactants and investigation of their adsorptive properties for the removal of the fluorescein dye. Journal of New Chemistry, 35(7): 4494-4500.
- Veglio, F. and Beolchini, F. 1997. Removal of metals by biosorption: A review. Journal of Hydrometallurgy, 44(3): 301-316.
- Wang, J. and Chen, C. 2009. Biosorbents for heavy metals removal and their future. Journal of Biotechnology Advances, 27(2): 195-226.